

THE CHEMISTRY OF DEGRADATION AND CONSERVATION OF PLASTIC ARTEFACTS

*OF PRE-SYNTHETIC “ERA”
BASED ON NATURAL OR ARTIFICIAL POLYMERS*

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PREFACE

The success of plastics started already in nineteenth century when it was recognized that by using, at that times primitive but efficient processing devices (presses, extruders, moulds, calendars, etc.,), was possible to shape, by means of pressure and temperature, artefacts from materials originated by natural pre-formed macromolecules present in the vegetal and animal world (animal horn and hoof, bois durci, gutta-percha, rubber, shellac, and casein, etc.).

The discovery, on 1839, by Charles Goodyear, of the process of vulcanisation of natural rubber, that led to the industrialization of soft and hard rubber (Ebonite), is considered as the milestone of the so called “ *Pre synthetic Era*” of plastic industry. This invention contributes to the advance of the “*art*” of moulding. As matter of facts the moulds and presses set up for rubber vulcanisation were also used for shellac, gutta-percha and finally, following of course some improvements, also for synthetic polymers.

The discovery , on 1862, of the celluloid, the first artificial plastic, based on cellulose nitrate, represented the real “*big bang*” for the plastic industry. As matter of facts since then the applications of plastic materials in many fields increased enormously. Many traditional materials (wood, glass, metals, etc.) were gradually substituted in several uses by this new polymer-based compound.

Such a trend was further on accelerated when in 1909 the *Bakelite*, the first “*Man-made synthetic polymer*” (based on phenol-formaldehyde resins) was developed by Leo Baekeland.

Such an event represented the beginning of the “*Synthetic Era of polymers*”.

Initially the manufacturers coined the term “*Plastics*” to define < *the property of a substance by virtue of which it can be formed or molded into any desired shape, as opposed to non plastic substances which must be cut or chiselled* >, that is <...*any material that by its nature or in its process of manufacture is at some stage, either through heat or by the presence of a solvent, sufficiently pliable, and flowable, in other words, plastic, so that it can be given its final shape by the operation of molding or pressing* > [from industry’s first magazine *Plastics*, March (1926)].

Once the macromolecular nature of polymer was assessed, then the term “*plastics*” more correctly was used to signify a multicomponent-compound made of a polymer, as main constituent, and low molecular weight additives, fillers and pigments capable to be moulded in artefacts.

The years from 1920 to 1940, saw the birth of a new branch of the science, namely the “*Chemistry of Macromolecules*” and then of the “*Polymer Science and Technology*”.

The scientific achievements following the vast amount of studies performed brought to the development of new physical methods of characterization of materials (for example: the x-ray diffraction, ultramicroscopy, viscosimetry, ultra-centrifuge, etc.) as well as to innovative diagnostic procedures based on analytical chemical analysis.

Moreover new polymerization techniques, characterized by a high yield, starting from new and more cheap monomers, were developed. Methodologies for the characterization of polymers from molecular and structural point of view were discovered. The relationships between molecular structure and property of polymers were investigated. And finally the role of additives, reinforcing agents and fillers on the stabilization and functions of polymers was definitely assessed.

After the Second World War a large number of new polymers were still synthesized by the man. In 1979 the volume production of plastics for the first time resulted to be larger than that of steel. Plastics and synthetic rubbers were more and more used in a wide range of application fields where they substituted more traditional materials. In this called "Century of Plastics" the "plastic revolution" determined very relevant social and economical changes. Many industrial sectors were abandoned new ones were opened.

Since the beginning of the *Pre-synthetic Era*, plastics were adopted by many artists as materials suitable to be used for the creation of important pieces that are recognized nowadays as real masterpieces. Such a tendency was furtherly confirmed, during the twentieth century, with the appearance on the market of the early synthetic polymer based plastics (Poly(vinylchloride), Poly(methyl methacrylate), Polystyrene, Poly(vinyl acetate), Nylon, Polyethylene, Polyester, Silicones, Polyurethanes, Epoxies, Polypropylene, Polycarbonate, etc.).

The importance of plastics in determining so many changes involving industrial, economical, social as well as artistic relevant aspects accounts why so many objects manufactured in plastics or in rubbers, since the earlier times, especially from the end of the Second World War are more and more collected in private and public houses or museums. As matter of facts those objects representing a witness not only of the industrial and scientific evolution of countries but also of the modifications of the uses and costumes of people needed to be protected and saved from deterioration and destruction.

Now a days many private and public museums and similar organizations, assuming that plastics have been and still are integrant part of our history as they deeply changed the way of life of all humanity, acquire, collect and display artefacts in plastics being considered, rightfully, as part of our cultural heritage.

Those artefacts, for what they represent, must be preserved, protected and maintained to assure their fruition to the future generations.

Thus the development of procedures finalized to the inhibition and mitigation of intrinsic and external factors capable to induce deterioration processes of these artefacts must be considered an issue of great concern.

The present volume consists of two sections.

The first one concerns the following topics:

---The intrinsic characteristics of polymers of relevance as far as their degradation behaviour is concerned, including the influence of additives on properties, stability and degradation behaviour of plastics.

--- The mechanisms of degradation of plastics artefacts induced by environmental chemical agents in relation to molecular structure of polymer constituent, nature and function of additives, composition and processing conditions.

--- Possible general remediation measures suitable to mitigate the degradation of plastics artefacts.

In the second section the subjects taken into examination are hereafter summarized:

--- Processing, structure, composition and properties of Plastics, used as components of artefacts of cultural interest, belonging to the pre-synthetic period, and based on:

- Natural pre-formed polymers (horn and hoof, bois durci, casein, hard and soft rubbers);

-Artificial polymers obtained by chemical transformation of cellulose (cellulose-nitrate and cellulose acetate) .

--- Degradation phenomena in relation to chemical composition and processing, history and use functions, exposition to the environmental factors of degradation.

--- Guidelines for conservation, preservation and storage of artefacts and active treatment for the protection mitigation and prevention against inherent and external factors of degradation.

The above topics were critical reviewed on the basis of up-to date literature information and of the analysis of a series of recent case studies.

The objectives of the work, whose results are henceforth presented, are essentially finalized to contribute to the:

--- Development of a more effective *Science-based* strategy, built on a platform of scientific studies gathered from researchers and conservatorists belonging to accredited public and private institutions particularly skilled in the field of the restoration, preservation and protection of artefacts in plastic materials.

--- Identification of more appropriate instrumental-based procedures capable to evaluate the risks associated to the displaying or storing of these kind of objects which for their nature result to be very sensitive to degradation.

SECTION-1

FIRST-CHAPTER

WITH THE GROWTH OF POLYMER INDUSTRY PLASTICS ARTEFACTS BECOME A RELEVANT PART OF THE CULTURAL HERITAGE

Many plastics artefacts have been recognised to be relevant part of the world of cultural heritage. As matter of fact items in plastic materials (radios, records, clocks, fountain pens, jewellery and hair accessories, robots, dolls, brooches, inkwell, perfume botles, sculptures and paintings based on synthetic varnishes and binders, etc.) have found place in artistic, historic and technological collections of the twentieth century.

The birth of the modern plastic industry goes back to the end of the nineteenth century and the beginning of the twentieth century following the development of Celluloid and Bakelite.

Because of the rapid expansion of plastics utilization in more and more different sectors the twentieth century was defined as the “Century of Plastics”.

The sweeping growth of plastic industry was originated by several factors some of them are hereafter listed:

- The understanding of the basic principle of the macromolecular chemistry;
- The development of new methods of molecular characterization;
- The set up of new controlled and reproducible procedures of chemical synthesis, favoured by the development of innovative and specific catalysts, suitable to obtain a great number of new “*man made*” polymers with widely different characteristics;
- The implementation of the chemistry of additives, fillers, pigments and colorants;
- The development of innovative methods of processing and transformation [1,2,3].

The term “*Plastics*” is commonly used to indicate polymer-based formulations (i.e. a compound made by a mixture containing at least one polymer, as main component, and additives, fillers, pigments etc.) suitable to be transformed and shaped with the aid of temperature and pressure.

Polymers, according to their behaviour to heating and pressure cycles, may be divided in:

Thermoplastics -A material constituted by linear macromolecules able to be repeatedly soften or melted when heated and to harden under cooling. Polymers such as polystyrene, polyethylene, nylons, etc., are examples of thermoplastic materials.

Thermosetting - A polymer that while is shaped, when is heated under pressure, forms, in presence of suitable catalysts, a three dimensional molecular network becoming permanently solid. The resultant material cannot be re-melted or remoulded. Epoxies, phenol-formaldehyde resins, unsaturated polyesters, etc., are typical thermosetting resins.

Plastics may be conveniently classified, according to the origin of the basic polymer constituent, in:

1) *Plastics obtained by physical and/or chemical transformation of natural macromolecules already present in the vegetal or animal world.*

These include horn, hoof, bois durci, natural rubber (hard and soft rubber), casein and cellulose derivatives (cellulose-nitrate and cellulose acetate).

2) Plastics deriving from low molecular weight natural compounds that only during manufacturing, due to the effects of heating and pressure, form polymer-like structures.

Typical example of such family is the Shellac.

3) Plastics- synthesised by the man starting from small molecules named monomers (Synthetic or Man made plastics).

The “Era” of synthetic plastics begun in 1908 when Leo Hendrix Baekeland patented the synthesis procedure and the method of processing of the phenol formaldehyde thermosetting resins (comonly called *Bakelite* in honour of its inventor).

The number of synthetic polymers developed since the beginning of the twentieth century is enormous. These compounds differ dramatically from each other as far as their properties are concerned. Thus the identification of the type of plastics from which an artefacts is made represents one of the main problem that one must afford for the sake of their conservation.

Plastics, since the birth of the polymer industry, were preferred, in many applications, to traditional materials such as, wood, metal, glass, ceramics, ivory, etc.

The chronology of commercial availability of some common plastics until 1991 is hereafter reported:

- 1839 Rubber vulcanized - (Ebonite, Vulcanite)
- 1855 Bois Durci
- 1862 Cellulose nitrate - (Parkesine)
- 1869 Cellulose nitrate - (Celluloid)
- 1900 Casein - (Galalith, Erinoid)
- 1909 Phenol-formaldehyde - (Bakelite, Catalin)
- 1912 Cellulose acetate based photographic film
- 1922 Cellulose acetate moulding material
- 1926 Thiourea and urea formaldehydes - (Beetle resin)
- 1930 Poly(vinylchloride) - (PVC)
- 1933 Poly(methyl methacrylate) - (Perspex, Plexiglass, Lucite, Diakon)
- 1934 Melamine formaldehyde - (Melamine)
- 1935 Polystyrene
- 1936 Poly(vinyl acetate)
- 1938 Nylon
- 1942 Polyethylene - (Polythene); Polyester
- 1943 Silicones; Fluorocarbons; Polyurethane
- 1947 Epoxies; Poly(ethylene terephthalate)
- 1954 Polypropylene
- 1955 Polycarbonate - (Makrolon, Lexan)
- 1959 Polyformaldehyde - (Acetal resin, Delrin)
- 1965 Polysulphone
- 1966 Poly(phenylene oxide)
- 1970 Poly(butylene terephthalate)
- 1970.Kevlar
- 1982 Poly (etherimide)
- 1983 Poly (etherketone)
- 1985 Liquid crystalline polymers
- 1986 Polycarbonate/ABS blends
- 1987-1991 Poly(aniline)
- 1990 Buckminsterfullerene
- 1991 Poly(pyrrole)

The *advantages* in using *plastics materials*, constituted by polymer based formulations, rather than traditional materials, were essentially the following:

- Easy processing;
- Low production cost;
- Weight saving;
- Colourability;
- Innovative performances and design;
- High rate of production.

The *disadvantages* in using items in plastics were mostly related to the:

- Instability against environmental and internal degradation factors;
- Necessity to use additives (stabilizers, plasticisers, fillers, aid processing etc.).

Artefacts in plastics, in exhibition or stored in private collections and in many museums including the art museums and the science museums, may be subdivided in the following two broad categories: **artistic objects** and **items of historical, scientific and cultural interest**.

A) Artistic objects in plastics

Plastics had (still have) an important function in the structuration of works of art. They represented (represent) an important means of expression of artists and designers. According to G. Williams, the reasons which convinced artists and designers, since the beginning of polymer *Era*, in using plastic materials for their works, may be summarized as follows:

< It is amongst the most versatile group of materials known, with different varieties notable for their relative strengths, ranging from total rigidity to complete flexibility, not to mention inertness and stability. Plastics enabled the development of an infinite number of novel shapes and colours which were impossible to achieve using natural materials. The moulding of plastic requires expensive tooling and a high degree of industrialisation, yet the resulting products can be mass-produced cheaply and in great quantity. Versatility, novelty and the potential for replication were the perfect qualities of any material for the manufacturers of new consumer goods > [4].

Early attempts in using plastics as materials for making works of art go back to the end of nineteenth century when processes, suitable to shape by compression moulding compounds based on natural polymers were invented [5].

The main reasons that contributed to the success of plastics as means of expression for artists and designers were related to the following factors:

- Easy availability, low weight and cost;
- Innovative mechanical and chemical characteristics;
- Mouldability alternative to carving;
- Easy colourability by using natural or synthetic pigments (see figure 1) [6];



FIGURE 1: The development of new plastics and pigments led to the production of materials having a wide variety of colors.
Left, a catalogue (1936) of the *Catalin Company* showing “*the colored Gem of the modern industry*” based on phenol-formaldehyde resins.
Right, set of samples in poly vinyl acetate with different coloration [6].

Polymer formulations were used by artists essentially in two different forms of art, namely in sculptures, by molding, casting and carving methods, and in paintings.

Plastics in artistic sculptures

From historical point of view plastics begun to be part of the repertory of materials suitable to be used for artistic sculptures at early decennia of twentieth century when Naum Gabo (1890-1977), < known for his sculptural experiments with constructivism >, experienced the use of celluloid in making innovative works of art [7].

Previous to that artistic artifacts, as shown in figures 2 and 3, were also produced by using different type of natural plastics, in the so called *pre-synthetic Era* [8,9].

Examples of different types of artificial and synthetic plastics used in artistic sculptures belonging to various time periods are reproduced in figures 4 to 8.

Plastics as components in artistic paintings

Formulations based on synthetic polymers are more and more used as binders and protective varnish in the manufacture of artistic paintings. The binders and the protective varnishes, as schematically shown in figure 9 are the main component of paintings that are structured according to the following different layers:

1) The support: The most common used supports, characterized by a high level of stability, are wood, walls and canvas.



FIGURE 2-left: Artistic object in ebonite (hardened rubber) 1878-1900 [8].

FIGURE 3-right: exemplary of daguerreotype, (period of American civil war) obtained by compression molding of a mixture of shellac and sawdust [9].

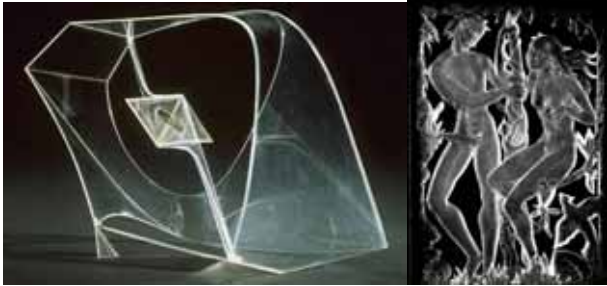


FIGURE 4-left: Work by Naum Gabo “Construction in Space with Crystalline Centre” (1938-40), in polymethylmethacrylate (PMMA) and celluloid [10].

FIGURE 5-right: Sculpture, “Adamo e Eva”, obtained by carving a sheet in polymethylmethacrylate, by Marcel Ronay, (I. C. I.).



FIGURE 6-left: Marcello Morandini, sculpture in PMMA [12].

FIGURE 7-right: Guido Drocco, Franco Mello, *Cactus*, expanded polyurethane (Gufam, 1972) [13].



FIGURE 8: Sculpture in epoxy resin by Frank Gallo, *Awakening Beauty*, USA, 1933 [14].

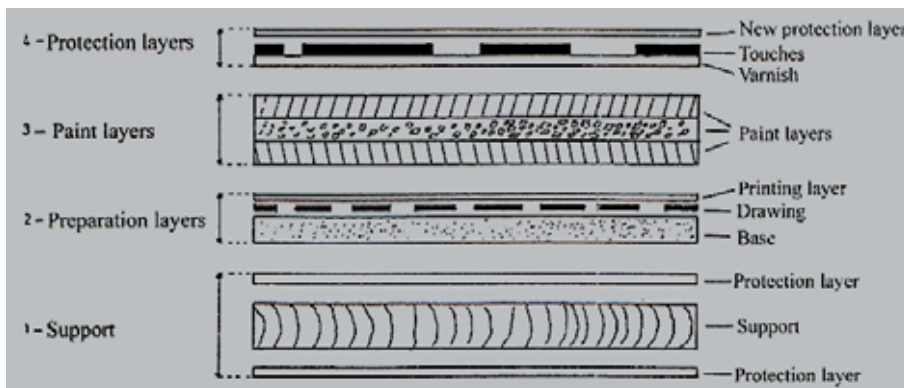


FIGURE 9: Model showing the layer structure of a painting [15].

2) *The preparation layers*: Are composed of a mixture containing binders (animal glues, Arabic gum, casein, oils, eggs, waxes, etc.) and white pigments [gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), chalk (CaCO_3), lead white ($2\text{PbCO}_3 \cdot \text{Pb}(\text{OH})_2$), zing white (ZnO)] or other opaque pigments such as, red and yellow hearth. The artists normally use such a layer for their drawing and template [15,16].

3) *The Painting layers*: Are constituted by pigments/colorants mixed with binders and a vehicle agent (oil or water) which all together form a liquid or paste to be applied to a surface to provide an adherent coat that imparts color to the preparation layer. Generally the binders used in painting layers and in preparation layers have the same nature and chemical structure [15].

4) *The Protective layers*: Are transparent and translucent films, obtained by solidification from a suitable varnish formulation, having as main function that of protecting the underlining painting layers against the environmental factors of degradation (H_2O , SO_x , NO_x , UV light, smog, soot, etc.) [15].

Binders are defined in reference [17] as follows:

< A resin or other cement like material used to hold particles together and provide mechanical strength or to ensure uniform consistency, solidification, or adhesion to a surface coating; typical binder are resin, glue, gum, and casein > [17].

In painting art the binders, while are hardening forming a transparent coat, should be able to fix the pigments and dyes to the preparation layer without influencing their colors.

Binders should also have the capability to:

- Give to paints a high chromatic yield, brightness and brilliancy;
- Implement the solidity of the paints against the physical and chemical factors of deterioration [15,16].

Varnish formulations, used for coating the surfaces of the paintings, according to reference [17] can be defined as follows:

< A transparent surface coating which is applied as a liquid and then changes to a hard solid; all varnishes are solutions of resinous materials in a solvent > [17].

Before the development of synthetic resins several types of natural substances that derived from animal or vegetal world were used as binders in the painting art (as example, terpenes, proteins, polysaccharides, drying oils, etc.).

Just before the Second World War several types of synthetic binders with innovative performances and properties and tailored to be used also in the field of painting art were developed by the chemistry industry.

Such a new products very soon began to replace natural materials. According to R. Mustalish this substitution process happened essentially because:

< They were cheaper and more readily available, especially during World War II, when natural raw materials were difficult to obtain.

They also appealed to artists who wanted to experiment with non traditional materials to create non traditional art > [18].

Some of the characteristics of synthetic binders are below summarized:

- i) Can be easily used;
- ii) Are able to induce brightness;
- iii) Their hardening is very fast;
- iv) The painting film is high elastic;
- v) They may be applied directly on no pre-treated canvas;
- vi) In some cases they may be used also as protective surface varnish.

The denomination and the chemical structure of monomers and of repetitive units of polymers that are the constituents of the most common synthetic binders are shown in figures 10 [16].

Among those reported in figure 10 the most used synthetic binders for artistic paints definitely were the alkyd, vinyl and acrylic resins whose molecular structures are depicted in figure 11 [19].

In 1946 the *Bocour Artists Colors Inc.* developed a line of paints, specific for artistic use, based on acrylic resin dissolved in organic solvent, marketed as *Magna*.

< these highly pigmented paints, which could be thinned with turpentine and used with oils, made them immediately attractive to modern artists such as Morris Louis, Kenneth Noland, Jules Olitski, and Roy Liechtenstein > [18].

In 1955 the *Permanent Pigments Inc.* commercialized the first paint for artists based on acrylic resins dispersed in water (marketed as *Liquitex*). *< Andy Warhol and Helen Frankenthaler were among the first artists to use this new medium > [18].*

The most relevant peculiarities of paints, based on water emulsions of acrylic resins, have been summarized as follows by R. Mustalish [18]:

< --- They can be diluted in water instead of turpentine or paint thinner.

--- They dry very quickly, and, unlike Magna color, they do not resolubilize with the addition of other layers of acrylic. This allows the artist to paint layer upon layer without disturbing the previously applied paint.

--- Acrylics also cause less change to paper and textiles, giving the artist more freedom in choosing supports for the work of art > [18].

Starting from 1950s the acrylic water emulsion based paints were more and more used by artists substituting most of polyvinyl acetate emulsion paints.

According to G. Martinez the introduction of acrylic resins represented a revolution in the field of artistic paintings comparable only to the first use of oil painting by the Flemish painter Van Eyck [14].

It is interesting to point out that now a days most of commercial canvas are prepared by using acrylic emulsion able to impart a higher flexibility in comparison to more traditional substances [20].

The reproductions of three modern paintings based on the utilization of acrylic binders and varnishes are shown in figure 12 [21,22,23].

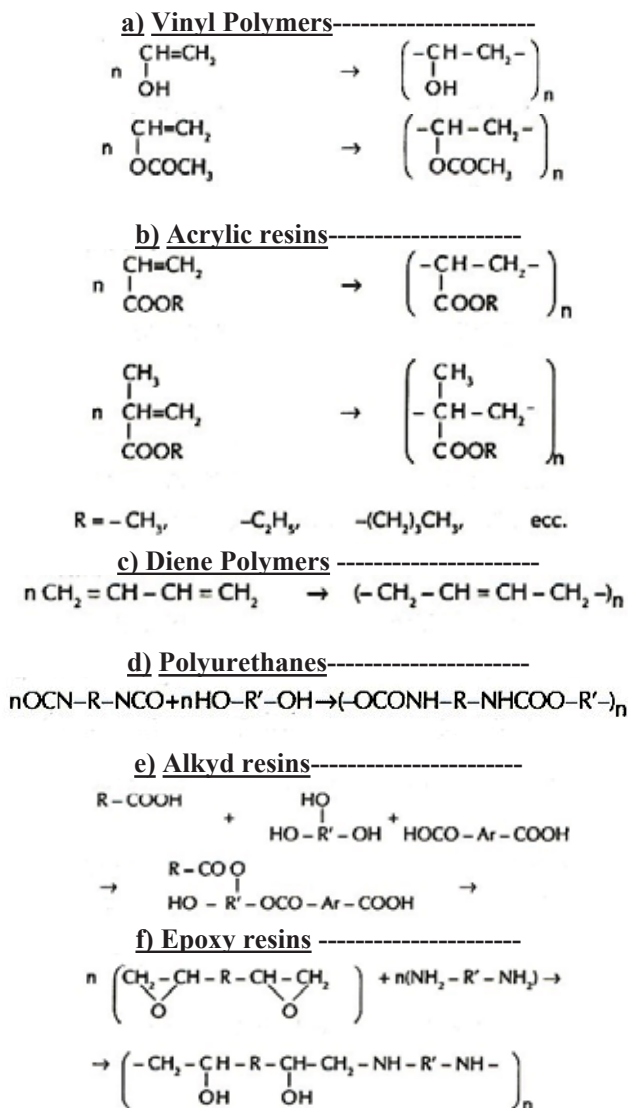


FIGURE 10: Chemical structure of monomers and repetitive units of polymers constituents of most common synthetic binders.

a) Vinyl polymers (vinyl alcohol and poly vinyl alcohol; vinyl acetate and polyvinyl acetate);

b) Acrylic resins (acrylic esters and polyacrylates, meta acrylic esters and poly meta-acrylates); **c)** Diene polymers, butadiene and polybutadiene;

d) Polyurethanes, di-isocyanate and diol, polyurethane; **e)** Alkyd resins (fat acid, polyol and aromatic di-carboxylic acid, alkyd resins);

f) Epoxy resins (di-epoxy monomer and di-amine, epoxy resin cross-linkable) [16].

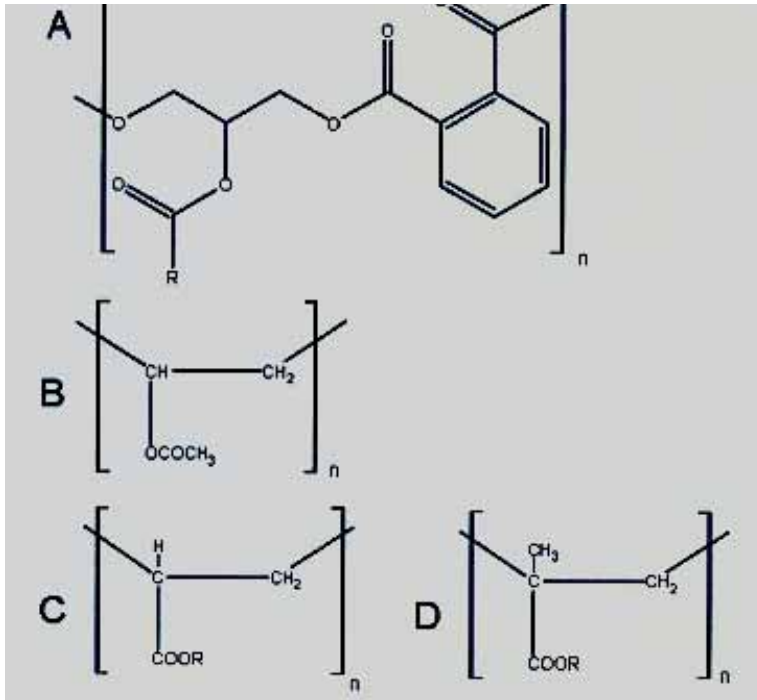


FIGURE 11: Molecular structure of the most used synthetic binders for artistic paints and varnishes.
 A) Alkyd resin based on glycerol; B) Vinyl resin: polyvinylacetate;
 C) Acrylic resin: polyacrylate;
 D) Acrylic resin: poly-meta-acrylate [19].



FIGURE 12: Paintings on canvas of modern artists which used acrylic binders and varnishes.
Left, Riccardo Pierallini, “Festa del’uva a Mendrisio”, [21].
Centre, Pierluigi Pusole, “Noi cannoni”, 1986 [22].
Rigth, Stefano Fiorese, “Medusa” [23].

B) Plastics in items of historical, scientific and cultural interest

Plastics represent an important part of our cultural heritage also for the role they had as components of artefacts, of the latest decades of nineteenth century and of the twentieth century, of historic, scientific and technological relevance [24].

Items produced in plastics or rubber like materials are becoming increasingly present in museum collections essentially because they are a witness of:

1) The evolution of:

- Science, technology and industry;
- Innovative industrial design;
- The production of artefacts with new advanced functions.

2) Events relevant for the history of peoples and nations.

Some significant examples of plastic objects satisfying the above criteria are hereafter presented and described.

Objects in plastics testifying the substitution process of traditional natural materials

Plastics formulation, due to their lower production costs, easier workability and higher rate of production, larger design versatility and possibility to realize items aesthetically more agreeable and light, at the beginning of the “*Plastic Era*”, were largely used for the production of artefacts of large consumption that at the times were made of traditional materials such as ivory, wood, glass, metals, leather, etc.

This phase of *imitation and substitution* [5] led to the birth of new industrial activities while old and consolidated activity were forced to an irreversible crisis that was the origin, quite often, of deleterious and dramatic effects of economical and social nature.

Some interesting examples, which testify this important phase of industrial and technical transformation of our society are below reported and commented in relation to the substituted materials.

--- Objects attesting the substitution of ivory, tortoise-shell and horn with plastics

In 1870 the patent concerning the synthesis of celluloid (the first semi-synthetic plastics invented by J. W. Hyatt, based on a mixture of cellulose nitrate and camphor) was registered in USA. In 1872-1878, Hyatt built the first machines for the manufacturing of celluloid including the first multiple injection mould [8]. As documented by figure 13 celluloid substituted natural materials, such as ivory, tortoise-shell (both materials very expensive and difficult to find on the market) and horn, in making combs and other hair accessories [9].

Ivory was also substituted in the manufacture of billiard balls by the bakelite (first synthetic thermosetting resin, obtained by the controlled reaction of phenol with formaldeide, invented and developed by L. H. Baekeland in 1909) (see figure 14-left) [9].

In figure 14-right is shown the case of the replacing of ebony and ivory with Styrene-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene (ABS) resins (more resistant to household and body chemicals factor of deterioration) in making organ keys.



FIGURE 13: Left, combs manufactured in horn, Leominster, Massachusetts, USA, (latest 1800s) [9].
Right, artistic combs produced in celluloid (early 1900s) [9].

The ABS resins, introduced in the 1940s, are constituted by a two phase systems characterized by a styrene-acrylonitrile copolymer (SAN) co-continuous phase and a dispersed elastomeric phase of a butadiene based rubber. Such a family of resins combines the hardness and the strenght of vinyl plastics with the toughness and impact resistance of the rubbery component.

The manufacturing of billiard balls represents also an interesting case of an intercompetition process between natural, artificial and synthetic plastics. As matter of fact ivory was first substituted by filled guttaperca (*trans*-polyisoprene: a natural polymer extrated from leaves and bark of trees native of Malay, Borneo and Sumatra), then guttaperca was replaced first by celluloid and afterwards by bakelite and ABS.



FIGURE 14: Left, billiard balls made in bakelite [9]. Right, styrene-acrylonitrile (SAN) and acrylonitrile-butadiene-styrene (ABS) resins replaced ebony and ivory in making organ keys [26].

-- Objects attesting the substitution of glass with polymethylmethacrylate (PMMA) and then with polycarbonate (PC)

Polymethylmethacrylate (PMMA, synthesized for the first time by the Rohm and Hass in 1927, Germany) obtained by polymerization of the monomer methyl methacrylate, is one of the most important member of the family of the acrylic resins. The characteristics that led PMMA to substitute in many application glasses were essentially the following:

- High optical clarity (about 92% light transmission);
- High weathering resistance;
- Excellent impact resistance;
- Tasteless and non toxic [27].

Two examples where glass was replaced by PMMA are documented in figure 15 [6,11].

In many sophisticated applications glass was substituted by polycarbonate (on the market since 1957). One of the methods of production of PC is based on the phosgenation of dihydric phenols, usually bisphenol A.



FIGURA 15: Left, decorative artefacts made in PMMA (year 1940) [6]. Right, an aircraft “*gun-sighting*” blown from a sheet of PMMA (I. C. I. Plastics Division, second world war) [11].



FIGURE 16: Example of application of polycarbonate in substitution of glass. Casket for museum collections [28].

Polycarbonate based plastics are recommended for their high degree of transparency, very hard surface, high resistance against environmental factors of degradation and excellent aesthetic qualities [8,27].

Typical application of PC for the production of objects previously made in glass is shown in figure 16 [28,29,30].

--- Records testifying the earlier applications of plastics in the field of sound registration and reproduction.

In 1887 Emile Berliner (a German-born American inventor, 1851-1929) invented and developed the first gramophone whose innovative principles are described as follows in reference [31]:

< The gramophone imprinted grooves on the flat side of a disc rather than the outside of a cylinder. Instead of recording by varying the depth of the groove (vertically), as with the phonograph, the vibration of the recording stylus was across the width of the track (horizontally). The depth of the groove remained constant > [31].

The invention and development of the gramophone led to the birth of the industry of sound registration and reproduction.

In 1893 Berliner introduced a fundamental innovation to the duplication step characterized by the use of a moulding process where a metal master image was pressed on a plastic plate obtained by using a formulation based on shellac (a moldable compound containing a natural resin exuded by red larvae of the insect, *Laccifer lecca*, living on trees twigs of some indian trees, and sawdust as filler). The introduction of such innovation allowed the mass production of records for sound reproduction.

The photograph of a very rare record in shellac is shown in figure 17 [32].



FIGURE 17: A very rare exemplar of record made in shellac [32].

As documented by figure 18-left, in 1912, records in bakelite were successively used. These records according to what reported in literature were characterized by the following properties:

- Hard and practically unbreakable;
- High fidelity;
- High resistance against the wear and tear due to usage.

In 1933 were introduced on the market the first long playing records in vinyl materials, especially in polyvinylchloride (see exemplaries in figure 18-right) [9].

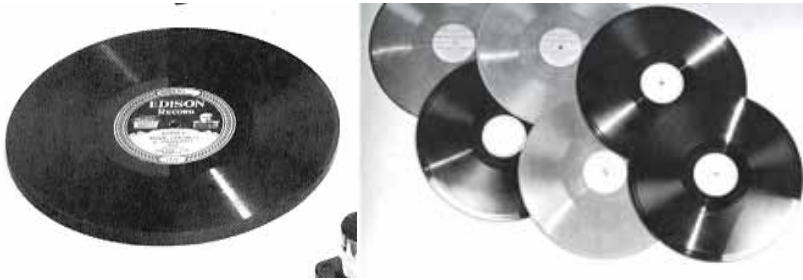


FIGURA18: Left, a record exemplar in bakelite molded in 1912 by Edison. Right, long playing records in vinyl resins presented in 1933 to the “*Century of Progress, the World Fair*” [9]

--- Plastic applications in the sector of reproduction of images.

Plastics strongly contributed to the development of the industry of picture and of motion picture film [8,9].

The history becomes in 1889 when George Eastman (1854 –1932), the founder of the *Eastman Kodak Company*, developed an emulsions coated film made in celluloid, flexible and unbreakable, suitable to be rolled that substituted in potography the rigid coated glass plate. This invention allowed the production of the first box camera for photography.

< *Using box cameras, amateur photographers began to document everyday life in America. Eastman's first simple camera in 1888 was a wooden, light-tight box with a simple lens and shutter that was factory-filled with film. The photographer pushed a button to produce a negative. Once the film was used up, the photographer mailed the camera with the film still in it to the Kodak factory where the film was removed from the camera, processed, and printed. The camera was then reloaded with film and returned* > [33].

The development of the modern cinema industry (the cinema was invented by Louis Le Prince and successively developed by Léon Bouly, Thomas Edison, the Lumière Brothers and Georges Méliès followed by many others) was made possible by the invention of flexible celluloid roll film. This explains why the world of movie past to history as the “*world of the celluloid*”.

Early bobin of flexible celluloid, used by T. Edison for its *kinetoscope* are shown in figure 19.



FIGURA 19: Left and center, early bobbin of flexible celluloid used also by T. Edison for its *kinetoscope* (on left) [8].

FIGURE 20: Right, early magnetic tape in flexible plastic films (see text).

The high flammability of celluloid (*lightninglike burning*) together with the property to deteriorate over time releasing oxidants and acidic gasses (especially HNO_3) led to the development of self extinguish substitutes of celluloid film especially for application in the field of cinematography. In the period 1909-1918 the Eastman Company succeeded in producing cellulose triacetate films more stable, flexible, and fireproof in comparison with those in celluloid. The process of replacement of celluloid films with those made in cellulose triacetate started, following years of research c/o the Kodak Research Laboratory, in 1925. Celluloid films for applications in the field of cinematography and photography were used until the early 1950s. Since then only films in cellulose triacetate were used for the above applications. Tapes produced by BASF (1934) consisting of a foil of cellulose acetate as carrier material, coated with a lacquer of iron oxide as magnetic pigment and cellulose acetate as binder were used in the field of magnetic recording following the development of the first magnetophone machine, in 1930, by the Allgemeine Elektrizitätsgesellschaft [AEG] in Berlin (see figure 20).

Since 1970 flexible films, still more stable than those in cellulose triacetate, and not fire hazard, made in polyester (polyethylene terephthalate-PET) started to be widely used for gelatin coated films for movie and photos applications [34]. From what above reported it emerges the intercompetition between plastics, process that historically followed that of substitution of traditional materials with plastics [2,3,25].

--- Evidences of substitution of wood and metals with plastics in different application sectors

Of great interest as far as the industrial design is concerned was the substitution of wood material with plastics in the manufacturing of cabinets for radio. An example of this interesting case is shown in figure 21 where is documented the replacing of wood with bakelite [35,36].

Plastics were also used in the production of furniture parts, previously made in wood, obtained by injection molding (see figure 22) [6].

An example of application of plastics in the field of electrical instruments in substitution of metals is reported in figure 23 [8].



FIGURE 21 Left: handsome mahogany wood cabinet for radio (*Channel Chief*) [35] **and center,** a bakelite cabinet radio [36].

FIGURE 22 Right: Chest with drawer fronts made by injection molded polystyrene that imitates wood [6].

The reproduction of the one of the first experimental car body, totally in thermoformed acrylonitrile-butadiene-styrene, made in 1970 is shown in figure 24 . This model pre-announced the future and intensive application of plastics in the car body industry [9].

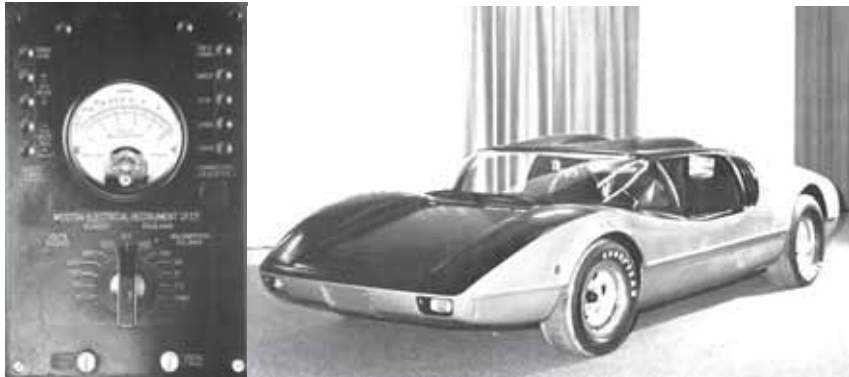


FIGURE 23, left: Application of plastics in the field of electrical instruments in substitution of metals [8].

FIGURE 24, right: Experimental car body totally in thermoformed acrylonitrile-butadiene-styrene made in 1970 [9].

--- Early plastic applications in the field of toys and jewelry

Early exemplaries of toys manufactured in celluloid are reported in figure 25 [37].
Plastics will be more and more used in such an application. Materials such as wood, ceramics, paper-pulp and others were substituted, giving rise to an industrial sector highly relevant from economic and social point of view.



FIGURE 25, left: Toys in celluloid, Italy, 1920-1930. [37].

FIGURA 26, right: The application of early plastics in the field of artistic *bijouterie*. Parure in bakelite and steel, France, 1925 [37].



FIGURE 27: The radio-field, kept at the “Museo dell'Arsenale della Marina Militare”, La Spezia”, used during the expedition of the aircraft “*Italia*” to the North Pole.
The frontal part is made in hardened rubber.

Because of their specific characteristics plastics were also successfully applied in the manufacturing of jewels with elegant coloured and innovative design. An exemplary is shown in figure 26 [37].

--- Objects in plastics attesting events relevant for the history of peoples and nations.

Many are the artefacts in plastics or containing parts in plastics that are exposed in museums as they represent a testimonancy of important pregnant events, mile stones of our history.

The radio-field (receiver and transmitter, called *Ondina*), kept at the “*Museo dell'Arsenale della Marina Militare*” (La Spezia), Italy, used during the famous expedition of the aircraft “*Italia*” to the North Pole (1928) represents a typical case of item being part of above mentioned category. As shown in figure 27 the frontal part of this radio was made in ebonite (hardened rubber).

DEGRADATION OF PLASTICS ARTEFACTS AND CONSERVATION ISSUES

The relevant number of objects made in plastics of artistic or technical and scientific interest, more and more collected in various museums all over the world, being recognized as part of our cultural heritage, need to be safeguarded in order to allow their fruition to the future generations.

Since the last decades the concern about the proper conservation of plastic artefacts is growing as many conservatorists noted alarming symptoms of degradation (discoloration, fading, blooming, crazing etc.) in most of objects collected.

The term “**degradation**”, in the case of plastics, includes a broad type of processes characterized by different mechanisms of action giving rise to modifications at molecular level able to determine in the long run relevant detrimental effects on the chemical, physical, mechanical and haestetical properties of the objects.

The understanding and then the prevention of degradation phenomena occurring in artefacts in plastics is particularly difficult for the following reasons:

- Plastics are based upon a wide range of polymer families having different chemical structure, molecular mass, types of interaction between macromolecules, functional groups, morphology, crystallinity and then use properties.
- Plastics are multicomponent systems. The basic polymer constituent is compounded with a variety of additives (varying in amounts from fractions of a % to tens of %) used to assist the manufacturing process, improve the service performance of the product, enhance the appearance of the material or reduce cost. Typical additives include, colorants, fillers, stabilizers, UV absorbers, plasticisers, lubricants, etc.
- All commercially used methodologies of polymer synthesis inevitably lead to the production of macromolecules with an unknown amount of chain defects that can be potential sites for the initiation of degradation reactions.
- The use of catalysts in most of polymerization reactions quite often leave in the polymer mass traces of metals such as aluminium, nickel, ecc. Such impurities even at very low concentration (ppm) may play an important role in catalysing degradation processes.
- Polymer materials undergo degradation already during the manufacturing processes (compression moulding, extrusion, injection moulding, ecc.) where they suffer the combined action of mechanical stresses, heat and oxygen.

< Polymers must usually be heated to high temperatures - considerably higher than their melting point - before they can be processed. Although thermal stabilisersare added to polymers during processing, some thermal degradation still takes place. Mechanical degradation due to chain-scission also occurs as a consequence of the high shear which the polymer melts are subjected to during injection moulding and extrusion moulding. These processes are often followed by rapid quenching, resulting in the formation of internal stresses > [38].

■ Plastics artefacts, according to their use functions in the course of the service life may be exposed to the action of various factors of degradation (heat, light, moisture, environment chemical pollutants and UV-radiation) which may contribute to the acceleration of deterioration phenomena and whose effects may overlap in an uncontrolled way. Thus it is not easy to distinguish who of the deterioration factors is/has been the one most effective.

■ Some plastics additives are able to induce degradation reactions by interacting with radiations, oxygen or other chemical agents. Some other additives may migrate towards the surface creating physical defects in the material.

Generally when artefacts in plastics are taken in the hands of conservatorists, becoming part of a private or public museum collection, they are already interested by degradation phenomena whose origins, causes and deepness of the damage are not easy to be assessed as they depends in a very complex manner by a combined action of several deterioration factors .

Thus the investigation of the degradation processes of plastics is made still more complicated by the observed concomitant attack of various factors of deterioration, which act with different mechanisms based on chemical reactions happening in solid phase and in heterogenous systems.

In order to adopt the most appropriate conservation actions (they include direct restoration, protection methodologies, the remotion of harmful contaminants and degradation products and the application of proper prevention techniques to control and reduce the rate of damaging) the plastic composition, including the nature and chemical structure of components as well as the manufacturing process must be preliminarily determined by using suitable analytical diagnostic techniques.

As shown by figure 28 the degradation, if not controlled, may lead to the total disruption of a plastic artefact [39].



FIGURE 28: An example of how similar artefacts, made by celluloid (an artificial plastics), may present different degree of degradation. Left, Fan (1920) with a good state of conservation. Right, Fan completely disintegrated [39].

Once the nature of constituents of the plastic material used for manufacturing an artefact has been determined then in order to protect the object from further damaging it is necessary to know how the external or environmental factors of degradation may still have detrimental effects on the objects.

Hereafter the typology, the nature and the properties of the most common external factors of damaging are described in relation to the chemical mechanisms that at molecular level lead to the modification and alteration of plastic materials. Moreover the mechanisms of action of the various ageing agents are also described in relation to:

--- The structure and the characteristics of the various families of polymers (that is, crystallinity, glass transition temperature, presence of functional groups, tertiary hydrogen atoms along the chains, ecc.).

- The chemical structure and function of additives used.
- The typology of manufacturing processes.
- The presence, eventually, of impurities [40,41].

The role of some of the most relevant intrinsic characteristics of the base polymers, as well as the role of the nature and function of additives against the inherent or external deterioration of plastics will be discussed in the next chapters of the present book.

It must be pointed out that in the present first-volume only plastics belonging to the “*Pre-Synthetic Era*” that is plastics obtained by physical and/or chemical transformation of natural macromolecules already present in the vegetal or animal world [i.e. horn, hoof, bois durci, natural rubber (hard and soft rubber), casein and cellulose derivatives (cellulose-nitrate and cellulose acetate)] will be taken into consideration leaving to a second volume the analysis of the most relevant plastics made by man thus belonging to the “*Synthetic Era*”.

REFERENCES

- 1) E. Martuscelli, *La Chimica e L'Industria*, RICHMAC-Magazine-**80**, 355 (1998).
- 2) E. Martuscelli, < *Dalla scoperta di Natta lo sviluppo dell'industria e della ricerca sulle plastiche in Italia* >, Consiglio Nazionale delle Ricerche, Serie Scienze Chimiche, Roma (2001).
- 3) E. Martuscelli, < *le plastiche nel terzo millennio* >, dossier le plastiche, *Ricerca & Futuro*, 23, 46 (2002).
- 4) G. Williams, *Conservation Journal*, October (1996).
http://www.vam.ac.uk/files/file_upload/42730_file.pdf.
- 5) E. Martuscelli, *La Chimica e L'Industria*, RICHMAC-Magazine-**77**, 538 (1995).
- 6) Jeffrey I. Meikle, < *American plastic, a cultural history* >, Rutgers University press (1995).
- 7) M. Derrick, S. Stulik, E. Ordonez, < *Cellulose nitrate deterioration in constructivist sculptures made by Gabo and Pevsner* >, Polymer Preprints, Division of Polymer Chemistry, Inc. , American Chemical Society, **33**, N.2, 637 (1992).
- 8) L. Scacchi Gracco, < *Pensieri di Plastica* > A. Mondatori Editore, Milano (1986).
- 9) J. Harry DuBois < *Plastics History USA* > Cahners Books, Boston (1972).
- 10) <http://fusionanomaly.net/naumgabo.html>, (2008).
- 11) J. Gordon Cook, < *Your guide to Plastics* >, Merrows Publishing CO LTD, England (1964)
- 12) [www.exibart.com/.../rev/723/rev50723\(1\)-ori.jpg](http://www.exibart.com/.../rev/723/rev50723(1)-ori.jpg), (2008).
<http://www.sapere.it/tca/minisite/arte/nonsolomostre/2004map/map06.html>, (2008).
- 13) G. Pettena < *arte/ architettura/ambiente 26, radical design: ricerca e progetto dagli anni '60 ad oggi* >,
http://www.ca.archiworld.it/riviste/rivista_arch/anno_2004/luglio/pag%2026-28.pdf.
- 14) G. Martinez, *Revista de Plasticos Modernos*, **89**,73 (2005).
- 15) A. C. Orti, < *Los Metodos de Analisis Fisico-Quimicos y la Historia del Arte* >, Universidad de Granada: Granada, chapter 2 (1994).
- 16) V. Massa, G. Scicolone, < *Le vernici per il restauro* >, Nardini Editore, Firenze (1991).
- 17) < *Dizionario Enciclopedico Scientifico e Tecnico* > , McGraw-Hill, Zanichelli, Bologna (1985).
- 18) R. Mustalish, "Modern Materials: Plastics". In *Heilbrunn Timeline of Art History*. New York: The Metropolitan Museum of Art (2000).
http://www.metmuseum.org/toah/hd/mome/hd_mome.htm (October 2004)
- 19) F. Cappelletti, *KERMES*, **47**, anno XV, 35, Luglio/Settembre (2002).
- 20) L. Borgioli, P. Cremonesi, < *Le resine sintetiche usate nel trattamento di opere policrome* >, il Prato, Padova (2005).
- 21) http://www.apst.ch/m_pieralliniriccardo_opere.htm, (2008).
- 22) http://www.artesegno.com/pgs_Operas/opr_Artist.asp?ID=59, (2008).
- 23) <http://www.arte-sanlorenzo.it/galleria2opere.php?id=12>, (2008).
- 24) A. Coppola, < *La legislazione sui Beni Culturali e Ambientali* >, Ed. Giuridiche Simone, Napoli (2000).
- 25) E. Martuscelli, < *Le fibre di polimeri naturali nell'evoluzione della civiltà: le fibre di seta* >, Consiglio Nazionale delle Ricerche, Serie Scienze Chimiche, Roma (1999).
- 26) J. H. duBois, F. W. Frederick, < *Plastics* >, Van Nostrand Rheinold Company (1981).
- 27) Lloyd R. Whittington, < *Whittington's Dictionary of Plastics* >, Technomic, USA (1978).
- 28) www.edilportale.com/.../prodotti-2995-fot7.jpg, (2008).
- 29) shop.dime-italy.com/catalogo/..%5CIMMAGINI%5C, (2008).
- 30) www.zavaluce.it/prod/img2/mini/sl-12.jpg, (2008).
- 31) http://en.wikipedia.org/wiki/History_of_sound_recording, (2008).
- 32) http://www.fonoteca.ch/yellow/soundCarriers/shellack_it.htm, (2008).
- 33) <http://inventors.about.com/library/inventors/blphotographytwo.htm>, (2008).

- 34) D. Matè, M. C. Sclocchi, D. Ruggiero, < *KERMES* >, **47**, 41 (2002).
- 35) www.geocities.com/.../bogen-bb1a-ivory.jpg, (2008).
- 36) www.radiolaguy.com/images/Belmont638s.jpg, (2008).
- 37) < *Gli anni di plastica* >, Gruppo Montedison, Electa, Milano (1983).
- 38) E. Then, V. Oakley, *Conservation Journal*, < A Survey of Plastic Objects at The Victoria and Albert Museum >, **Number 6**, January (1993)
http://www.vam.ac.uk/res_cons/conservation/journal/conservation_journal_6/plastic_objects/index.html, (2008).
- 39) S. C. Stinson, < *Chemical & Engineering News* >, September **9**, 34 (1996).
- 40) E. Martuscelli, < *Plastics in Art (in Cultural Heritage) - Plastics for Art (for Cultural Heritage)* >, Lecture presented at Programma Giornata AIM on “Il restauro e la diagnostica degli oggetti d’arte e di design in plastica”, 31/10/(2008).
- 41) E. Martuscelli, < *La Chimica Macromolecolare Applicata alla Conservazione dei Manufatti Lapidari* >, PAIDEIA, Firenze (2007).

SECTION-1

SECOND -CHAPTER

THE INTRINSIC CHARACTERISTICS OF POLYMERS OF RELEVANCE AS FAR AS THEIR DEGRADATION BEHAVIOUR IS CONCERNED

1) Morphology, Crystallinity and Glass Transition Temperature

Polymers may be divided in two classes:

- a) Crystallizable;
- b) Non-Crystallizable or Amorphous [1-3].

Crystallizable polymers are characterized by the fact that each of the constituent chains are regular from constitutional and configurational point of view. Moreover those chains are able to be associated in the crystals by assuming the same stable conformation (i.e. a three-dimensional geometry) with the minimum internal energy. For example in the case of crystals of polyethylene the chains assume in the crystals a trans planar conformation where all carbon atoms lay in a plane (see figure 1). In isotactic polypropylene the crystal structure is based on a close packing of macromolecules with a 3/1 helix conformation (see figure 2) [4].

Natural and man made crystallizable polymers are always characterised by the co-presence in the bulk of ordered and disordered phases (crystalline and amorphous regions respectively).

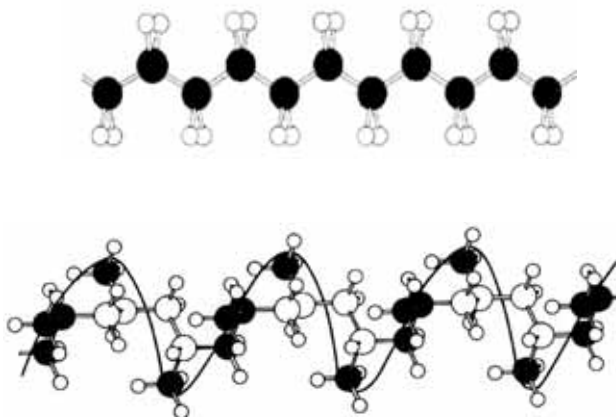


FIGURE 1, top: A regular polyethylene chain with a trans planar conformation [4].

FIGURE 2, bottom: An isotactic polypropylene regular chain with a 3/1 helix conformation [4].

The morphology and the structure of semi-crystalline polymers in the bulk may be qualitatively described by the modified fringed micelle model represented in figure 3. According to such model the crystalline phases are embedded in a continuous amorphous matrix. The model forecasts that segments of the same chain may be part of disordered regions and others of ordered ones. This means that crystals and amorphous phases cannot be physically separated.

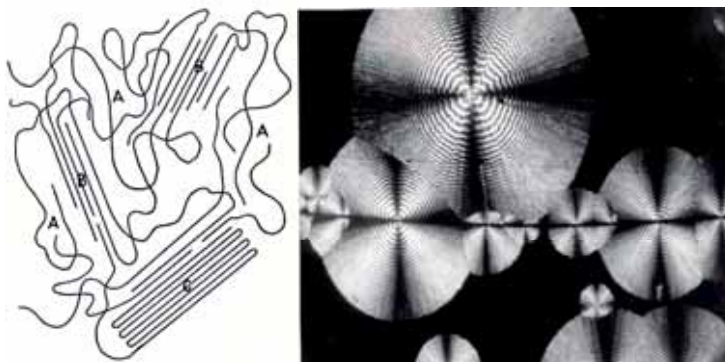


FIGURE 3, left: Modified “*Fringed micelle*” model for semicrystalline polymers. A= amorphous region; B= crystallite; C= crystallite with chain folding [4].

FIGURE 4, right: Crystalline polymers crystallize from the melt according to a complicated three dimensional branched spherulitic morphology. In figure is reported an optical micrograph showing spherulites of polyhydroxybutyrate grown isothermally in thin films from the melt [5].

In many polymers crystallized from the melt it has been observed that the crystalline regions may organize them self in larger and ordered structures ($> 10^{-4}$ cm), called spherulites, which can be easily seen under optical microscope (see example in figure 4) [4].

In the case of non-crystallizable polymers the chains form a random coiled interconnected structure ,often called *spaghetti like*, qualitatively described in figure 5.

The presence of two phase structure in crystalline polymers may be evidenced by means of methodologies based on wide angle X-ray diffraction (WAXS) and thermal analysis, especially differentials scanning calorimetry (DSC). The application of this methods also allows to stand out how polymers (amorphous and crystalline) quite often behave differently from low molecular mass compounds particularly as far as transitions and transformation, following heating or cooling, are considered.

In figure 6-left the Volume/Temperature relationships is schematically represented in the case of a low molecular weight crystalline and amorphous glassy substances (curve, a and b, respectively) [6]. From the trend of the curves it results that on cooling an abrupt volume change occurs at the crystallization temperature (first-order liquid-solid transition), see curve a) in figure 6-left).

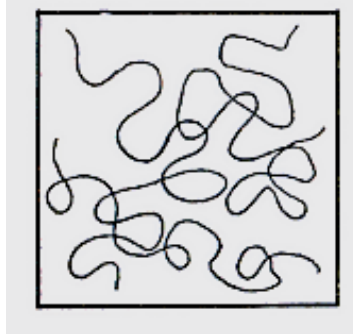


FIGURE 5: Random coiled structuration of macromolecules in the bulk for an amorphous non-crystallizable polymers.

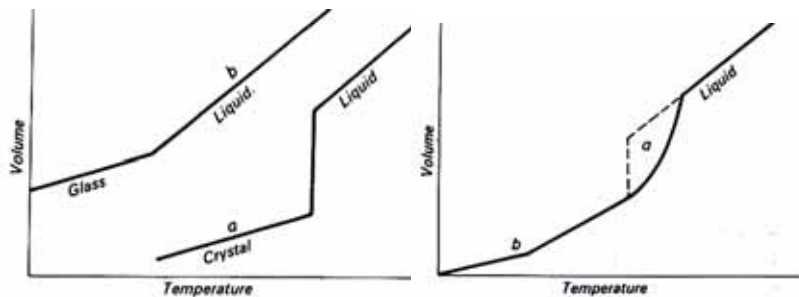


FIGURE 6: Volume/Temperature relationships for:
Left, Low molecular weight crystal [curve a)] and glass [curve b)].
Right, Semi-crystalline polymer. a) = first order transition due to the crystallization process, dashed line, and to the melting process, solid line; b) = second order transition, at T_g , related to the amorphous content in the polymer material [6].

In the case of glasses, being amorphous in nature, the Volume/Temperature curves present, at the glass transition temperature (T_g) only a change in the slope [see curve b) in figure 6, left]. It is well known that T_g represents, on cooling, the temperature where the molecules lose degrees of freedom and consequently their long range mobility is drastically reduced (the transition from liquid to glassy state is a second-order transition) [6]. As shown in figure 6, right, in the case of a crystalline polymers, the V/T curves show the presence of the two transitions (a) and b)).

The presence of both amorphous and crystalline phases in crystalline polymers may be easily evidenced also by DSC thermograms. As example in figure 7 is reproduced the DSC thermogram of polyethyleneterephthalate (PET), a typical crystallizable polymer. From such a diagram, as indicated in figure 7, the values of T_g and T_m are easily determined [7].

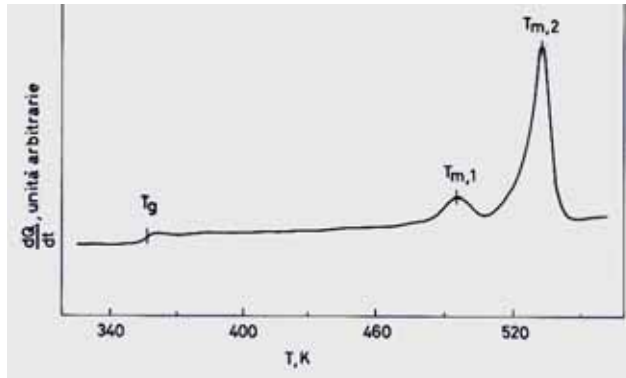


FIGURE 7: DSC thermogram of polyethyleneterephthalate crystallized from the glassy. Are visible the glass transition temperature(T_g) and the melting endotherms ($T_{m,1}$ and $T_{m,2}$) [7].

The wide angle X-ray diffraction technique turns to be very useful not only in to put in evidence the co-existence in crystalline polymer of ordered and disordered regions but also in determine the degree of crystallinity (X_c), hereafter defined.

In the case of validity for a semicrystalline polymer of a two phase model, characterized by the presence of amorphous and crystalline regions, then the crystalline mass fraction (usually named as mass degree of crystallinity X_c) is given by the following equation:

$$X_c = M_c / [M_c + M_a] \quad (1)$$

Were M_c and M_a are the masses of the crystalline and of amorphous regions respectively.

The X-ray diffractograms of semicrystalline polymers, as shown in figure 8, differ from those of low molecular weight substances as in the former the crystalline peaks are super-imposed to the continuous, diffuse scattering halo due to the amorphous component (compare diffractogram of NaCl with those of polymers).

Such a behaviour is the base for the determination of X_c from X-ray diffractograms. The method assumes that the overall intensity of X-ray diffracted by the crystalline regions is proportional to the number of electrons, that is, to the mass of the diffracting phase (M_c) and then to the sum of the peaks areas measured from the diffractograms. By analogy the whole intensity of the continuous scattering is assumed to be proportional to the amorphous mass in the material and then to the halo area. The separation methods of the areas corresponding to the crystalline and amorphous contribute are shown in figure 8 for low density polyethylene and isotactic polystyrene and in figure 9 for isotactic polypropylene [4,7,8, 9]. Thus from above the equation 1 becomes:

$$X_c = \sum A^{ic} / [\sum A^{ic} + \sum A^{ia}] \quad (2)$$

Where $\sum A^{ic}$ and $\sum A^{ia}$ are the summation of the areas of the crystalline peaks and of continuous scattering respectively (see figure 9).

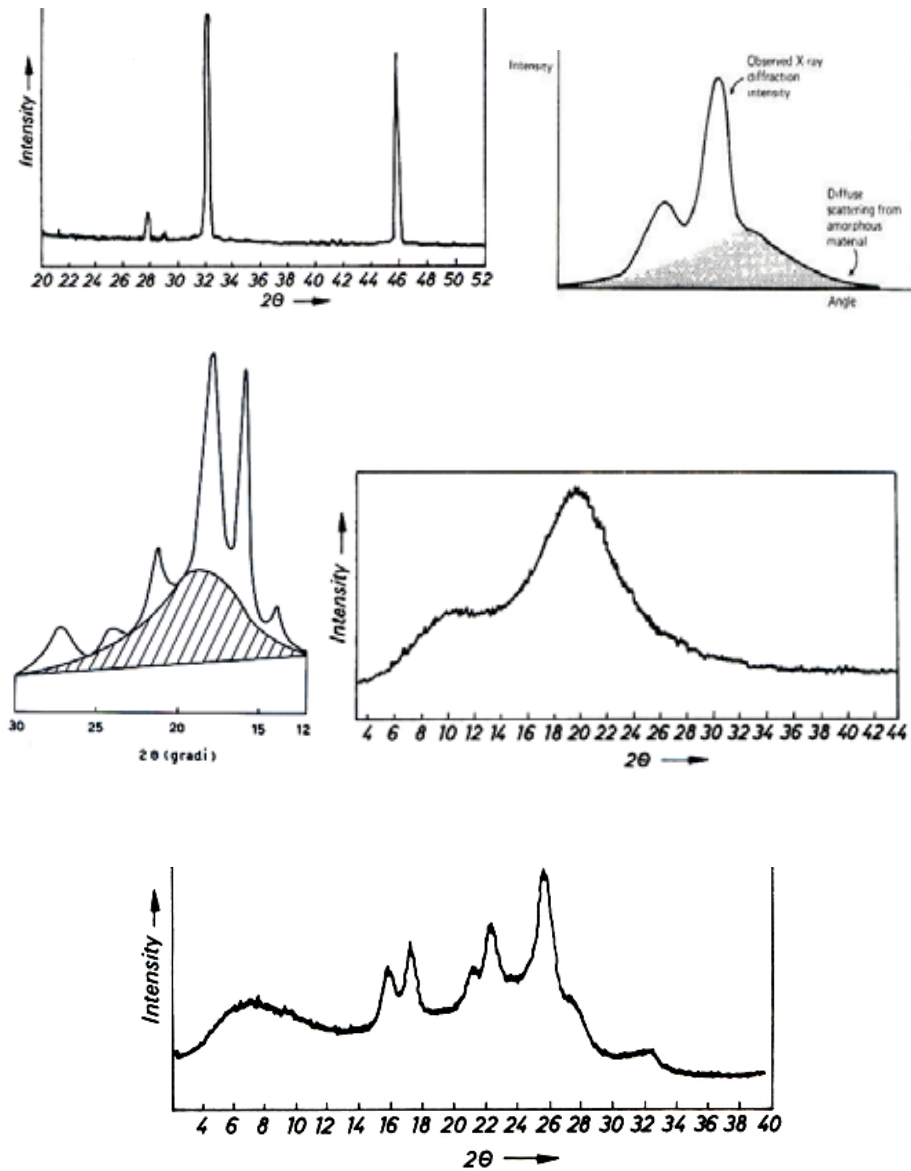


FIGURE 8: X-ray diffractograms of:
Top-left, table salt (NaCl).
Top-right, low density polyethylene (crystalline).
Centre-left, isotactic (crystalline) polystyrene.
Centre-right, atactic (amorphous) polystyrene.
Bottom, polyethyleneterephthalate (crystalline)
 [4,7,8].

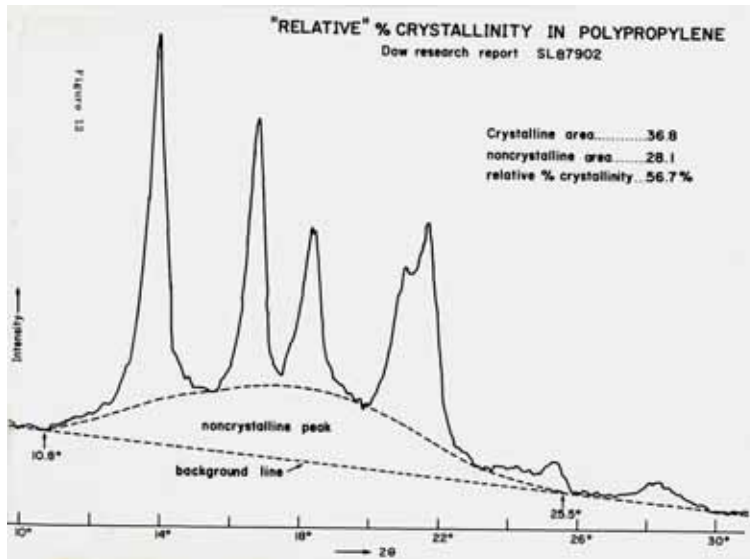


FIGURE 9: The method of peaks separation followed to determine the relative value of the degree of crystallinity in the case of isotactic polypropylene [9].

It is interesting to point out that the X-ray diffractometry is a very useful technique for the recognition of the nature of polymer constituent in a plastic artefact as every crystalline polymer, as shown in figure 8 and 9, exhibits diffraction peaks whose Bragg's angles and intensities are strictly related to their molecular and crystal structures and to the way macromolecules are packed in the solid state (see examples in figure 10) [10].

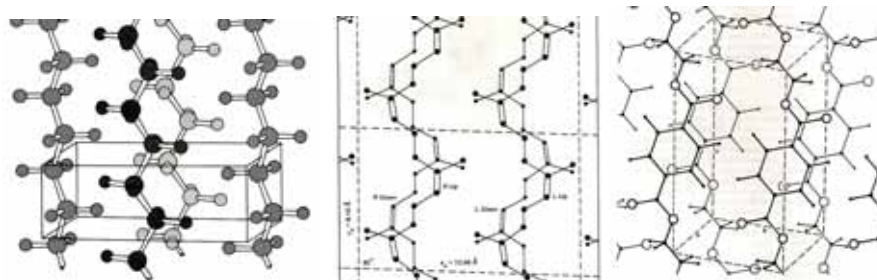


FIGURE 10: Chain arrangement of polymer macromolecules in the crystalline unit cell.
Left, Polyethylene. Centre, Natural rubber. Right, Polyethyleneterephthalate [10].

As for low molecular weight substances also for crystalline polymer the diffraction of X-rays may be interpreted, with reference to figure 11, assuming that the diffracted beams are reflected at specific angles by bundles of parallel lattice planes constituted by atoms or molecules or ions. According to Bragg's rule, for a given wave length λ of incident X-ray, reflections occur at precise values of θ only when the interplanar d-spacing of the diffracting bundles of parallel crystallographic planes satisfies the following equation:

$$n \lambda = 2d \sin\theta \quad (3)$$

where n = order of reflection; λ = X-ray wave length; d = interplanar spacing of the set of planes of this order; θ = angle between "diffracting plane" and "incident X-ray beam", and the "diffracting plane" and the "reflected beam" (see figure 11).

Equation (3), by including n in the *Miller* "reflection indices" (hkl) of the diffracting planes, becomes [9,11].

$$\sin\theta_{(hkl)} = \lambda / 2d_{(hkl)} \quad (4)$$

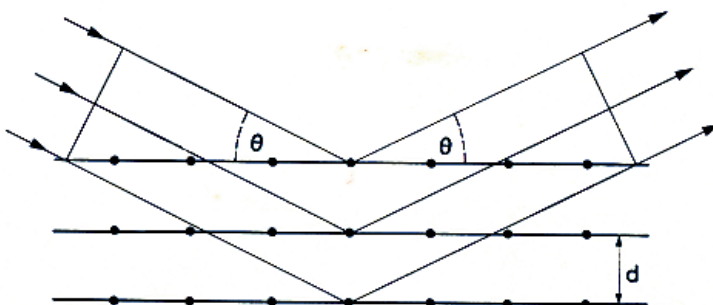


FIGURE 11: Geometry of X-ray diffraction by a bundle an atomic plane, belonging to a crystal lattice, according to the Bragg theory.

The angle 2θ of a reflection corresponding to a set of plane with hkl indices is function of the unit cell geometry, while the intensity of the peak diffraction depends upon the positions and nature of the atoms, molecules or ions in the crystal.

An example of an X-ray diffractogram, regarding a sample of highly crystalline polyethylene, on which all reflections have been indexed with *Miller* notation, and on which d-spacing have been calculated by means of the Bragg equation, is reported in figure 12 [9].

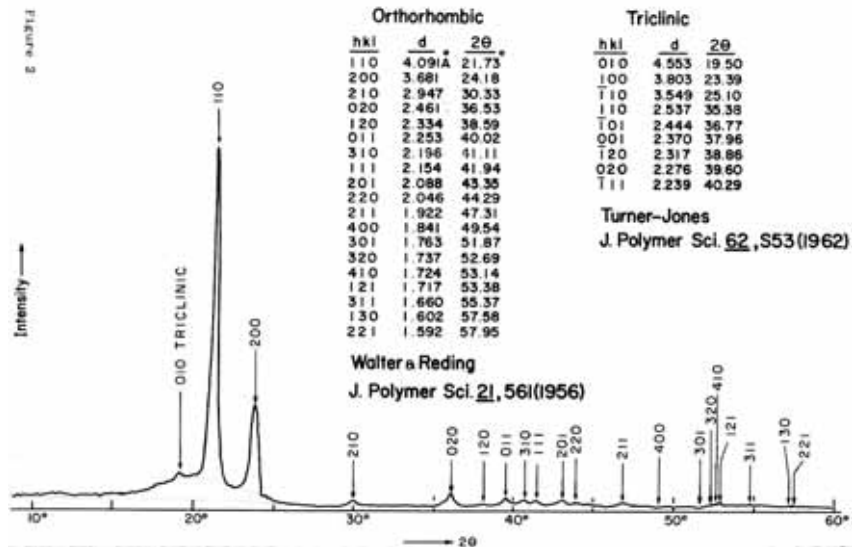


FIGURE 12: X-ray diffractogram of a highly crystalline polyethylene sample on which all reflections have been indexed with *Miller* notation, and on which d-spacing have been calculated by means of the Bragg equation [9].

Effect of crystallinity on polymer properties

The values of the degree of crystallinity for some common polymers are reported in table 1 [12]. For a given crystallizable polymer the X_c is not a constant as its value varies according to the:

- Conditions of polymerization;
- Method of processing;
- Mechanical treatment (e.g. drawing);
- Thermal treatment;
- Conditions of crystallization [12].

Correspondingly many of its properties (overall density and heat of melting, elastic modulus, permeability, ecc.) may change with the crystalline content (see examples in figure 13 concerning some polyethylene samples) [10,13].

Generally it is found, that under comparable conditions, polymer samples with higher density and crystallinity are more brittle and easily fracture at RT, while as the level of X_c is reduced they becomes tougher and more flexible. Such a behaviour is in agreement with the increasing trend of the elastic modulus with fraction crystalline observed in figure 13-bottom [10].

As will be widely discussed in one of the next paragraphs, in the case of polymers, also the barrier resistance to liquid and gaseous permeants is strongly dependent on crystallinity [13,14].

TABLE 1: Degree of crystallinity
(X_c 100) for typical polymers [12].

Natural rubber (crystalline)	20–30
Gutta-percha	55–60
Polythene (low-density)	55–75
Polythene (high-density)	80–95
Nylon (fibre)	50–60
Terylene (fibre)	60
Cellulose (cotton, flax)	70
Cellulose (viscose rayon)	40
Polypropylene (fibre)	55–60

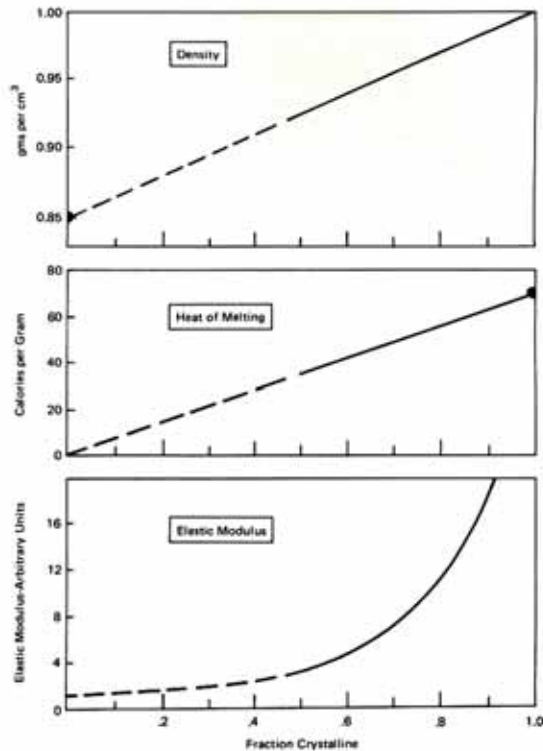


FIGURE 13: The dependence of density, heat of melting and elastic modulus upon crystallinity for polyethylene samples [10].

Relationships between glass transition temperature and polymer properties

The values of the glass transition temperatures of some common polymers, together with the molecular structure of the repeating units are reported in figure 14 [12].

The glass transition temperature T_g , associated essentially to the disordered phase of polymers < is usually interpreted as the temperature at which segments of polymer chains attain sufficient thermal energy to excute coordinate movement. Below T_g , the chain atoms, are as in a solid essentially frozen, and the polymer in consequence is hard and glass. Above T_g , the coordinated motion of several segments confers on the polymer the characteristic rubber-like properties > [11].

Polymer	Repeating unit	Transition temp. (°C)
Silicone rubber	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{Si}-\text{O}- \\ \\ \text{CH}_3 \end{array}$	-125
Polybutadiene	$-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}_2-$	-85
Polyisobutylene (butyl rubber)	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{C}-\text{CH}_2- \\ \\ \text{CH}_3 \end{array}$	-70
Natural rubber	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \\ \\ \text{Cl} \end{array}$	-70
Polychloroprene (neoprene rubber)	$\begin{array}{c} \text{Cl} \\ \\ -\text{CH}_2-\text{C}=\text{CH}-\text{CH}_2- \\ \\ \text{Cl} \end{array}$	-50
Poly (vinyl chloride) (P.V.C.)	$\begin{array}{c} \text{Cl} \\ \\ -\text{CH}_2-\text{CH}- \\ \\ \text{Cl} \end{array}$	+80
Poly (methyl methacrylate) (perspex)	$\begin{array}{c} \text{CH}_3 \\ \\ -\text{CH}_2-\text{C}- \\ \\ \text{C}=\text{O} \\ \\ \text{O} \\ \\ \text{CH}_3 \end{array}$	+100
Polystyrene	$\begin{array}{c} -\text{CH}_2-\text{CH}- \\ \\ \text{C} \\ / \quad \backslash \\ \text{HC} \quad \text{CH} \\ \quad \quad \\ \text{HC} \quad \quad \text{CH} \\ \backslash \quad / \\ \text{C} \\ \\ \text{H} \end{array}$	+100

FIGURE 14: Values of the glass transition temperature for some common polymers. The molecular structure of the repeating units is also represented [12].

The T_g represents an important characteristic for a polymer materials as its value determines, at a given reference temperature (T), if the polymer behaves like a rubber [$T_g < T$] or as a glass [$T_g > T$]. Thus according to the values reported in figure14, at room temperature, PVC, PMMA and PS behave as a glassy, on the contrary natural and silicon rubbers are rubbery. Of course PVC, PMMA and PS behave like a rubber at $T >$ than their T_g .

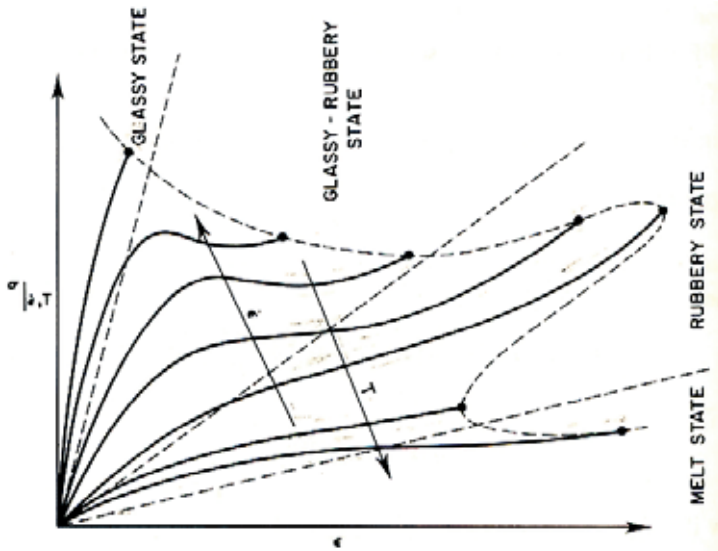


FIGURE 15: Extensibility (ϵ - abscissa) of a generic polymer as a function of temperature and strain rate (σ , T- ordinate) [15].

Such a behaviour results from figure 15 where typical tensile stress/strain curves for a generic polymer (tested at constant strain rate or stress under isochronous conditions) over a range of temperatures between the glassy state and the melt are shown [15].

From the trend of the curves it emerges that the extensibility of the polymer is high in the rubbery state while in the glass state the polymer presents a high rigidity and reduced extensibility.

For a given polymer the T_g is not a constant as it varies with the following factors:

1) Average molecular mass (M_{av}) - T_g decreases with the lowering of M_{av} . T_g and M_{av} are related through the following Flory-Fox equation:

$$T_g = T_g(\infty) - K_{FF} / M_{av} \quad (5)$$

Where $T_g(\infty)$ is the values of T_g for infinite value of M_{av} and K_{FF} is a constant [16].

2) Cross-links - T_g increases with the increase of the degree of cross-links. This behaviour is accounted for by assuming that the introduction of cross-links reduces the molecular mobility.

The dependence of T_g from the density of cross-links (x) may be described through the Fox and Lashaek equation:

$$T_g(x) = T_g(\infty) + K' x \quad (6)$$

3) Crystallinity – Samples with high values of X_c have higher T_g . It has been observed that for nylon-6 when the crystallinity rises from 5% to 50% the corresponding value of T_g increase of $\approx 13^\circ\text{C}$ [16].

4) Presence of monomer, solvent or plasticisers – All these substances, by decreasing interchain forces, cause a more or less pronounced lowering of T_g . For example in the case of PVC the addition of Dioctyl phthalate (Di-Ph) as plasticiser determines a reduction in T_g that is proportional to its content %. The values of T_g of PVC may decrease from $+80^\circ\text{C}$ to $\approx 0^\circ\text{C}$ for a formulations containing high % of Di-Ph ($> 40\%$).

5) Presence of water (Water absorption process) – All polymer materials absorb, to some extent, molecules of water. The amount of water absorbed depends upon molecular structure of polymers. As matter of fact it varies from about zero for polytetrafluoroethylene (PTFE) to complete solubility in the case of some types of polyvinylalcohol (PVA) and polyethyleneoxide (PEO). Water absorption may induce many different kind of deleterious effects such as:

- Swelling;
- Dissolving;
- Leaching (the process of extraction of additives from the bulk);
- Plasticizing;
- Hydrolyzing;
- Lowering the resistance to heat and to weathering;
- Stress cracking.

In the field of conservation of plastic artefacts the absorption of water may be the cause of further damaging effects as it may vehiculate dissolved environmental chemical reactive agents (acids, gaseous substances, ecc.).

For a given polymer, at constant temperature and pressure, the amount of water absorbed depends on the value of the:

- Environmental relative humidity (RH), that is the ratio of the quantity of water vapour present in the atmosphere to the quantity which would saturate it at the fixed temperature [at constant time and temperature, the amount of absorbed water increases with the increase of RH values (see example in figure 16, where isotherm curves of water absorption for nylon-66 are shown)].
- T_g ;
- Crystallinity and T_m [16,17,18,19,20].

Water absorption is a very important factors especially in the case of polyamides and proteins both being characterized by an high tendency in to absorb water from the environment.

For most of such polymers water is a swelling agent for the macromolecules located in the amorphous domains. Consequently the values of T_g decrease with the increase of the amount of absorbed water.

This conclusion find support in the data reported in table 2 from which it results that the influence of water content upon the T_g , in the case of various types of polyamides depends strongly on the molecular structure of the repeating units and moreover that for a given polymer T_g strongly decreases with the increase of RH (see the cases of polyamide 6 (PA-6) and Pa-66) [16].

The dependence of T_g of keratin wool fibers on the water regain, shown through the diagram in figure 17, represents an example of how the penetration H_2O molecules into the amorphous regions determines a reduction on the T_g of a protein based polymer material [18].

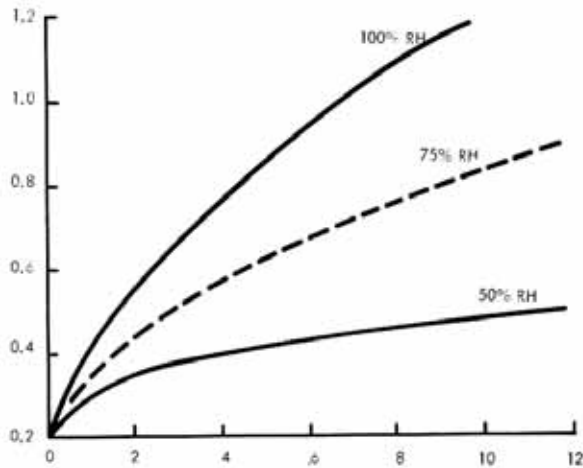


FIGURE 16: Moisture absorption of nylon-66 pellets. On abscissa is reported the exposure time (hours) to humid air at 23°C. On ordinate is reported the wt% of water absorbed [20].

TABLE 2: Tg of polyamides with different molecular structure and conditioned at three different values of the relative degree of humidity (U.R.) [16].

PA	essiccate		50% U.R.		100% U.R.		
	A	B	C	B	C	B	C
4,6	102	78	80	-	10	-	-
6,6	82	75*	47	35	15	-15	-37
6	56	66*	51*	20	3	-22	-32
12	29	58*	42	-	-	42	-
6/6,T	-	-	113	-	-	-	-

*) A, calculated according to the relation: $T_g = 2/3 T_m$,
 B, by using a torsion pendulum, C, by DSC thermograms

***) essiccate= dry

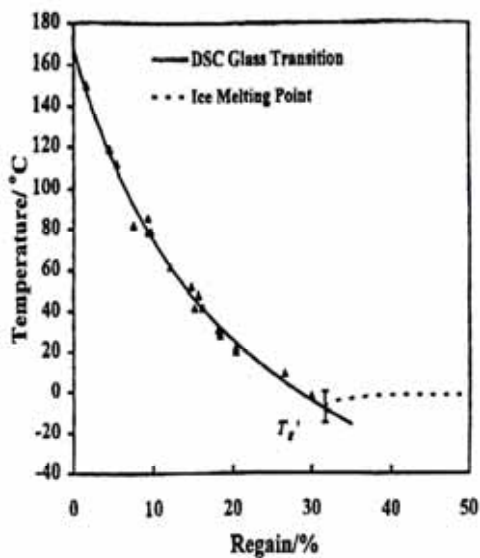


FIGURE 17: Dependence of the T_g of wool fibers from the water regain % (measured by the ratio between the weight of the H_2O absorbed and that of the dry fiber) [18].

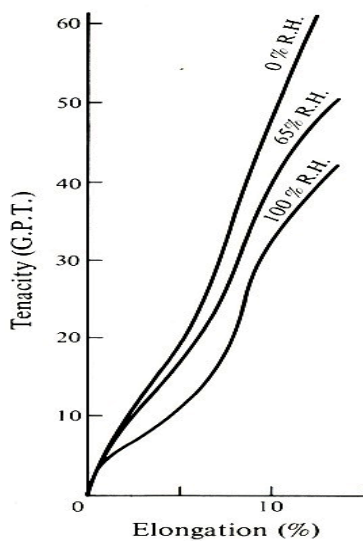


FIGURE 18: Tenacity/Elongation (%) curves, at constant temperature and for different values of RH%, for nylon-6 samples [21].

The influence of water up-take on the mechanical behaviour of a polymer is illustrated through the trend of Tenacity/Elongation diagrams reported for nylon-6 in figure 18 [21]. It can be seen that at constant elongation the value of tenacity decreases with the increase of the environmental RH as consequence of a related reduction in Tg values.

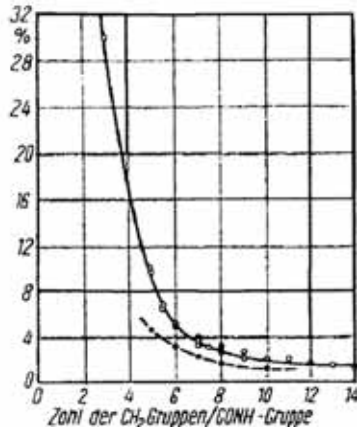


FIGURE 19: Amount of water absorbed by different samples of nylons as function of the ratio between the number of CH₂ groups in the repeat units and those of CONH (CH₂/CONH)
The experiments were performed at 65% RH and at 20°C [16].

TABLE 3: Water absorption of nylon samples with different CH₂/CONH values [16].

Polyamide	(CH ₂ /CONH)	water absorption%
	RH, 65%	in H ₂ O

6	5	3-4,2	9-11
6,6	5	3,4-3,8	7,5-9
6,8	6	3	4-4,5
8,8	7	1,8-2	3-4
6,10	7	2	3,5-4
6,12	8	2	2,5-2,8
6,1 ^(a)	-	-	6

In the case of polyamides, as shown by the data in figure 19, and in table 3, under the same experimental conditions, the amount of water absorbed decreases with the increasing of the ratio between the number of CH₂ groups in the repeat units and those of CONH (CH₂/CONH) [16]. Such observed behaviour suggests how strong is the influence of molecular structure of nylon against water absorption process (nylon 6 with CH₂/CONH=5, water absorption =3-4% (RH=65%); nylon-6.12, CH₂/CONH=8, Water absorption=2%).

6) Hydrogen bonds – In the case of polyamides every reaction that leads to elimination of intermolecular hydrogen bonds cause a drop in T_g values. For example in nylon 12, following methylation of –NHCO– groups, the T_g reduces from 42 to –34°C [16].

In literature, quite often the T_g of a given polymer has been qualitatively related to the melting temperature T_m by means of the hereafter reported empirical and approximated equation :

$$T_g = 2/3 T_m \quad (7)$$

As can be seen by the data in table 4 the melting temperature of polymers varies according to the chemical structure of the repeating units [10]. An analysis to define some of the molecular factors influencing the T_m of polymer materials leads to the conclusion that the more flexible chains are characterized by lower values of T_m (e.g. natural rubber), while the more rigid extended chains (see for example the case of polyethyleneterephthalate) have higher melting temperatures [10].

TABLE 4: Melting temperature for some common homopolymers (°C) [10].

Polydimethyl siloxane	Silicone rubber	– 40
Polyisoprene—1,4 <i>cis</i>	Natural rubber	28
Polyisoprene—1,4 <i>trans</i>	Gutta-percha	75
Polyisobutylene	Butyl rubber	5
Polyethylene—linear		145
Polyethylene—branched		115–120
Polytetrafluoroethylene	Teflon	330
Polypropylene		176
Polyacrylonitrile		317
Polymethylene oxide	Delrin	180
Polyhexamethylene adipamide	Nylon 6,6	270
Polyethylene terephthalate	Dacron	260
Cellulose triacetate	Acetate rayon	297

2) Resistance to Liquid and Gaseous Permeants (Concept of Permeability)

One of the most relevant property of polymer materials is represented by their resistance against the penetration, through the surfaces, of reactive gases, vapours and liquids.

The barrier efficiency against vapours and gases is particularly requested to polymer films used as wrapping materials with the function of protecting enclosed artefacts from contamination by the chemical constituents of the environmental atmosphere (oxygen, carbon dioxide, water vapour, ozone, chlorine, NO_x, SO_x, ecc.).

Usually the barrier efficiency of a given polymer against a well defined penetrant is measured by its permeability coefficient (P) that in case of gases may be defined as follows:

< Permeability coefficient (P) refers to the amount of gas, by volume, which penetrates unit thickness and area of specimen per unit time, under constant temperature and unit pressure difference when permeation is stable, expressed in cm³·cm/cm²·s·Pa. While permeation mass (Q) refers to the gas volume which permeates through unit area of specimen per unit time, under constant temperature and unit pressure difference when the permeation is stable. Its unit is cm³/m²·d·Pa. They satisfy the following formulas:

$$P=Qxd$$

d: material thickness > [22].

In case of water vapour the

< permeability coefficient (P_v) refers to water vapour volume that permeates through unit thickness and area of specimen per unit time, under specified temperature, relative humidity and unit vapour pressure difference, expressed in g·cm/cm²·s·Pa. Water vapor transmission (WVTR) refers to amount of water vapor, by volume that penetrates one square meter and specified thickness of specimen within 24 hours, under specified temperature and relative humidity and water vapor pressure difference. The unit is g/m²·24. They satisfy the following formulas:

$$P_v = WTRxd / \Delta p$$

d: thickness of specimen, Δp: water vapor pressure difference between two sides of specimen > [22].

Assuming that the steady-state diffusion process of permeant is in agreement with the Fick'law and moreover the gas or vapours dissolves in the polymer according to Henry's law then, in first approximation, it can be derived for P the following equation:

$$P = DS \quad (8)$$

Where D is the diffusivity and S the solubility [13].

According to reference [15] the process of permeation of low molecular weight substances through polymer films is essentially based on four different stages:

i) Absorption of the permeant molecules on the surface (related to permeant-polymer molecular interactions);

ii) Solution of the gas or vapour into the substrate (dependent upon both molecular attraction and polymer free volume) ;

iii) Diffusion through the wall by the concentration gradient;

iv) Desorption from the other surface [15].

Generally the similarity of solubility parameters of polymer and permeant as well as the presence of a polymer amorphous phase will encourage diffusion processes.

Starting from the relation:

$$\Phi = (d - d_a) / (d_c - d_a) \quad (9)$$

(with d , d_a and d_c being the density of the polymer with crystallinity volume fraction = ϕ , the density the 100% amorphous polymer and that of the 100% crystalline polymer respectively) then from theoretical considerations it has been possible to derive for semicrystalline polymer equations that relate P with crystallinity and density.

Such relations are hereafter reported:

$$P_{polymer} = P_{amorphous} (1 - \Phi)^2 \quad (10)$$

(where $P_{polymer}$ is the permeability of the polymer having a crystallinity volume fraction = ϕ and $P_{amorphous}$ being the permeability of the 100% amorphous polymer), and

$$P_{polymer} = Constant (d_c - d) \quad (11) \quad [23].$$

Equations 10 and 11 predict that for a given polymer-permeant pair the values of P should decrease with the increase of crystallinity and density [23].

The trends of the $P \rightarrow$ Density curves of figure 20 confirm, for polyethylene films, the above conclusions [23]. Moreover it emerges that for a given density P results to be strongly function of the chemical nature of permeants. In particular it can be seen that the permeability increases going from N_2 to O_2 to CO_2 (see figure 20).

The influence of chemical structure of repeat unit on P values is clearly demonstrated by the data reported in table 5 where the oxygen permeability of polyethylene films is compared with that of chain polymers where an hydrogen atoms has been substituted by different side functional groups [15,13].

The permeability of some polymers against different permeants (O_2 , CO_2 and H_2O -vapour) is reported in table 6 [24].

In general it is observed that water easily permeates films made of polymers with hydroxyl groups in the repeat unit (e. g. cellulose, polyvinylalcohol, ecc.) or with other polar groups such as amide and urethanes. On the contrary non polar polyolefins (e.g. polyethylene and polypropylene) are characterized by good water barrier efficiency but by poor barrier properties against non polar gases (e. g. oxygen and nitrogen) [15].

W.L. Hawkins, et Al., found that the % of O_2 absorbed by polyethylene films resulted to be inversely proportional to the % of crystallinity [14]. Such observation is confirmed by the trend of the curves $P/(Amorphous\ content)$, shown in figure 21 [13].

Thus it may be concluded that the penetration of O_2 occurs preferentially through the amorphous regions of the polymers where the degradation reactions of oxidation preferentially take place.

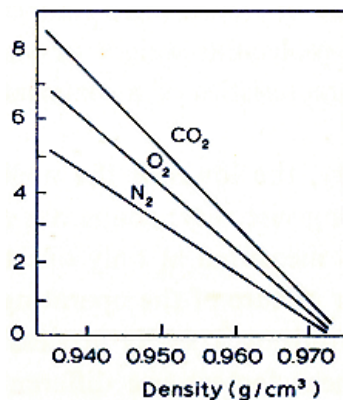


FIGURE 20: Dependence of permeability (P) of polyethylene films from density, according to relation (11), and from the chemical nature of gaseous permeant. In coordinates is reported the quantity: $P \cdot 10^{10}$ ($\text{cm}^3/\text{mm}/\text{cm}^2/\text{sec}/\text{cm-Hg}$) [23].

TABLE 5: Effect of primary structure on O_2 permeability P ($\text{cm}^3/\text{mil } 100\text{in}^2 \text{ day atm}$) of carbon chain polymer $[-\text{CH}_2-\text{CHX}-]_n$ [13,15].

Effects of functional groups

<i>Nature of X in</i> $-(\text{CH}_2-\text{CHX})_n$	$P_{O_2}^a$
—OH	0.01
—CN	0.04
—Cl	8.00
—F	15.00
—COOCH ₃	17.00
—CH ₃	150.00
—C ₆ H ₅	420.00
—H (LDPE)	480.00

TABLE 6: Permeability for some common polymers [24].

POLYMER	O ₂ ^{a)}	CO ₂ ^{a)}	H ₂ O-vapour ^{b)}
PVC-plasticized	6-400	20-600	25-188
PE-low density	50-100	200-500	2.5-3.7
PE-high density	20-50	150-400	0.7-1
PS	50	-	17.5
PET-polyester	0.6-0.8	3-5	2.5-5
Nylon-6	0.4-0.6	2-2.4	40-55
Cellophane	0.1-0.16	0.2-1.2	1-300
Poly vinylidene chloride	0.16-0.22	0.76-1.2	0.5-1.5
Ethylene-cop-vinyl alcohol	> 0.02	>0.02	7.5

a) mol/(m.s.Pa)x10²⁵, at 25°C, 50% RH;

b) mol/(m.s.Pa)x10²⁵, at 25°C, 100% RH

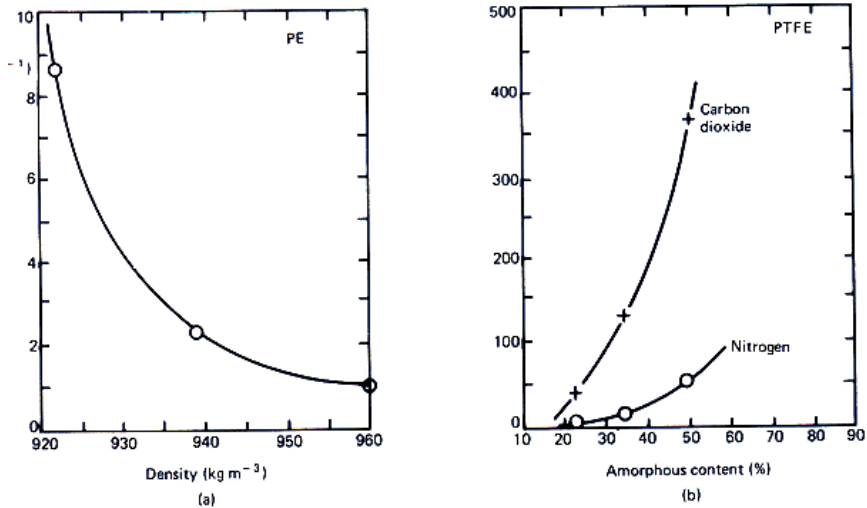


FIGURE 21: Permeability (P) to nitrogen of polyethylene film as function of density (left) and degrees of crystallinity (right) [13].

The data reported in table 7-left, demonstrate that for a given polymer the absorption of water determines a reduction of the barrier to O₂ while the orientation degree of the polymer film produces a lowering in the values of P (see table 7-right) [15].

TABLE 7: Effect of humidity (left) and of monoaxial orientation on permeability of polymer films. P, units: cm³/mil 100in² day atm [15].

	<i>Dry</i>	<i>100% RH</i>		<i>Draw ratio</i>	<i>P_{O₂}</i> ^a
PVA	0.01	25.00	PP	1:1	150
Cellulose	0.13	200.00		4:1	80
Nylon 6	1.0	5.00	PS	1:1	420
PVAC	55.0	150.00		4:1	300
SAN	1.0	1.00	PET	1:1	10
PET	7.0	6.00		6:1	5
PVDC	0.1	?	SAN	1:1	1.0
PAN	0.04	?		4:1	0.9

All the above observations must be taken into consideration when polymer artefacts, stored or in display in museum collections, may be in contact with chemical pollutants having the capacity to diffuse towards the surface penetrating inside the object where they may cause permanent damages. Thus the knowledge of the nature of the polymer constituent and its permeability turns to be useful in predict, when in presence of a known chemical gaseous pollutant, the entity of the possible degradation and the actions to be undertaken necessary to mitigate negative effects.

3)Dissolving tendency of polymers against liquid agents

The dissolving tendency of polymers represents an important issue as the first phase of conservation very often consists in solvent cleaning of plastic artefacts.

Solvent cleaning is necessary for the removal of soluble soiling such as: tars, bituminous materials, waxes, fatty, oily or grease dirt, etc..

A right cleaning methodology first of all requires that the liquid to be used must be unable to dissolve the polymer component.

The solubility of polymers depends on their physical properties (crystallinity, melting and glass transition temperature, etc.) and also on their chemical characteristics (polarity, molecular mass and its distribution, branching, cross-linking degree, etc.).

Hereafter the influence of the most effective factors upon solubility of polymers are briefly described [25,26].

a) Polarity

Polar polymers (poly (acrylic acid), poly (acryl amide), polyvinyl alcohol, etc.), are more soluble in polar solvents as water. On the contrary, polymers with low polarity (polystyrene, poly(methyl methacrylate), poly(vinyl chloride), poly (isobutylene), etc.) are more soluble in non polar solvents

b) Molecular weight and degree of cross-links

It is observed that, at constant temperature and for a given solvent, as molecular weight and cross linking degree increases, the solubility of a polymer decreases (figure 22) [27].

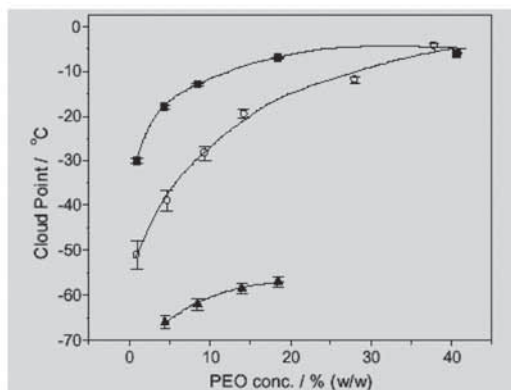


FIGURE 22: Dependence of the cloud point temperature of polyethylene oxide (PEO), in chloroform solution, with concentration. The curves refer to PEO samples having different molecular mass: (▲) PEO, 200; (○) PEO, 3350; (■) PEO, 10000. From the trend of the curves it can be concluded that at a given concentration the solubility of PEO increases with decreasing the molecular mass (phase separation occurs at lower temperature) [27].

c) Crystallinity

The solubility of a polymer in a given liquid decreases with its crystalline degree.

Crystalline, non polar, polyethylene is soluble in suitable solvents only at elevated temperature close to its melting point, above 100°C (PE, $T_m = 135^\circ\text{C}$). On the contrary highly polar nylons 6.6 ($T_m = 265^\circ\text{C}$), may be easily dissolved even at room temperature provide that a polar solvent, able to interact with its chains by forming for example also hydrogen bonding, is used.

d) Branches

The presence of short length branches along the macromolecular chains generally determines an increase in the solubility of polymer materials as, by disturbing the association of chains in the crystals, they cause a lowering in the crystal content.

On the contrary in the case of long side branches that may pack together giving rise to ordered structure oriented more or less perpendicular to the polymer chain backbone an increase in the solubility is usually observed.

Due to the high molecular mass, the coiled structure and molecular entanglements the dissolution of a polymer is a slow process. According to figure 23 it consists in two different steps: Swelling and Dissolution.

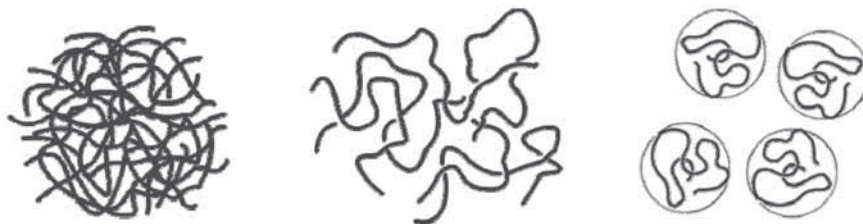


FIGURE 23: Schematic representation of the dissolution process for polymer molecules.

Left, polymer molecule in the condensed state. Centre, first step with gel formation:

Right, solvated polymer molecules dispersed in the solvent [26].

From thermodynamical point of view the process of dissolution of an amorphous polymer is governed by the free energy of mixing (ΔG_m) that is related, at a given value of the absolute temperature (T), to the enthalpy and entropy of mixing (ΔH_m and ΔS_m respectively) through the following equation:

$$\Delta G_m = \Delta H_m - T\Delta S_m \quad (12).$$

According to equation [12], the dissolution will occur only if ΔG_m assumes negative values. The dissolution of polymer macromolecules is always accompanied by an increase in entropy, thus ΔS_m is usually positive and consequently the term, $-T\Delta S_m$, is negative being T positive for definition.

On the contrary ΔH_m may be either positive or negative. Thus *< the sign and the magnitude of ΔH_m is the deciding factor in determining the sign of the Gibbs free energy change.....In order for ΔG_m in eq.12 to be less than zero, the heat of mixing must be smaller than the entropic term >* [28].

From theoretically consideration Hildebrand and Scott and Scatchard developed for ΔH_m the following semi-empirical equation [28].

$$\Delta H_m/V = (\delta_1 - \delta_2)^2 \varphi_1 \varphi_2 \quad (13)$$

In equation (13) δ_1 and δ_2 are the solubility parameters for solvent and polymer, whereas ϕ_1 and ϕ_2 are the volume fractions of solvent and polymer, respectively.

The solubility parameter δ is related to the value of the cohesive energy density (CED) through the hereafter reported relation:

$$\delta_i = (CED)_i^{1/2} = [\Delta E_i^v / V_i]^{1/2} \quad (14)$$

where ΔE_i^v is the energy of vaporization per cm^3 and V_i is the molar volume of the i species.

From equation (13) one may predict solubilization of the polymer if the term $(\delta_1 - \delta_2)$ is small.

In case of $\delta_1 = \delta_2$ the two components will be miscible in all proportion [28].

Thus from the knowledge of δ_1 and δ_2 it is possible to predict solubility of an amorphous polymer in a given liquid.

It is important to point out that equation (13) is valid, in principle, only for solutions where weak polymer-solvent interactions occur.

The solubility parameter δ of polymers can be also determined by using indirect methods. One of this methods is based on the measurements the degree of swelling (DS) of samples of slightly cross-linked polymer immersed in liquids having different and known values of δ .

< The extent of swelling can be plotted versus the solubility of the swelling liquids. This gives rise to a gaussian shaped curve centering around a certain value of solubility parameter δ_p at which the swelling is maximum.....The value of δ_p is taken as the solubility parameter of the polymer > [30].

An example of application of such method for natural and synthetic rubbers is represented in figure 24 [30].

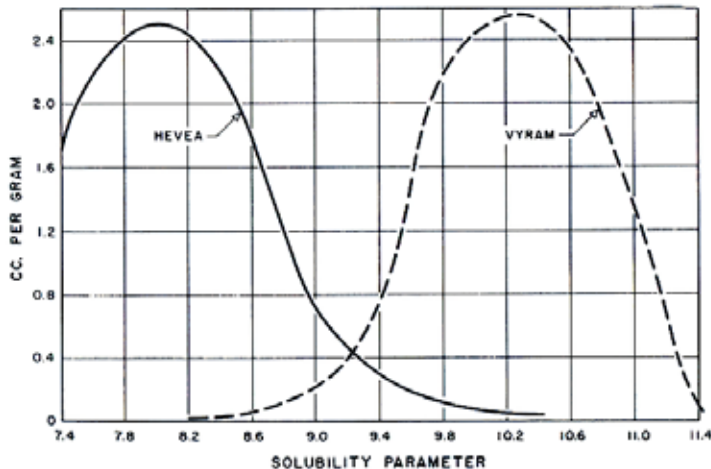


FIGURE 24: Swelling (in cubic centimeters of solvent imbibed per gram of rubber) versus δ (in $[\text{calories/cubic centimeters}]^{1/2}$) of the solvents for Hevea (natural rubber) and Vyram, synthetic rubber [30].

Another interesting method (known as “Group Contribution Method”, [28]) is *< based on the assumption that the contribution of different functional groups to the thermodynamic properties are additive. The energy of vaporization of solvent or polymer is*

$$\Delta E_i^y = \sum_i n_i \Delta \varepsilon_i \quad (15)$$

In equation (15) $\Delta \varepsilon_i$ is the contribution to the vaporization energy of i group while n is the number of i groups present in the macromolecule repeat unit.

Starting from the above assumptions the following relation was derived for δ :

$$\delta = \sum_i F_i / \sum_i V_i = p \sum_i F_i / M \quad (16)$$

where F_i is the molar attraction constant, V_i is the molar volume for each subsegment of the polymer repeating unit, p is the density of the polymer and M is the polymer molecular weight [25, 28].

On the basis of equations (16) it is possible to calculate the value of δ *< by using group contribution calculations for the molar volume and the cohesive energy density or molar attraction constants >* [28].

The values of the the molar attraction constant (F_i) as calculated by different Authors according to the Group Contribution Method are reported, for several types of functional groups, commonly present in polymers, in table 8 [28].

An example of application of the group-contribution approach, by using equations (16), to estimate the solubility parameter of polyethylene terephthalate (PET), is described in figure 25 [31].

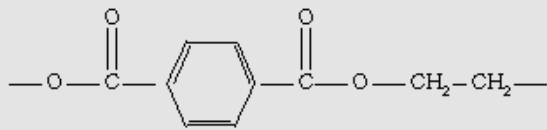
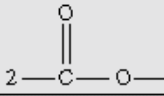
		
Subsegment	Molar Attraction Constant, F cal ^{1/2} cm ^{3/2} mol ⁻¹	Molar Volume, V cm ³ mol ⁻¹
2 CH ₂	2 (132)	2 (16.5)
o-phenylene	652	58.8
	2 (298)	2 (19.6)
Totals	1512	131
$\delta = \frac{1512}{131} = 11.5 \text{ cal}^{1/2} \text{ cm}^{-3/2} = 23.5 \text{ MPa}^{1/2}$		

FIGURE 25: Estimation of solubility parameter of polyethylene terephthalate (PET) by using the group-contribution approach (see equation (16)). The molecular structure of PET repeat unit is shown at top. The functional groups are indicated on the left part of the figure [31].

TABLE 8: The molar attraction constant F_1 [$\text{Mpa}^{1/2} \text{cm}^3 \text{mol}^{-1}$], for functional groups as derived by different Authors, see text [28].

CARBON CONTAINING GROUPS			
-CH ₃	437	420	303
=CH ₂	272	280	269
=CH-	57	140	176
=C=	-190	0	65
=CH ₂	388	—	259
=CH-	227	222	249
=C <	39	82	173
-CH=(aromatic)	—	—	240
-C=(aromatic)	—	—	201
-CH(CH ₃)-	495	560	(479)
-C(CH ₃) ₂ -	685	841	(672)
-CH=CH-	454	444	497
-C=CH-	265	304	421
-(CH ₃)-CH-	(704)	724	(725)
HC≡C-	583	—	—
-C≡C-	454	—	—
Cyclopentyl	—	1380	1300
Cyclohexyl	—	1660	1470
Phenyl	1500	1520	(1400)
Phenylene	1350	1380	(1440)
Naphthyl	2340	—	—
OXYGEN-CONTAINING GROUPS			
-O-(ether)	143	255	235
(epoxide)	—	—	360
-OH	—	754	462
(aromatic)	—	—	350
-CO-	562	685	538
-CHO	—	—	599
-COO-	634	511	688
-COOH	—	651	(998)
-O-(C=O)-O-	—	767	(904)
-(C=O)-O-(C=O)-	—	767	1160
NITROGEN-CONTAINING GROUPS			
-NH ₂	—	—	464
-NH-	—	—	368
-N <	—	—	125
-CHCN	(896)	1120	(901)
-CN	839	982	725
-(C=O)-NH-	—	1290	(906)
-O-(C=O)-NH-	—	1480	(1040)
-N=C=O	—	—	734
OTHER GROUPS			
-H	164-205	140	-103(acidic d
-S-	460	460	428
-SH	644	—	—
-F	(250)	164	84
-Cl(primary)	552	471	420
-Br(primary)	695	614	528
-I	870	—	—
-CF ₃ -	307	—	—
-CF ₂ -	561	—	—
-O-N=O	900	—	—
-NO ₂	900	—	—
-PO ₄	1020	—	—
-Si-	-77	—	—

The solubility parameters (δ) of several homo polymers, the solubility parameters (δ) of different solvent and plasticizers and the list of solvents for representative homopolymers are reported respectively in table 9, 10 and 11 respectively [28, 29].

TABLE 9: Solubility parameters (δ) for homo polymers
Left: alphabetical sequence of starting monomers.
Right: increasing δ value sequence [28,29].

Repeating Unit (Alphabetical Sequence)	δ (cal/cm ³) ^{1/2}	Repeating Unit (Increasing δ Value Sequence)	δ (cal/cm ³) ^{1/2}
Acrylonitrile	12.5	Tetrafluoroethylene	6.2
Butyl acrylate	9.0	Isobutyl methacrylate	7.2
Butyl methacrylate	8.8	Dimethylsiloxane	7.5
Cellulose	15.6	Propylene oxide	7.5
Cellulose acetate (56% Ac groups)	27.8	Isobutylene	7.8
Cellulose nitrate (11.8% N)	14.8	Stearyl methacrylate	7.8
Chloroprene	9.4	Ethylene	8.0
Dimethylsiloxane	7.5	1,4-cis-Isoprene	8.0
Ethyl acrylate	9.5	Isobornyl methacrylate	8.1
Ethylene	8.0	Isoprene, natural rubber	8.2
Ethylene terephthalate	10.7	Lauryl methacrylate	8.2
Ethyl methacrylate	9.0	Isobornyl acrylate	8.2
Formaldehyde (Oxymethylene)	9.9	Octyl methacrylate	8.4
Hexamethylene adipamide (Nylon 6/6)	13.6	n-Hexyl methacrylate	8.6
n-Hexyl methacrylate	8.6	Styrene	8.7
Isobornyl acrylate	8.2	Propyl methacrylate	8.8
1,4-cis-Isoprene	8.0	Butyl methacrylate	8.8
Isoprene, natural rubber	8.2	Ethyl methacrylate	9.0
Isobutylene	7.8	Butyl acrylate	9.0
Isobornyl methacrylate	8.1	Propyl acrylate	9.0
Isobutyl methacrylate	7.2	Propylene	9.3
Lauryl methacrylate	8.2	Chloroprene	9.4
Methacrylonitrile	10.7	Tetrahydrofuran	9.4
Methyl acrylate	10.0	Methyl methacrylate	9.5
Methyl methacrylate	9.5	Ethyl acrylate	9.5
Octyl methacrylate	8.4	Vinyl chloride	9.5
Propyl acrylate	9.0	Formaldehyde (Oxymethylene)	9.9
Propylene	9.3	Methyl acrylate	10.0
Propylene oxide	7.5	Vinyl acetate	10.0
Propyl methacrylate	8.8	Methacrylonitrile	10.7
Stearyl methacrylate	7.8	Ethylene terephthalate	10.7
Styrene	8.7	Vinylidene chloride	12.2
Tetrafluoroethylene	6.2	Acrylonitrile	12.5
Tetrahydrofuran	9.4	Vinyl alcohol	12.6
Vinyl acetate	10.0	Hexamethylene adipamide(Nylon 6/6)	13.6
Vinyl alcohol	12.6	Cellulose nitrate (11.8% N)	14.8
Vinyl chloride	9.5	Cellulose	15.6
Vinylidene chloride	12.2	Cellulose acetate (56% Ac groups)	27.8

¹Values reported are for homopolymers of the Repeating Unit. Reported δ values vary with the method of determination and test conditions. Averaged values are given in this table.

TABLE 10: Solubility parametyers (δ) of solvent and plasticizers (increased δ value sequence) [28, 29].

Solvent	δ (cal/cm ³) ^{1/2}	H-Bonding Strength [†]	Solvent	δ (cal/cm ³) ^{1/2}	H-Bonding Strength [†]
Dimethylsiloxanes	4.9-5.9	p	Di(ethylene glycol) monobutyl ether (Butyl Carbitol®)	9.5	m
Diisodecyl phthalate	7.2	m	Chlorobenzene	9.5	p
Hexane	7.3	p	Methylene chloride	9.7	p
Diamyl ether	7.3	m	Dipropyl phthalate	9.7	m
Diethyl ether	7.4	m	1,1,2,2-Tetrachloroethane	9.7	p
Dioctyl phthalate	7.9	m	Ethylene dichloride	9.8	p
Butyl butyrate	8.1	m	Acetone	9.9	m
Ethyl amyl ketone	8.2	m	1,2-Dichlorobenzene	10.0	p
Ethylene glycol diethyl ether	8.3	m	Diethyl phthalate	10.0	m
Butyl acetate	8.3	m	Ethylene glycol diacetate	10.0	m
Methyl isobutyl ketone	8.4	m	Di(propylene glycol)	10.0	s
Methyl amyl ketone	8.5	m	Carbon disulfide	10.0	p
Amyl acetate	8.5	m	1,4-Dioxane	10.0	m
Ethyl <i>n</i> -butyrate	8.5	m	Propylene glycol methyl ether	10.1	m
Ethylene glycol dimethyl ether	8.6	m	Di(ethylene glycol) monoethyl ether (Carbitol®)	10.2	m
Carbon tetrachloride	8.6	p	Cresol	10.2	s
Dioctyl sebacate	8.6	m	Aniline	10.3	s
Dioctyl adipate	8.7	m	Ethylene glycol monoethyl ether (Cellosolve®)	10.5	m
Isopropyl alcohol	8.8	m	Pyridine	10.7	s
Diethyl carbonate	8.8	m	Dimethyl phthalate	10.7	m
Propyl acetate	8.8	m	<i>N,N</i> -Dimethylacetamide	10.8	m
Diethyl ketone	8.8	m	Cyclohexanol	11.4	s
Dimethyl ether	8.8	m	Butyl alcohol	11.4	s
Toluene	8.9	p	Acetonitrile	11.9	p
Di- <i>n</i> -hexyl phthalate	8.9	m	Dimethyl sulfoxide	12.0	m
Ethyl acetate	9.1	m	Di(ethylene glycol)	12.1	s
Diamyl phthalate	9.1	m	<i>N,N</i> -Dimethylformamide	12.1	m
Tetrahydrofuran	9.1	m	Furfuryl alcohol	12.5	s
Dibutyl sebacate	9.2	m	Propylene glycol	12.6	s
Benzene	9.2	p	1,2-Propylenecarbonate	13.3	m
Tetrachloroethylene (perchloroethylene)	9.3	p	Methanol	14.5	s
Di(propylene glycol) monomethyl ether	9.3	m	Ethylene glycol	14.6	s
Chloroform	9.3	p	Ethylene carbonate	14.7	m
Dibutyl phthalate	9.3	m	Glycerol	16.5	s
Methyl ethyl ketone	9.3	m	Water	23.4	s
Dibenzyl ether	9.4	m			
Ethylene glycol monobutyl ether (Butyl Cellosolve®)	9.5	m			

[†]H-Bonding: p = poor; m = moderate; s = strong

Carbitol and Cellosolve are registered trademarks of Union Carbide Corp.

TABLE 11: Solvents of some representative homopolymers [28, 29].

Repeating Unit	Solvents
Acetylene	Isopropylamine, aniline
Acrylamide	Morpholine, water
Acrylate esters	Aromatic hydrocarbons, chlorinated hydrocarbons, THF, esters, ketones
Acrylic acid	Alcohols, water, dilute aqueous alkali
Acrylonitrile	Phenylenediamines, ethylene carbonate, sulfuric acid
Alkyl vinyl ethers	Benzene, halogenated hydrocarbons, methyl ethyl ketone
Amic acids	DMF, DMSO, tetramethylurea
Aryl sulfonates	DMF
Butadiene	Hydrocarbons, THF, higher ketones
ϵ -Caprolactam (Nylon 6)	<i>m</i> -Cresol, chlorophenol, formic acid
Cellulose	Trifluoroacetic acid, aqueous solutions of cupriethylenediamine
Cellulose ethers	Aqueous alkali
Cellulose triacetate	Methylene chloride, THF, ethylene carbonate
Chloroprene	Benzene, chlorinated hydrocarbons, pyridine
Ethylene	Above 80°C: halogenated hydrocarbons, higher aliphatic esters and ketones
Ethylene phthalamide	Sulfuric acid
Ethylene terephthalate	Trichloroacetaldehyde hydrate, phenol, chlorophenol
Ethylene oxide	Chloroform, alcohols, esters
Formaldehyde	At elevated temperature: phenol, aniline, ethylene carbonate
Hexamethylene adipate (Nylon 6/6)	Trichloroethanol, phenols, sulfuric acid
Isobutene	Chlorinated hydrocarbons, THF, aliphatic ethers
Isoprene	Hydrocarbons, THF, higher ketones
Lactic acid	Chloroform, dioxane
Maleic anhydride	Dioxane, ethers, ketones
Methacrylate esters	Benzene, methylene chloride, methyl ethyl ketone
Methacrylic acid	Alcohols, water, dilute aqueous sodium hydroxide
1,4-Phenylene ethylene	Biphenyl, phenyl ether
Phenylene sulfone	Methylene chloride, DMSO
Phenyl glycidyl ether	Xylene (hot), 1,2-dichlorobenzene (hot)
Propylene	Above 80°C: halogenated hydrocarbons, higher aliphatic esters and ketones
Propylene oxide	Benzene, chloroform, ethanol
Pyromellitimides	<i>m</i> -Cresol, conc. sulfuric acid
Siloxanes	Aromatic and chlorinated hydrocarbons, esters
Styrene	Benzene, chlorinated aliphatic hydrocarbons, methyl ethyl ketone, ethyl acetate
Tetrafluoroethylene	Perfluorokerosene (350°C)
Thiophenylene	Biphenyl, dichlorobiphenyl
Ureas	Phenol, <i>m</i> -cresol, formic acid
Urethanes	Phenol, <i>m</i> -cresol, formic acid
Vinyl acetal	Benzene, chloroform, THF
Vinyl acetate	Toluene, chloroform, methanol
Vinyl alcohol	Glycols (hot), water, piperazine
Vinyl butyryl	Methylene chloride, alcohols, ketones
Vinyl chloride	THF, methyl ethyl ketone
Vinyl carbazole	Chloroform, chlorobenzene, dioxane
Vinylidene chloride	THF(hot), trichloroethane
Vinylidene fluoride	Cyclohexanone, ethylene carbonate
<i>N</i> -Vinyl pyrrolidone	Chloroform, ethanol, pyridine

¹ A more extensive selection is found in "Polymer Handbook", Eds. Brandrup, J.; Immergut, E.H.; Grulke, E.A., 4th Edition, John Wiley, New York, 1999, VII /497-535. Aldrich Catalog Number Z41,247-3.

As shown by the trend of the curves represented in figure 26 generally an increase in polymer concentration determines an increase in the temperature where the polymer starts to precipitate (cloud point). Of course the entity of the phenomena depends upon the nature and structure of both polymer and solvent [27]. From the comparison of the curves it can be observed that at a given concentration the solubility of PEO is lower in the case of methanol (higher cloud point temperature), a solvent with a relatively higher δ value (14.5 [calories/cubic centimeters]^{1/2}) and with a strong tendency in to form hydrogen bonds (see tables 9, 10).

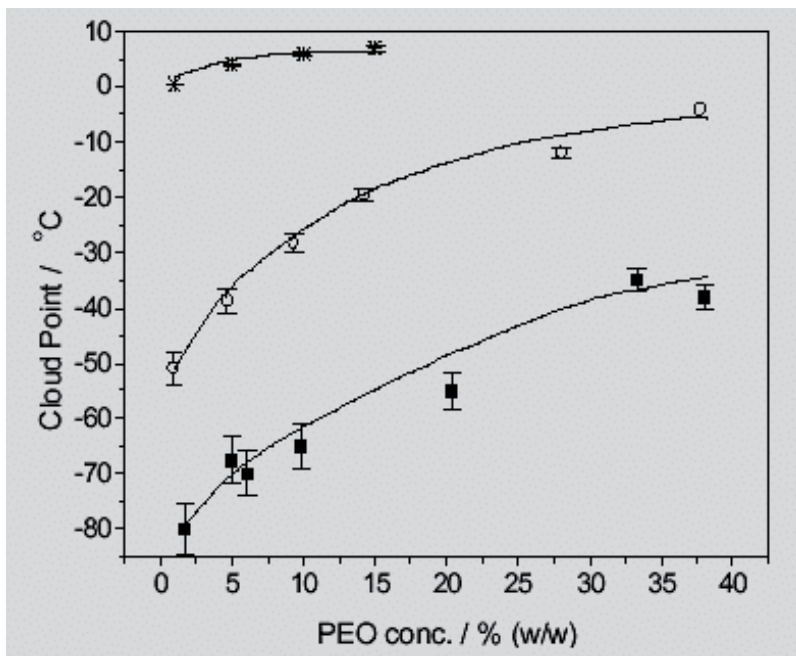


FIGURE 26: Effect of concentration and temperature on the solubility of PEO (Mw=3350) in (*) methanol ($\delta=14.5$, s), (o) chloroform ($\delta=9.3$, p), and (■) dichloroethane ($\delta=9.8$, p) [27].

In the case of no specific interactions between a polymer and a solvent then the polymer will have chance to be dissolved if term $(\delta_s - \delta_p)^2$ turns to be smaller than 4.0.

< Thus, for example,.....if we are trying to dissolve nylon 6.6 in water, we will see that it is not possible thermodynamically, since $(\delta_{water} - \delta_{nylon6.6}) = (47.9 - 27.8) \text{ MPa}^{1/2} = 20.1 \text{ MPa}^{1/2} \gg 4.0$. However, nylon 6.6 will dissolve in toluene, since $(\delta_{toluene} - \delta_{nylon6.6}) = (18.2 - 27.8) \text{ MPa}^{1/2} = -9.5 \text{ MPa}^{1/2} \ll 4.0$. Making similar calculations, we will see that nylon 6.6 can also be dissolved in n-hexane and carbon tetrachloride..... In polar systems or when polymer-solvent interactions occur, for example hydrogen bonding, the calculation of the solubility parameters is carried out by means of more complicated equations > [25].

From solubility tests it is possible to obtain interesting information about polarity and the presence of specific functional groups along the polymer backbone.

For this reasons solubility tests are quite often used to distinguish one polymer family from another one (see table 11).

REFERENCES

- 1) E. Then, V. Oakley, *Conservation Journal*, < A Survey of Plastic Objects at the Victoria and Albert Museum >, Number 6, January (1993)
http://www.vam.ac.uk/res_cons/conservation/journal/conservation_journal_6/plastic_objects/index.html, (2008).
- 2) S. C. Stinson, < *Chemical & Engineering News* >, September 9, 34 (1996).
- 3) E. Martuscelli, < *Plastics in Art (in Cultural Heritage) - Plastics for Art (for Cultural Heritage)* >, Lecture presented at Programma Giornata AIM on “Il restauro e la diagnostica degli oggetti d’arte e di design in plastica”, 31/10/(2008).
- 4) E. Martuscelli, < *La Chimica Macromolecolare Applicata alla Conservazione dei Manufatti Lapidei* >, PAIDEIA, Firenze (2007).
- 5) E. Martuscelli, personal archive.
- 6) A. Sharples, < *Introduction to Polymer Crystallization* >, E. Arnold Publishers, Ltd., London (1966).
- 7) E. Pedemonte, G. C. Alfonso, < *Lo Stato Cristallino* >, in < *Macromolecole, Scienza e Tecnica* >, a cura di F. Ciardelli et Al., Sez. V, pp. 227-276, Pacini Editore, Pisa (1983).
- 8) G. Bodor, < *Structural Investigation of Polymers* >, Akademiai Kiado, Budapest (1991).
- 9) J. W. Turley, < *X-Ray Diffraction Patterns of Polymers* >, The Dow Chemical Company (1965).
- 10) L. Mandelkern, < *An Introduction to Macromolecules* >, Springer-Verlag, New York, USA (1972).
- 11) J. A. Allen, < *An Outline of Polymer Chemistry* >, Oliver & Boyd, Edimburg (1968).
- 12) L. R. G. Treloar, < *Introduction to Polymer Science* > Wykeham Publications, London (1970).
- 13) C. Hall, < *Polymer Materials* >, the Macmillan press LTD, London (1981).
- 14) W. L. Hawkins, et Al., et Al., *J. Polymer Sc.*, **41**, 1 (1959).
- 15) L. Mascia, < *Thermoplastics* >, Elsevier Applied Science, London (1989).
- 16) A. Ciaperoni, A. Mula, < *Chimica e Tecnologia delle Poliammidi* >, Pacini Editore, Pisa (2001).
- 17) E. Martuscelli, < *Degradazione delle Fibre Naturali e del Tessuti Antichi* >, PAIDEIA, Firenze (2006).
- 18) J. M. Kure, *Textile Res. J.*, **67**, 18 (1997).
- 19) E. Martuscelli, < *Relazioni Proprietà Struttura nelle Fibre di Lana* >, Collana di Trasferimento e Diffusione, Vol. Primo, CAMPEC, Napoli (2003).
- 20) C. M. Baranano, < *Injection Molding of Nylons* >, in *Nylon Plastics*, Cap. 5, Edited by M. I. Kohan, John Wiley & Sons, New York (1973).
- 21) J. M. Shultz, < *Polymer Materials Science* >, Prentice-Hall, Inc., New Jersey (1974).
- 22) <http://www.labthink.cn/service/show567.html>, (2009).
- 23) H. V. Boenig, < *Polyolefins: Structure and Properties* >, Elsevier Publishing Company, London (1966).
- 24) J. L. Mateo, *Revista de Plasticos Modernos*, 89,459 (2005).
- 25) S. B. Grassino, < *Polymer Solutions* >, <http://pslc.ws/macrog/property/solpol/ps1.htm>, (2009).
- 26) B.A. Wolf, *Pure & Appl. Chem.*, **57**, No. 2, 323 (1985).
- 27) M. Spitzer, L. H.M. da Silva, W. Loh, < *liquid biphasic systems formed in ternary mixtures of two organic solvents and ethylene oxide oligomers or polymers* >, *Journal of the Brazilian Chemical Society*, http://www.scielo.br/scielo.php?script=sci_arttext&pid=S0103-50532000000400009&lng=e&nrm=iso&tlng=e, (2009).
- 28) E. A. Grulke, < *Solubility parameters factors* >, in “Polymer Handbook”, Edited by J. Brandrup, E. H. Immergut, John Wiley & Sons, New York(1989).
- 29) < *Polymer Solutions: Solvents and Solubility Parameters* >, from Aldrich catalogue (2009)

- 30) A. V. Tobolsky, < *Properties and Structure of Polymers* >, John Wiley & Sons, New York (1962).
- 31) E. J. Moskala, M. Jones,< *Evaluating Environmental Stress Cracking of Medical Plastics* >, *Medical Plastics and Biomaterials Magazine* (MPB Article Index), May (1998), <http://www.devicelink.com/mpb/archive/98/05/001.html>, (2009).

SECTION-1

THIRD-CHAPTER

INFLUENCE OF ADDITIVES ON PROPERTIES, STABILITY AND DEGRADATION BEHAVIOUR OF PLASTICS

Since the beginning of the development of plastic industry it was recognized that to improve processing and material performance and stability it was necessary to make use of suitable additives.

In plastic industry the term additive is used to indicate a substance that is added in minor amounts to a basic resin or compound in order to enhance the properties without altering the chemical structure of the base polymer constituent.

According to reference [1-a] additives should provide to plastics:

► Stability (to retain the original molecular architecture of the polymer under the effect of heat, light, etc.);

► Functionality (to provide additional properties to the polymer which add value for end use application) [1-a].

As reported in table 1, polymer additives may be conveniently classified according to their function [1-b].

TABLE 1: Polymer additives classified
According to their function [1-b].

<i>Main classification</i>	<i>Subdivision</i>
1. Processing additives	a. Processing stabilisers b. Lubricants c. Viscosity depressants d. Fusion promoters
2. Flexibilisers	a. Plasticisers
3. Anti-ageing additives	a. Antioxidants b. Ultraviolet stabilisers
4. Surface properties modifiers	a. Antistatic agents b. Antiblocking additives
5. Optical properties modifiers	a. Pigments and dyes b. Nucleating agents
6. Fire retardants	a. Ignition inhibitors b. Self-extinguishing additives c. Smoke suppressants
7. Foaming additives	a. Blowing agents

Additives may be dissolved, forming a unique phase in the polymer mass or alternatively they may be insoluble thus giving rise to a separated phase in the compound.

Hereafter some of most important classes of additives are discussed in order to put in evidence their role especially in the case of plastic artefacts involved in degradation phenomena.

1) Processing additives

1-a) Processing stabilizers

They are used to interfere with oxidation reactions during transformation of polymers in presence of oxygen. Are subdivided in:

--- Primary stabilizers or antioxidants, having the function to react with propagating free radicals forming stable products thus interrupting the chain reactions process.

--- Secondary stabilizers or peroxide decomposers, able to convert reactive hydro peroxides in inactive species.

The molecular structures of some antioxidants and peroxide decomposers are described in table 2 and 3 respectively [1-b].

TABLE 2: Chemical name and molecular structure of anti oxidants used for polymers [1-b].

Chemical name	Structure
A. <i>Antioxidants</i>	
(a) 1,1,3-tris(2 methyl-4 hydroxy-5- <i>tert</i> butyl phenyl) butane	(a)
(b) Tetra, tris methylene 3-(3',5'-di- <i>tert</i> butyl-4' hydroxy phenyl) propionate methane	(b)
(c) 0, <i>o</i> -di- <i>n</i> -octadecyl-3,5-di- <i>tert</i> butyl-4-hydroxybenzyl phosphonate	(c)

TABLE 3: Molecular structure and name of hydro peroxide decomposers used in polymer formulations [1-b].

Chemical name	Structure
(a) Dilaurylthio-dipropionate	(a)
(b) Tris(<i>n</i> onyl phenyl) phosphite	(b)
(c) Zinc dithiocarbamate	(c)

1-b) lubricants and mold release agents

The functions of lubricant agents may be summarized as follows:

- To improve the property of fluidity and inhibit clinging to the walls of the machines with which the melt comes into contact.
- To assist flow in calendaring, molding and extrusion by lubricating the metal surfaces in contact with plastic compound.
- To assist in knitting and wetting of the resin in mixing and milling operations;
- To impart lubricity to finished products [2]

Lubricants by improving fluidity also develop positive additional properties and serve to support other additives [3].

According to their main function lubricants are classified in External and Internal lubricants.

External lubricants: *< do no interact with polymer but function at the surface of the molten polymer between the polymer and the surface of the processing equipment and are generally incompatible with the polymer itself. These lubricants function by coating the process equipment and reducing friction at the point of interface. They delay fusion and give melt control and the desired polymer flow... > [4].*

Internal lubricants: *< are usually chemically compatible with the polymer and act by reducing friction between polymer molecules. They reduce Van der Waals forces, leading to lower melt viscosity and lowering energy input needed for processing > [4].*

Hereafter some of the most used families of lubricants are briefly presented [4].

---- Metallic stearates

They are used for PVC (predominantly), polyolefins, ABS, polyesters and phenolics (calcium stearate is widely used).

---- Esters

Fatty esters, polyol esters and wax esters are all part of this family of lubricants. Are used for PVC, polystyrene and acrylic polymers.

---- Fatty amides

Are used essentially as slip and mold release agents predominantly in polyolefins. The ethylene-bis-stearamide find application as internal and external lubricant in the case of PVC and ABS.

---- Fatty alcohols

They are used for rigid PVC.

---- Waxes

Being non-polar find application as external lubricant for PVC.

Fatty acid esters and amides, fluoropolymers and silicones are the commonly used as mold release agents.

2) Plasticisers

A plasticiser is a substance able to increase the flexibility, softness, and extensibility of inherently rigid thermoplastics and thermoset resins [4,5]. Moreover plasticisers have also the function to improve the processability, impact resistance and reduce the value of the glass transition temperature (see the case of PVC in table 4). This means that generally plasticisers should be soluble in the polymer matrix thus forming a unique thermodynamic phase.

As shown also by table 5, the most used plasticisers belong to the following families:

- Phthalate esters;
- Aliphatic esters;
- Epoxy esters;
- Phosphate esters;
- Trimellitate esters;
- Polymeric plasticisers [1-b].

TABLE 4: Dependence of the Tg of PVC from the % of Di-octyl phthalate (DOP) added as plasticiser [6].

PVC (w/w%)	DOP (w/w%)	Tg (°C)
100	0	85
90	10	60
80	20	35
70	30	0

TABLE 5: Some common plasticisers used in the case of thermoplastic polymers [1-b].

Plasticiser	Polymer
Di-octyl phthalate (DOP)	Polyvinyl chloride and copolymers
Tricresyl phosphate (TCP)	Polyvinyl chloride and copolymers
Di-octyl adipate (DOA)	Polyvinyl chloride, cellulose acetate butyrate
Di-octyl sebacate (DOS)	Polyvinyl chloride, cellulose acetate butyrate
Adipic acid polyesters (MW = 1500 3000)	Polyvinyl chloride
Sebacic acid polyesters (MW = 1500 3000)	Polyvinyl chloride
Chlorinated paraffins ("n"Cl = 40- 70) (MW = 600 1000)	Most polymers
Bi- and terphenyls (also hydrogenated)	Aromatic polyesters
N-ethyl <i>o,p</i> -toluene sulphonamide	Polyamides

In first approximation the T_g of a plasticized polymer ($T_g^{(plast)}$) may be related to those of plain polymer ($T_g^{(pol.)}$) and plasticiser additive ($T_g^{(add.)}$), assuming mutual solubility, through the Fox equation hereafter reported:

$$1/T_g^{(plast)} = W^{(pol.)}/T_g^{(pol.)} + W^{(add.)}/T_g^{(add.)} \quad (1)$$

where $W^{(pol.)}$ and $W^{(add.)}$ are the weight fraction of the polymer and additive respectively.

Dynamic Mechanical Analysis (DMA) can be used to study the effects of adding plasticisers to polymer systems as from the corresponding diagrams the T_g values, as function of the composition of the formulation, can be easily derived.

It is well known that from DMA technique it is possible to measure, due to the visco-elastic behaviour of a polymer, the following quantities:

- < - G' , the storage modulus, which represents the degree of elasticity and the degree of structure of the material, to which extent the material can store and restore deformation energy;
- G'' , the loss modulus, which informs on the ability of the material to flow and indicates to which extent the material can lose deformation energy;
- $Tan \delta = G''/G'$, the loss tangent, which peaks when the material experiences a phase transition (glass transition, melting point) > [7].

A typical DMA diagram, showing the trend of G' and $\tan \delta$ in the case of nylon-6, is reported in figure 1 [8]. The three peaks observed in the $\tan \delta$ curve indicate that the material following heating undergoes secondary transitions at a well-defined temperature. In particular the peak labeled as α in figure 1 is related to the glass transition of the nylon-6.

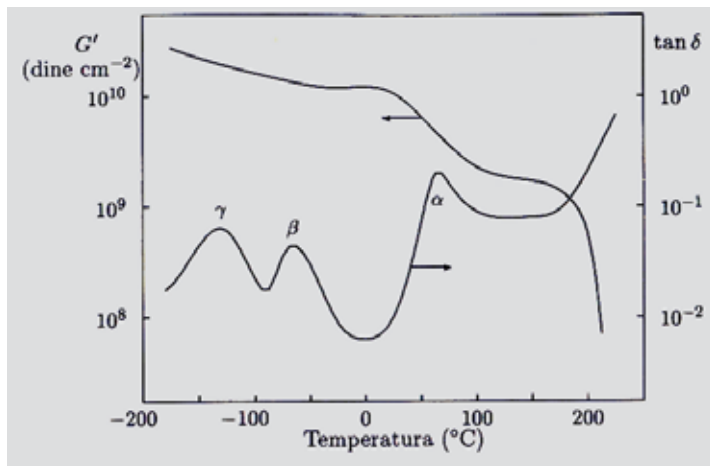


FIGURE 1: Diagrams obtained by Dynamic Mechanical Analysis (DMA) showing the trend of G' and $\tan \delta$ in the case of nylon-6. The α peak corresponds to the T_g of the sample (see text) [8].

As shown by figure 2, in agreement with the data of table 4, the DMA peak temperature of $\tan \delta$, for PVC samples, decreases systematically with increasing plasticiser content [9].

The presence of a plasticiser, as represented by the diagrams reported in figure 3, determines in PVC an increasing permeability against water vapors [9].

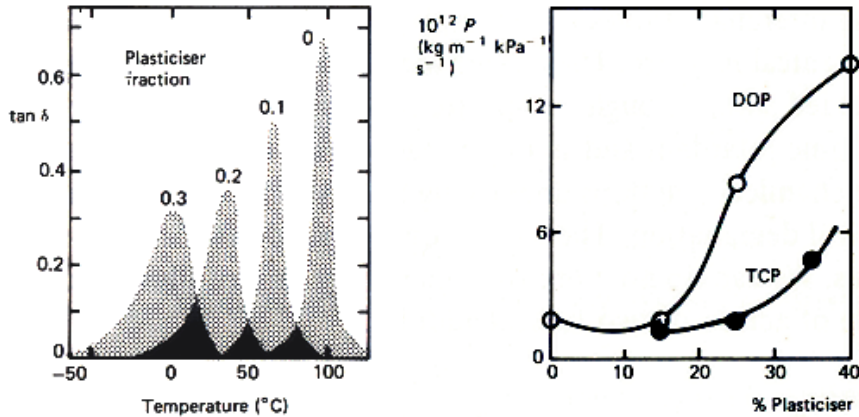


FIGURE 2, left: Dependence of the DMA peak temperature of $\tan \delta$ upon the plasticiser content in the case of PVC [9].

FIGURE 3, right: Water vapor permeability of PVC samples as function of plasticiser content (dioctyl phthalate, DOP, and tricresyl phosphate, TCP) [9].

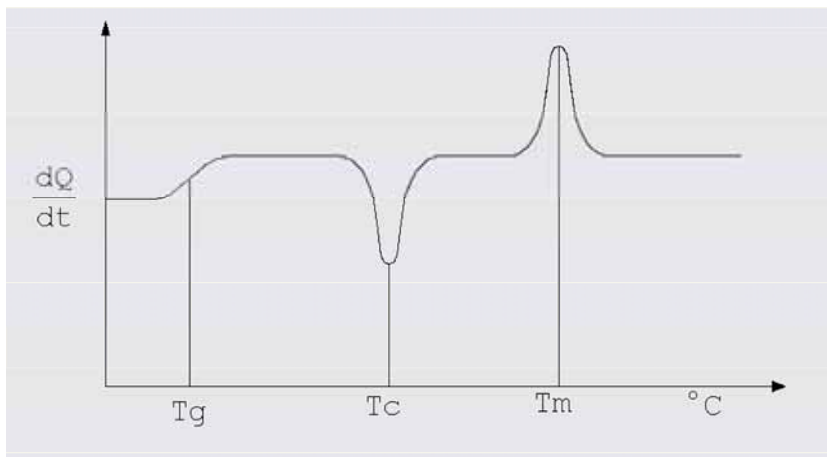


FIGURE 4: A typical DSC thermogram for polymer samples showing glass transition temperature (T_g), temperature of crystallization (T_c) and melting temperature (T_m) [9-b].

Differential Scanning Calorimetry (DSC), one of the most widely used technique to study the thermal transitions of polymers, turns to be very effective also in determining the dependence of T_g of a plastics from plasticisers content.

As shown by figure 4 when a plastic sample, on heating, reaches T_g, then the sudden change in heat capacity, due to the fact that more heat can be absorbed because of the increased molecular motion, determines an abrupt change in the slope of the thermogram [9-b].

As can be seen DSC is also suitable in deriving the temperature of the exothermic crystallization process and of the endothermic transition related to the fusion of polymer (figure 4) [9-b].

3) Anti-ageing additives- Light-Stabilizers

Ageing is the consequences of exposure of plastics to natural or artificial environmental factors of degradation. According to reference [1]:

< Ageing may be defined as the process of deterioration of materials resulting from the combined effects of atmospheric radiation, temperature, oxygen, water, micro-organisms and other atmospheric agents (e.g. gases) > [1-b].

Is well known that the exposure of plastics to UV-light, in presence of oxygen, produces the major effects of ageing causing deep modifications in the artefacts such as: loss of gloss, crazing, chalking, discoloration, changes in electrical characteristics, embrittlement, loss of function and breakdown.

To reduce those effects generally UV stabilizers are used which, according to their specific activity and the mechanism through which they prevent degradation, may be grouped into three different families, hereafter briefly described.

--- UV-Absorbers

Are additives capable to protect polymer materials by preferentially absorbing UV-radiations, in a wave range of 290-400 nm, and to convert this light energy into harmless heat [1,2,10].

Carbon blacks and iron oxide have been often used as UV-absorbers. The chemical name and molecular structure of some common organic UV-absorbers belonging to the families of 2-hydroxybenzophenone and hydroxyphenyl benzotriazoles are reported in figure 5 [1].

--- Excited State Quenchers

They are additives with the ability to remove the energy absorbed by plastic artefacts before photo-chemical degradation reactions start [2].

The most common used excited state quenchers are nickel based complexes (see examples in figure 6) [1-b].

< These deactivating metal ion quenchers stop energy before it can break any molecular bonds and generate free radicals > [4].

--- Radical Scavengers

It is well established that the absorption by a polymer material of light, especially UV radiations, may gives rise to photo induced degradation processes with the production of radical species. These radicals by initiating chemical reactions, cause polymer degradation as well as the generation of more radicals (see later). The propagation of radical attack not only determines the degradation of polymer macromolecules but also produces unsaturated and conjugated products able to act as chromophores groups that by absorbing solar light cause effects of discoloration.

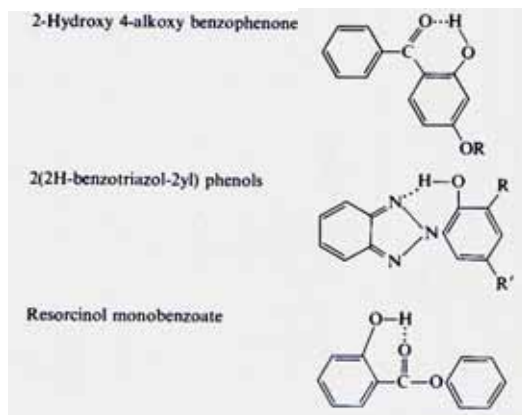


FIGURE 5: Chemical name (left) and molecular structure (right) of some common UV-Absorbers used for plastics [1-b].

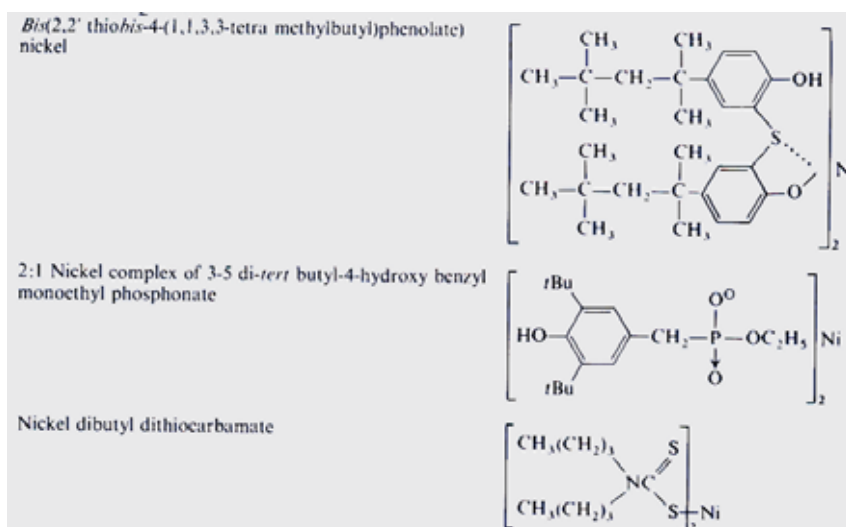


FIGURE 6: Name (left) and molecular structure (right) of nickel complexes commonly used as excited state quenchers for polymers [1-b].

From above it emerged the necessity by chemical industry to develop radical quenching additives. Radical scavengers, do not absorb UV-light, they have the ability of trapping radicals. Lactones (benzo furanone derivatives) and acrylated bis-phenols, are powerful carbon centered radical scavengers. As matter of fact these compounds, even at low concentration, help in controlling melt stability during polymer processing [11].

The mechanism through which a substituted benzofuranone is effective in radical quenching is described in figure 7 [11].

Hydroxylamines, very active as both primary and secondary antioxidants, are also able, especially in combination with hindered amines, to act as radical scavengers, see mechanism in figure 8 [12].

Hindered amine light stabilizers (HALS), introduced by Ciba and Sankyo in 1975, are capable to stabilize polymer resins via free radical termination. These additives, derivatives of 2,2,6,6-tetramethyl piperidine (see molecular structure in figure 9), are widely used in most polymers for their cost effectiveness and performances [4,13].

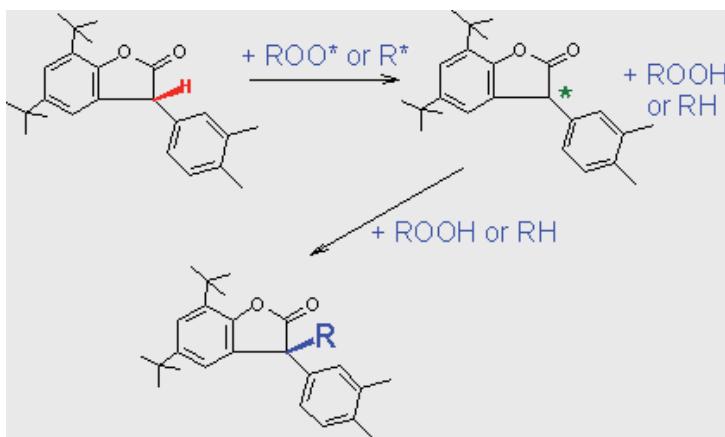


FIGURE 7: The mechanism of radical scavenger of lactones (benzofuranone derivatives) [11].

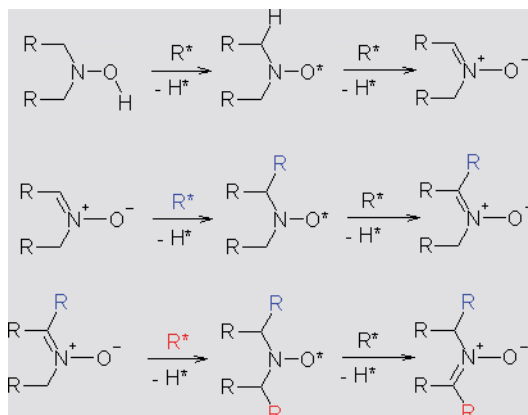


FIGURE 8: The mechanism of radical scavenging shown by hydroxylamines [12].

The mechanism of action of HALS in entrapment reactions of carbon radicals is described in figure 10 [13].

< Because of the regenerative nature of this process, as well as the typically high molecular weights of the stabilizers, hindered amine stabilizers are capable of providing extreme long-term thermal and light stability > [13].

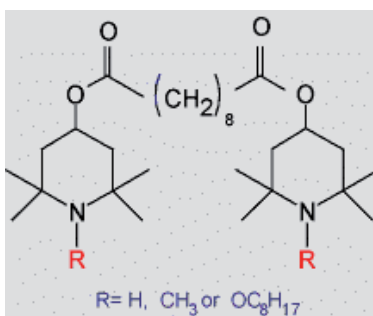


FIGURE 9: Molecular structure of hindered amine light stabilizers (HALS). These additives are derivatives of 2,2,6,6-tetramethyl piperidine [13].

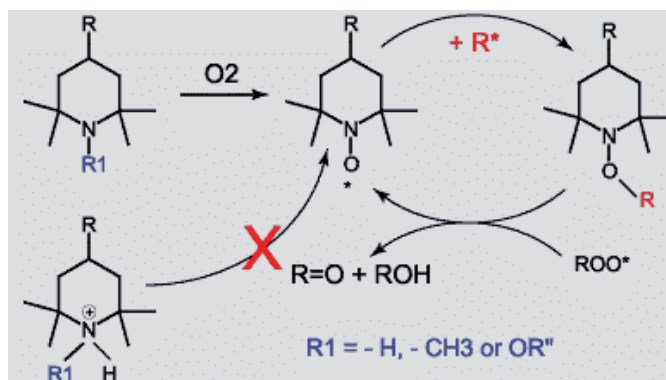


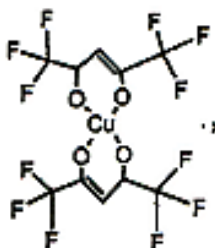
FIGURE 10: The mechanism action of HALS in radical entrapment reactions of carbon radicals [13].

According to reference [3] < the maximum possible protection against the ageing process triggered by radicals, is provided by the synergistic combination of UV absorbers and oxygen stabilizers in one package. In combination the protective effect is even better than the total protection afforded by the individual components > [3].

Quite recently I. Luzinov et Al., proposed a radical scavenger system, to be employed to trap radicals in fluoropolymer films, based on the incorporation of < nanoparticles made of a Cu(II) substance in a polymeric pellicle, because this material can effectively undergo reactions with radical species. Reaction of CuCl₂ with radicals proceeds according to the following scheme:



Copper (II) hexafluoro-2,4-pentanedionate (CuHAA, see molecular structure below) soluble in many fluorinated solvent was used to cast Teflon AF films containing copper compound.



In one of the two procedures developed to obtain film of fluorinated polymers containing dispersed Cu-nano particles Cu metal particles were synthesized directly in the solvent (Vertrel® XF) by chemical reduction. This procedure was based on the following steps:

<--- CuHAA was dissolved in ca. 70mL of Vertrel® XF;

--- 2mL of a 1% Teflon AF solution was added;

--- excess of NaBH₄ was dissolved in methanol and added to the copper solution with rapid stirring;

--- Upon NaBH₄ addition mixture immediately becomes dark yellow and then a green-orange color due to the Ostwald ripening of the particles;

--- Teflon coated particles quickly fall out of solution due to the insolubility of Teflon AF in Methanol > [14].

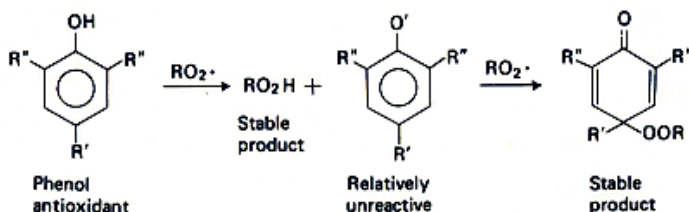


FIGURE 11: Thermal antioxidant mechanism of a phenol derivative agent [9].

It is interesting to point out that carbon black is a very efficient additive against ageing of polymers acting at the same time as UV absorbers, excited state quenchers and as radical scavengers [1-b]. The mode of action of a typical thermal antioxidant additive (phenol derivative) in trapping a propagating radical species is represented in figure 11 [9].

4) Surface properties modifiers

They may be divided in Antiblocking and Antistatic agents.

--- Antiblocking additives

They are < agents which are incorporated in plastic compounds to reduce the adhesion of surfaces of products made from the compounds to each other or to other surfaces, and which function by producing a slight roughening of the surface.....Antiblocking agents are usually finely divided, solid infusible materials, usually minerals but sometimes waxes. They function by forming small protruding asperities on surfaces which maintain small air spaces which reduce the coefficient of friction and prevent surface from sticking together > [2].

The four major types of antiblocking agents belong to the following families of materials:

- Diatomaceous earth;
- Talc;
- Calcium carbonate;
- Synthetic silicas and silicates [4].

--- Antistatic agents

Are substances able to impart < a slight to moderate degree of electrical conductivity to plastics compounds, thus preventing the accumulation of electrostatic charges on finished articles. They may be incorporated in the materials before molding, or applied to their surfaces after molding > [2].

The most common external or topical antistatic agents are quaternary ammonium salts (QUATS), usually applied from a water or alcohol solution [2].

Internal antistatic may be of migratory or permanent types.

The migratory antistatic agents (MAS), with a chemical structure composed of hydrophilic and hydrophobic components, tend to migrate or bloom to the surface of the molded plastic artifact.

The hydrophilic portion is able to bind water at the surface of the article. If the surface is wiped the MAS is removed causing the migration of additional agent towards the surface. These types of MAS can be cationic (long-chain alkyl quaternary ammonium, phosphonium, or sulphonium salts with chloride counter ions), anionic (alkali salts of alkyl sulfonic, phosphonic, or dithiocarbamic acids), and non ionic compounds (ethoxylated fatty alkylamines) [2].

Permanent polymeric antistatic agents have been lately developed which are compounded into the plastic matrix. The advantages of such permanent antistatic agents are:

- Insensitivity to moisture;
- Long-term performance;
- Minimal opportunity for surface contamination;
- Low off gassing;
- Color and transparency capability [2].

Hydrophilic polymers such as polyether block copolymers and inherently conductive polymers (based on polyaniline, neoalkoxy zirconates and polythiophenes) have been tried as permanent antistatic agents [2].

5) Flame retardants

It is well known that plastics are more or less easy to catch fire, thus since the beginning of their use research efforts have been developed in find out anti-flammable agents [10].

Flame retardants are additives (organic or inorganic in formulation) used *< to reduce the ease of ignition smoke generation and rate of burn of plastics >* [2].

According to their mechanism of action flame retardants may be conveniently classified in:

- Ignition inhibitors;
- Char formers;
- Smoke suppressors [1-b].

--- Ignition inhibitors

Are additives effective in increasing the ignition temperature of polymers being *< capable of forming large amounts of incombustible gases, which would also inhibit the free radical oxidation reaction in the flame zone >* [1-b].

Formulations constituted by mixtures between organic halogenated substances (see table 6) and oxides of antimony and molybdenum are often used as ignition inhibitors. As matter of fact such compounds have the capacity to *< form volatile oxychloride gases which expel oxygen from the flame zone and at the same time, they produce free radicals which by interfering with the chain reactions in the gaseous phase, will reduce the net rate of the reactions leading to CO₂ and H₂O >* [1-b].

TABLE 6: Some halogenated compounds that in Combination with antimony oxides are used as ignition inhibitors for polymers.
Left: chemical names. Right: suggested applications.
[1-b].

Chlorinated paraffins	General usage
Perchlorocyclopentadiene	High melting point polymers
Decabromo diphenylene oxide	Most polymers
Tris(2,3 dibromopropyl) phosphate	General usage
Poly(β chloroethyl triphosphate)	General usage
Bromophthalimide	High melting point polymers

Other types of ignition inhibitors are based on formulations containing aluminum trihydrate or magnesium hydroxide or zing borate or melamine derivatives. *< These function primarily by emitting incombustible gases, i.e. H₂O from the inorganic compounds, and by removing heat from the substrate through endothermic vaporization or sublimation phenomena >* [1-b].

The capacity of melamine (see molecular structure in figure 12-left) and its derivatives to act as flame-retardants for polymers is described, in reference [15]. In this report the mechanism of action is described as follows:

< In the initial stage melamine can retard ignition by causing a heat sink through endothermic dissociation in case of a melamine salt followed by endothermic sublimation of the melamine itself at roughly 350°C. Another, even larger, heat sink effect is generated by the subsequent decomposition of the melamine vapors. Melamine can be regarded as a "poor fuel"..... Furthermore, the nitrogen produced by combustion will act as inert diluents > [15].

The molecular structures of some derivatives of melamine used as flame-retardants for polymers are illustrated in figure 12 [15,16].

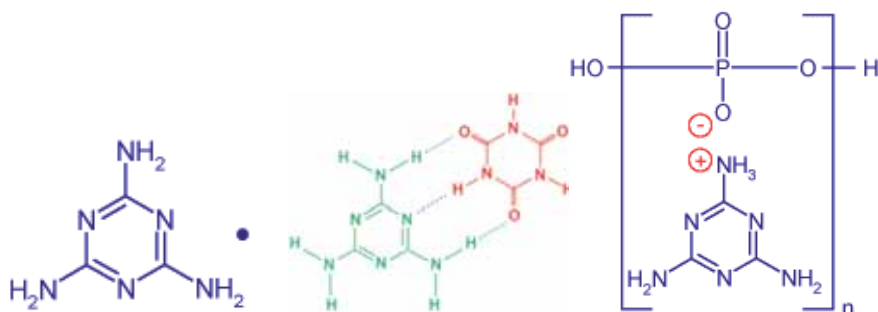


FIGURE 12: Molecular structures of:
Melamine (left);
Melamine cyanurate (center);
Melamine-phosphate (n=1), melamine-
pyrophosphate (n=2) and melamine-
polyphosphate (n>2) (right) [15,16].

--- *self-extinguishing (Char formers)*

They are additives, usually phosphorous compounds, which by producing chars remove the carbon fuel source forming as well an insulating layer protecting against the fire heat [4].

Some polymers (poly vinyl chloride, vinyl chloride-acetate copolymers, poly vinylidene chloride, nylons and casein plastics) are intrinsically self-extinguishing as they have the ability to cease burning once the source of flame has been removed [2].

It has been found that polymers forming during pyrolysis products with structures similar to that of graphite are also able to produce a major amount of char. Thermogravimetric analysis, as shown in figure 13, represents an effective methodology to determine the amount of char residue in a plastic material [1-b].

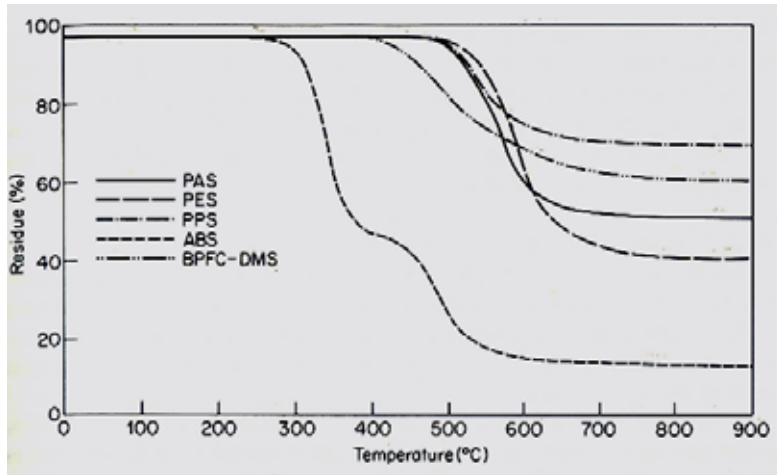


FIGURE 13: Thermo gravimetric diagrams for several plastics. PAS=polyaryl sulphones; PES=polyether sulphones, PPS=polyphenylene sulphide; ABS=acrylonitrile-butadiene-styrene terpolymer blends; BPFC-DMS=polycarbonate-silicone block copolymers [17].

From the trend of the thermograms it can be seen that the % of char residue, for some thermoplastics belonging to the acrylonitrile polymer family, depends upon the molecular structure of repeat unit being larger in the case of those polymers with aromatic rings in the backbones of the chains [1-b, 17].

< Melamine can also show considerable contribution to the formation of a char layer in the intumescent process. The char layer acts as a barrier between oxygen and polymeric decomposition gases > [15].

--- *Smoke Suppressants*

Are additives capable to reduce the amount of toxic smokes generated during the process of burning of polymers. Silica flour, molybdenum oxide, magnesium oxide, aluminum tri-hydrate etc., are typical examples of substances used as smoke suppressants for plastics [1-b].

6) **Foaming additives (Blowing Agents)**

Foaming additives may be defined as follows: < Any substance which alone or in combination with other substances is capable of producing a cellular structure in a plastic or rubber mass > [2].

The above definition includes a wide range of systems, some of which are hereafter mentioned:

- Gases, which expand when the pressure is reduced;
- Solids miscible with polymer that leave pores when leached out;
- Liquids that by passing to the gas state are able to form cell in the polymer matrix;
- Chemicals that following heating react or decompose forming gases [2].

Thus blowing agents are substances that, during the processing of plastics or rubbers, have the capability to give rise to the formation of gases such as N_2 , CO_2 or H_2O that been < *trapped in the polymers, turn the material into foam, thus increasing the insulation and energy absorption properties and reducing weight. These foams can be seen in everyday use such as protective food packaging, cushioning in sports shoes and in automobile parts where lower weight saves fuel* > [18]. Foaming additives can be conveniently classified in: *Physical* and *Chemical* types.

--- *Physical blowing agents*

< *Are volatile liquids or compressed gases that change state during processing to form a cellular structure within the plastic matrix... The compounds themselves do not experience any chemical changes* > [4].

Liquid aliphatic hydrocarbons, with low boiling temperature, and their chlorine and fluorine analogs together with N_2 , CO_2 and air are typical examples of such kind of agents.

--- *Chemical blowing agents*

Are compounds (mostly solid hydrazine derivatives) able to decompose, usually at the temperature close to that of polymer processing, giving rise to the formation of at least a gas product which by expanding the polymer mass produces the cellular structure. According to the mechanism of action chemical blowing agents may be divided in:

Exothermic (azodicarbonamide AZ), modified AZ-systems, sulphonyl hydrazides, sulphonyl semicarbazides, dinitropentamethylene tetramine, etc.) or *Endothermic* (sodium borohydride [$NaBH_4$], sodium bicarbonate [$NaHCO_3$], etc.) according to whether the production of gases occurs through physical transition (i.e. evaporation or sublimation) or by a chemical process (for example a decomposition reaction generating gaseous products) [4, 1-b].

The molecular structure of some of cited chemical blowing agents are described in figure 14.

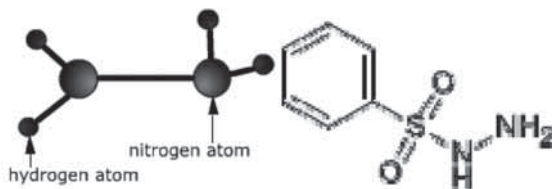


FIGURE 14: The molecular structure of: Left, hydrazine, N_2H_4 , a compound made up of nitrogen and hydrogen. Right, benzenesulphonyl hydrazide.

Cellular polymers can be flexible or rigid, thermoplastic or cross-linked.

< The most familiar examples of both rigid and flexible cross-linked and chemically foamed materials (where the polymeric structure develops via chemical reactions along with expansion into a foam) are polyurethane foams manufactured from different formulations by using different process conditions. The most familiar example of a physically foamed system (where a previously synthesized molten polymer is expanded into a foam) is an expanded atactic polystyrene rigid foam > [19].

Foaming processes may lead to polymer materials with *open* or *closed-cell* (see figure 15)

< The foam cells adopt polyhedral shapes which result from the combination of the physical factors governing the foaming process and the geometrical constraints of packing > [19].

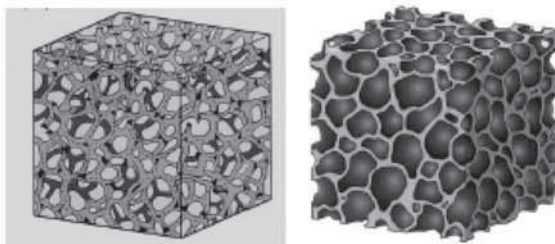


FIGURE 15: Models of slabs of typical open-cell foams (left) and closed-cell foams (right) [19].

7) Biocides agents

It is well known that environmental conditions characterized by the presence of moisture, warmth, and soil may induce in many plastics the growth of microbial agents able to cause embrittlement, discoloration, loss of light transmittance or odors, etc. To avoid such a phenomena suitable additives have been developed to protect plastic products against unwanted growth of micro-organism such as mold, mildew, fungi and bacteria.

Biocides additives are usually used in < a wide variety of plastic materials such as plastic foils and sheets, molded plastic parts, paints and laminates, adhesives and sealants for specific applications. Other applications in which the end product can be protected are artificial fibers for clothing and for industrial and household products > [19].

The most common biocides include the following types of products:

- 1) 10,10'-oxybisphenoxarsine (OBPA);
- 2) 2-*n*-octyl-4-isothiazolin-3-one;
- 3) 4,5-dichloro-2-*n*- octyl-4-isothiazolin-3-one (DCOIT);
- 4) Zinc 2-pyridinethianol-1-oxide (zinc OMADINE);
- 5) Trichlorophenoxyphenol (TCPP or TRICLOSAN);
- 6) N-trichloromethylthio-4-cycloesene-1,2-dicarboximide (CAPTAN);
- 7) N- (trichloromethylthio)phtalimide (FOLPET) [4].

The molecular structure of some of the above mentioned biocides are described in figure 16.

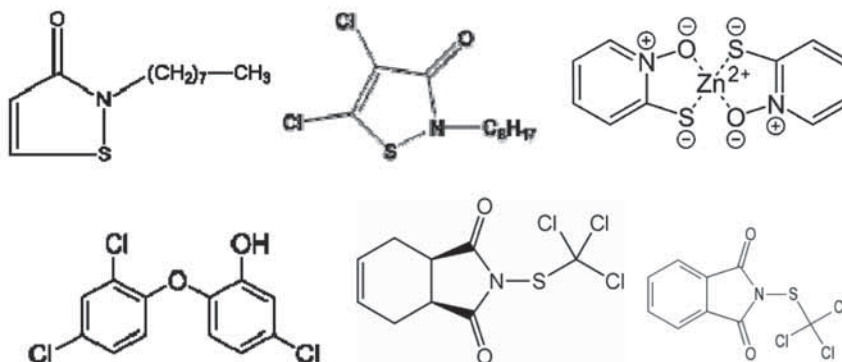


FIGURE 16: The molecular structure of some biocides used in the case of polymer materials.

Top:

Left - 2-n-Octyl-4-isothiazolin-3-one [20];

Center - 4,5-dichloro-2-n-octyl-4-isothiazolin-3-one (DCOIT) [21];

Right - Zinc 2-pyridinethiol-1-oxide (zinc OMADINE) [22];

Bottom:

Left - Trichlorophenoxyphenol (TCPP or TRICLOSAN) [23];

Center - N-trichloromethylthio-4-cycloesene-1,2-dicarboximide (CAPTAN) [24];

Right - N-(trichloromethylthio)phtalimide (FOLPET) [25].

A biocide to be effective should be able to migrate towards the surface of the plastic object in order to contrast the attack of microbial agents.

Biocides, initially were essentially developed to protect polyurethane-foams and flexible polyvinylchloride, where plasticizers are a key food source for fungi, bacteria, and algae. At the present antimicrobial additives are also widely used < in polyolefins and other plastics, thanks to consumer demand for "germ-free" products > [26].

Two inorganic antimicrobials agents, heat stable and resistant to migration, with the following composition:

--- 98% zinc oxide with a small amount of silver and other inorganics;

--- 98% TiO₂ with small amounts of silver, zinc, and copper [26], were developed.

< Both are off-white powders. They are effective in PP, PE, PET, PBT, ABS, and nylons 6 and 66,..... Potential applications include household articles, appliance components, computer keyboards, phone sets, gymnastic equipment, and fibers for bath mats or carpeting > [26].

8) Organic and inorganic pigments

Pigments according to reference [2] are defined as follows:

< ..all colorants, organic or inorganic, natural and synthetic, which are insoluble in the medium in which they are used. Organic pigments are those which contain carbon as the basic part of the molecule. The inorganic pigments, most of which are derived from natural minerals, contain a metal as the basic part of the molecule > [2].

The main characteristics of pigments reside on the capability to impart color to plastics by scattering light having well defined wavelengths (λ) while absorbing light with different values of λ (see figure 17-left).

Examples of inorganic and organic pigments used in the case of thermoplastic polymers are reported in table 7 and 8 respectively.

TABLE 7: Inorganic pigments used in the case of thermoplastic polymers [1-b].

B. PIGMENTS		
(i) <i>Inorganic</i>		
(a) Oxides	White titanium oxide Yellow iron oxide Red iron oxide Black iron oxide Green chromium oxide	TiO_2 $Fe_2O_3 \cdot H_2O$ Fe_2O_3 Fe_3O_4 Cr_2O_3 and $Cr_2O_3 \cdot 2H_2O$
(b) Chromates	Moly orange Chrome orange	$PbCrO_4$ - $PbSO_4$ - $PbMoO_4$ $(PbCrO_4)_x \cdot (PbO)_y$
(c) Sulphides	Cadmium yellow Cadmium red	(c) Mixed CdS, ZnS Mixed CdS, CdSe

TABLE 8: Organic pigments used in the case of thermoplastic polymers [1-b].

Chemical nature	Type	Structure
Organic Yellows	Dichlorobenzidine derivatives	(a)
Oranges	Dianisidine derivatives	(b)
Reds	Toluidine reds	(c)

Quite recently Ciba®, now part of BASF, developed a family of inorganic pigments (IRGACOLOR®) based on bismuth vanadate which *< exhibit excellent performance and end-use properties in many different demanding polymers. These pigments are characterized by their outstanding resistance to heat, weather and chemicals, even at very low concentrations, which makes them extremely useful for tinting purposes > [27].*

The IRGACOLOR® pigments also characterized by a very good dispersibility; they are suitable to be used in many type of plastics (see figure 17).



FIGURE 17: Inorganic pigments suitable to be used in many type of plastics [27,28].

High performance organic pigments suitable for a wide range of polymers and processes were also developed by Ciba®. *< These pigments exhibit excellent all-round properties, which result in their being used in many different automotive applications. They are used in engineering plastics, styrenics, flexible and rigid PVC, and for a broad range of polyolefins, depending on the specific product chemistry. The properties exhibited by these products are*

- High heat stability
- Very good migration resistance
- Excellent lightfastness
- Very good weather resistance > [28].

These pigments are market as: CROMOPHTAL® DPP (red pigment); IRGALITE®; IRGAZIN®; and CINQUASIA® [29].

The molecular structures of some recently developed organic high performance pigments are represented in figure 18

It is interesting to point out that many pigments are obtained by using organic dyes *< which are insolubilised into brittle thermosetting resins and micronised into particles of the desired dimensions > [1-b].*

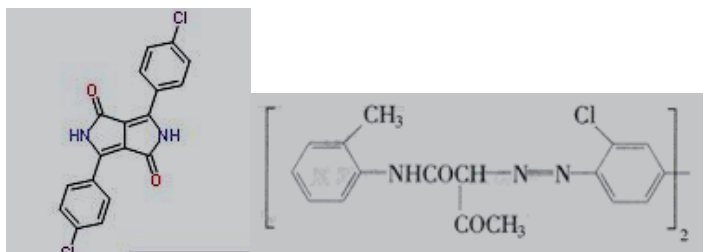


FIGURE 18: Molecular structures of some recently developed organic high performance pigments [27,28].

From optical point of view pigments to be able to scatter and absorb light have to satisfy the following conditions:

- Their particle size should be larger than the λ of the incident light;
- Their refractive index should be much higher than that of polymer matrix;
- They have to show a very good dispersibility in the polymer matrix [1-b].

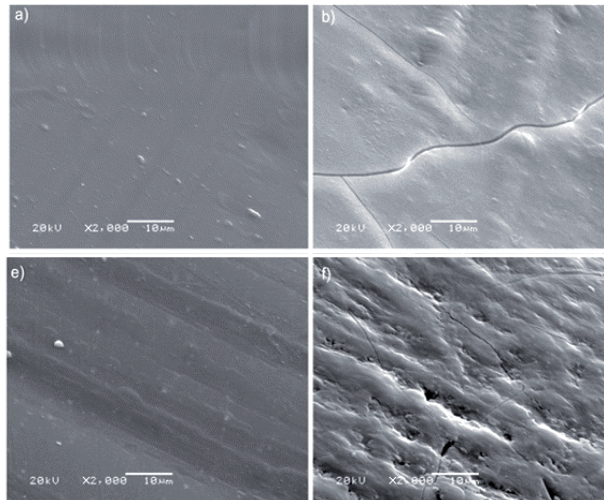


FIGURE 19: Scanning electron photomicrographs of: Top-left, polycarbonate before artificial aging; Top-right, polycarbonate after 3360hrs of aging. Bottom-left, polycarbonate containing bismuth vanadate pigment before artificial aging; Bottom right polycarbonate containing bismuth vanadate pigment after 3360hrs of aging [30].

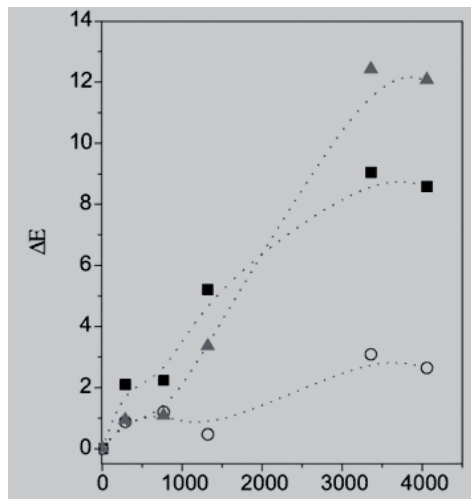


FIGURE 20: Color variation parameter (ΔE) as function of aging time for polycarbonate ■ and polycarbonate containing bismuth vanadate pigment ▲ [30].

In some circumstances it was found that pigment additives may influence the mechanism and the kinetics of the photodegradation behaviour of the polymers. C. Saron and Others while studying the photochemical aging of polycarbonate containing bismuth vanadate (BiVO_4) observed that the presence of the pigment determines:

< a faster drop in the mechanical properties and an increase in the hydroperoxide concentration during the aging process > [30].

Such a conclusions were in agreement with the following observations:

1) The presence of voids, sinks and cavities on the surface of samples (see electron micrographs in figure 19) *< caused by matrix corrosion around aggregates of the pigment due to a photocatalytic action of the pigment under polycarbonate degradation when the material is exposed to the aging conditions > [30].*

2) The coloring ability of the pigment, as shown by figure 20, is influenced by the time of aging [30].

The findings of C. Saron and Others were accounted for by assuming that:

< The presence of bismuth vanadate pigment makes polycarbonate more susceptible to photodegradation under accelerated aging with UVA radiation. The possible mechanism of the bismuth vanadate pigment on polycarbonate photodegradation involve a direct chemical reaction between polymer and pigment, resulting in both polymer and pigment degradation > [30].

From all above reported it can be concluded that by using suitable additives several and important plastic functions and properties may be tailored and implemented.

As already shown additives may be used to fulfill several and different aims some of which are herewith summarized:

- Retention of properties of polymer component (i.e., plasticizers, etc.);
- Extension of polymer properties (i.e., light stabilizers, slip agents, anti aging, etc.);
- Protection of customers polymer properties (i.e., antimicrobials, colorants and pigments, anti statics, etc.).

REFERENCES

- 1-a) B. van Beusichem, M. A. Ruberto, < *Introduction to Polymer Additives and Stabilization* >, http://www.pqri.org/workshops/leach_ext/imagespdfs/posters/Polymer_Additives_PQRI_Poster.pdf, (2009).
- 1-b) L. Mascia, < *Thermoplastics* >, Elsevier Applied Science, London (1989).
- 2) L. R. Whittington, < *Dictionary of Plastics* >, Technomic, USA, (1978).
- 3) <http://www.bm-chemie.de/content/en/polymeradditives/index.shtml>, (2009).
- 4) C. A. Harper, < *Modern Plastics Handbook* >, McGraw-Hill, New York, (2000).
- 5) <http://www.pvc.org/PVC.org/What-is-PVC/How-is-PVC-made/PVC-Additives/Plasticisers>, (2009).
- 6)
http://www.google.com/search?hl=it&lr=lang_it&q=glass+transition+temperature+pvc&revid=1380424856&ei=h9q8SYfDdiRsAadxMToDg&sa=X&oi=revisions_inline&resnum=0&ct=broad-revision&cd=7, (2009).
- 7) A. Neau, *Pittura e Vernici - European Coatings*, 10, 49, (2007)
http://www.gbp.it/copiasitopv_inlinea/archivio_pdf/ANNO2007/10_plastiNaft.pdf, (2009).
- 8) < *Fondamenti di Scienza dei Polimeri* >, a cura di M. Guaita et Al., Pacini Editore, Pisa (1998).
- 9) -a) C. Hall, < *Polymer Materials* >, The MacMillan Press LTD, London (1981).
-b) <http://repositories.tamu.edu/bitstream/handle/1969.1/1611/etd-tamu-2003C-MEEN-Book1.pdf?sequence=1>, (2009).
- 10) <http://www.bm-chemie.de/content/en/polymeradditives/index.shtml>, (2009).
- 11)
<http://www.specialchem4adhesives.com/tc/antioxidants/index.aspx?id=acrylatebphenols>, (2009).
- 12) <http://www.specialchem4adhesives.com/tc/antioxidants/index.aspx?id=hydroxylamine>, (2009).
- 13) <http://www.specialchem4adhesives.com/tc/uv-light-stabilizers/?id=hals>, (1009).
- 14) I. Luzinov, V. Klep, B. Zdyrk, G. Chumanov, D. D. Evanoff, Jr., *Nanocomposite Polymer Pellicles for 157 Nm Photolithography*, International Sematech,
www.semtech.org/meetings/archives/litho/immersion/20040803/Posters/B-02_Luzinov-Clemson_Nanocomposite_polymer_pellicles.pdf, (2009).
- 15) <http://www.specialchem4polymers.com/tc/Melamine-Flame-Retardants/?id=4004>, (2009).
- 16) <http://www.varianinc.com/image/vimage/docs/products/chrom/apps/SI-01842.pdf>, (2009).
- 17) D. A. Kourtides, et Al., *SPE Regional Tech. Conf. Connecticut Sect.*, p. 113, (1977).
- 18) http://poweradditives.com/polymer_additive.htm, (2009).
- 19) www.polymerexpert.biz/PolymersandComposites.html, (2009).
- 20) www.dermacom.ch/private/alindex/OC000.htm, (2009).
- 21) L. Sadasivan, Usha Gandhi, < *A 'Two-For-One' Biocide For Latex Coatings Provides Effective In-Can and Dry Film Preservation* > www.pcimag.com/Articles/Cover_Story/430c3548f, July 1, (2003),
- 22) en.wikipedia.org/wiki/Zinc_pyrrithione, (2009).
- 23) www.answers.com/topic/triclosan, (2009).
- 24) [wikimedia-CAPTAN](http://wikimedia.org/wiki/CAPTAN), (2009).
- 25) [wikimedia-FOLPET](http://wikimedia.org/wiki/FOLPET), (2009).
- 26) S. Lilli Manolis, < *Biocides keep the bugs off your plastics* >, *Plastics Technology*, February 1 (1998),
<http://www.allbusiness.com/manufacturing/plastics-rubber-products-manufacturing/732590-1.html>, (2009).

27)

http://images.google.com/imgres?imgurl=http://www.ciba.com/inorganic-pigments.jpg&imgrefurl=http://www.ciba.com/index/ind-index/ind-automotive/products-9/ind-pla-eae-pro-colorants-3/ind-pla-eae-prod-color-inorganic_pigments-2.htm&usg=__49gXcYwQLRQ76nlPzTnt7L6Z-A0=&h=134&w=200&sz=9&hl=it&start=1&tbnid=V2BPgF4ZU4kUcM:&tbnh=70&tbnw=104&prev=/images%3Fq%3DCiba%25C2%25AE%2BIRGACOLOR%25C2%25AE%26hl%3Dit, (2009. 28)

http://images.google.com/imgres?imgurl=http://www.lookchem.com/300w%255C2008-11%255Caa35a8ff-ec34-49cf-9622-000ba3a538e6.jpg&imgrefurl=http://www.lookchem.com/cas-846/84632-65-5.html&usg=__KT5v2ssyhgynDDiMUFwj_hQ5Ok=&h=144&w=142&sz=4&hl=it&start=11&tbnid=V6c7OJIyyz00kM:&tbnh=94&tbnw=93&prev=/images%3Fq%3DCROMOPHTAL%26hl%3Dit, (2009).

29) K. Pianoforte,

http://images.google.com/imgres?imgurl=http://www.inkworldmagazine.com/articles/2006/08/images/Pigments_violet.jpg&imgrefurl=http://www.inkworldmagazine.com/articles/2006/08/high-performance-pigments.php&usg=__c9x9y3tQH9d3GwyN4SFGNntu5-g=&h=200&w=150&sz=76&hl=it&start=178&tbnid=_aJmFkzdU82FpM:&tbnh=104&tbnw=78&prev=/images%3Fq%3DCiba%25C2%25AE%2BCROMOPHTAL%25C2%25AE,%26ndsp%3D20%26hl%3Dit%26sa%3DN%26start%3D160, (2009).

30) C. Saron, M. I. Felisberti, F. Zulli, M. Giordano, < *Effects of bismuth vanadate and anthraquinone dye on the photodegradation of polycarbonate* >, *Journal of the Brazilian Chemical Society*, Web Release Date: July 24, (2007), 2009 Brazilian Chemical Society.

31) <http://xoomer.virgilio.it/hmxjhn/dir14/plastiche.htm>, (2009).

SECTION-1

FOURTH-CHAPTER (PART-1)

DEGRADATION OF PLASTIC ARTEFACTS IN RELATION TO MOLECULAR STRUCTURE OF POLYMER CONSTITUENT, NATURE AND FUNCTION OF ADDITIVES, COMPOSITION AND PROCESSING CONDITIONS.

From a general point of view the degradation behaviour of a multicomponent polymer-based material (plastics) depends on several and different kind of internal and external factors which, according to their origin, may be conveniently grouped as follows [1-5]:

A) Factors depending on polymer component and processing conditions

- Molecular structure of repeat unit;
- Molecular mass (average values and distributions);
- Aggregation state of macromolecules in the condensed state (degree of crystallinity/amorphicity, glass transition temperature, melting temperature, ecc.);
- Catalytic residues, metal ions, impurities and structural defects.

B) Factors depending on Additives

- Type, chemical nature, function and concentration.

C) Factors depending on Interactions with other materials

D) Factors depending on Exposure to environmental degradation agents

- Heat;
- Humidity;
- Oxygen and ozone;
- Sun light especially ultraviolet radiations;
- Chemical pollutants;
- Bacteria, fungi and insecta.

E) Factors depending on Mechanical stresses

- during manufacturing
- following life cycle and use function.

From another point of view the deterioration of plastic items may be taken back, essentially, to the following three main causes:

- Physical and mechanical;
- Chemical;
- Biological [1-7].

1) Physical or mechanical degradation (Physical aging)

Usually such type of degradation is associated with incorrect utilization and handling of the plastic items during their life especially in relation to the use functions for which they have been manufactured.

Typical mechanical damaging, that do not forecast chemical reactions, may arise from: surface scratching, repeated bending, dropping, volume expansion/contraction due to heat/cold cycle, swelling due to the absorption of moisture or other kind of liquids and vapours, migration of additives towards the surface, ecc. It is worthy to note that mechanical damages may accelerates many chemical degradation processes [6,7].

Plastic artefacts showing different types of mechanical damages are shown by figures 1 and 2 [7].

Some of the effects produced on plastic items by mechanical and physical degradation are below listed:

- stress crazing or environmental stress crazing;
- increasing rigidity due to plasticiser leaching or migration;
- an oily or solid bloom on the surface caused by migration of additives;
- distortion phenomena associated to uneven loss of plastisers [7].

Transparent sheets of thermoplastics polymers such as polystyrene and poly (methyl methacrylate), due to the high values of the glass transition temperature, are rigid at room temperatures. Consequently those objects quite often show clear evidences of non haesthetic forms of environmental stress crazing phenomena (see figure 1-right) [7].

Plastics based on polyvinylchloride and on cellulose nitrate (celluloid), being formulised with a high content of additives, especially plasticisers, are typical examples of plastics that easily show migration of additives that in some circumstances being uneven causes distortion of the objects (see figure 2-left)[7].



FIGURE 1, right: Environmental stress crazing observed in objects made by rigid transparent thermoplastics such as polystyrene and poly(methyl methacrylate) [7].

FIGURE 2, left: Uneven loss of plasticiser from artefacts manufactured in celluloid is responsible for heavy distortion [7].

Physical aging, connected to migration of additives and plasticizers, produces in the materials loss of flexibility, brittleness, soil accumulation and staining, while molecular relaxations, and polymer crystallization may induce phenomena of deterioration characterized by shrinkage, hardening, breaks, opacity and dullness, delamination and cracks.

Optical and mechanical effects have been quite often observed in the case of composition changes determined by preferential extractions and solubilization processes [8].

Examples of damages caused by physical aging are clearly evidenced through the electron scanning micrographs reproduced in figure 3 [8].

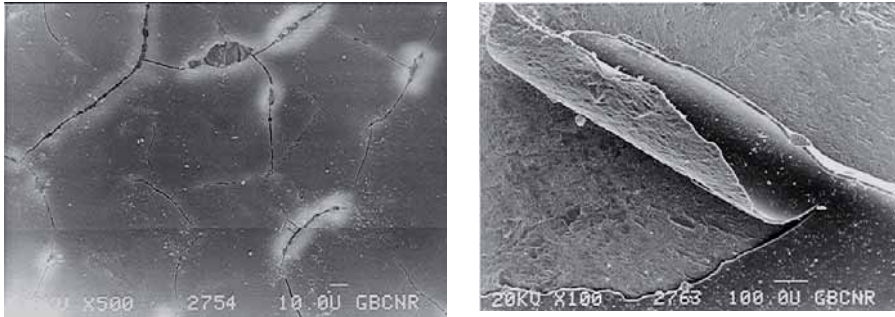


FIGURE 3: Electron scanning micrographs showing examples of mechanical damages caused by physical aging in polymer materials (delamination, cracks and crazes, whitening and blooming phenomena are evidenced) [8].

2) Chemical degradation

The main factors able to induce chemical changes in polymer materials are essentially the following:

- Light
- Heat
- Oxygen
- Moisture
- Ozone or other atmospheric contaminants
- Contact with chemical agents during life cycle utilization, exhibition, storage, cleaning and restoration treatments.

The main processes responsible of chemical transformation in polymer materials are essentially the following:

- Thermal degradation (*Factor*: heat);
- Photodegradation (*Factor*: light);
- Thermo-oxidation(*Factors*: heat and oxygen);
- Photo-oxidation (*Factors*: light and oxygen);

The chemical mechanisms related to the above cited processes are below described together with the most effective type of damages they are capable to produce.

2.1) Thermal degradation of polymers

It is a process of degradation, produced by heat in absence of oxygen, particularly relevant during the manufacturing of polymers. As matter of facts it is well known that many polymers are processed in conditions which exclude oxygen while high temperatures are used.

In the case of carbon based polymers, following exposure to increasing temperatures, between 150-500°C , it can be observed that most of common present chemical bonds (C-C, C-H, C-N, C-O, ecc.), according to their dissociation energy (see table 1), may be broken.

TABLE 1: Dissociation energy for some common interatomic bonds.

BONDS	ENERGY (kJ mol ⁻¹)
C—H	416
C—C	348
C—O	361
C—F	485
C—Cl	329
C—N	292
C=C	612
C=O	732

The process of polymer thermal degradation occurs through three main steps, namely:

Primary or Initiation step:

Depolymerization step:

Termination step.

In the case of polymers with the backbone chain constituted by C-C bonds, as shown by figure 4, the *Primary or Initiation step* of the process of thermal degradation consists in the thermolysis of C-C bonds with formation of radical species.

This *primary step* is followed by a series of reactions that according of the nature of the polymer and of the temperature may be classified according to the following two different categories:

1) Reactions involving the chain backbone, named “*depolymerization*”, which foresee the cleavage of C-C bonds of the backbone of polymer chain leading to the fragmentation of the macromolecules and or to the formation of volatile low molecular mass products (monomers).

2) Reactions that forecast the “*elimination, condensation or cyclisation of the side groups*” present along the macromolecules. The backbone structure remains unaltered while small molecules are produced (H₂O, NH₃, ecc.) [3,4].

Generally it is observed that on heating the reaction involving side substituents occurs at lower temperatures than those causing chain depolymerization [3,4].

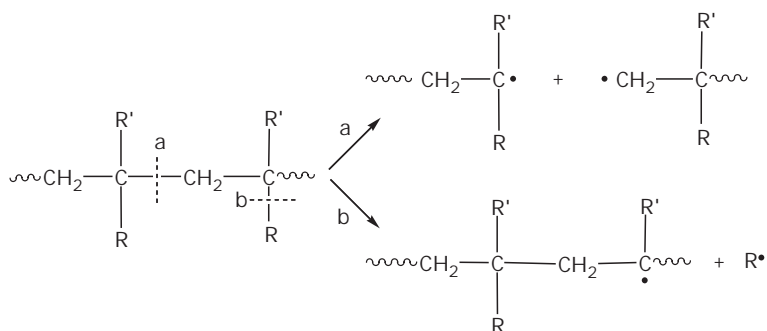


FIGURE 4: The primary step of the thermal degradation process of a carbon-carbon chain polymer.

Top-right: homolysis of backbone C-C bonds.

Bottom-right: homolysis of side group C-C bonds [3].

Reactions of depolymerization

In the case of a generic vinyl polymer the reactions responsible of depolymerization occur through a chain-radical mechanism initiated by an homolytic scission of a carbon-carbon intra chain bond (see scheme reported in figure 5) [3,4,5,9].

The depolymerization may be propagated through successive scission reactions in β , against the carbon radical atom, through an *unzipping* mechanism leading to the production of monomer molecules (see figure 6) [3,4,5,9]

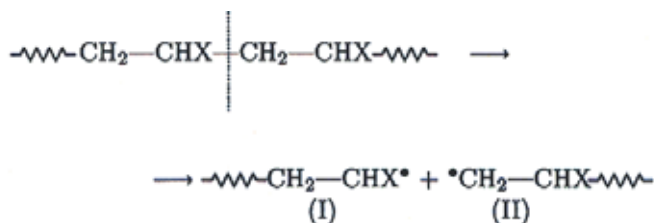


FIGURA 5: The scheme of the homolytic scission of a carbon-carbon intra chain bond that represents the initiation step of depolymerization. The mechanism leads to the formation of reactive macroradical species [9].

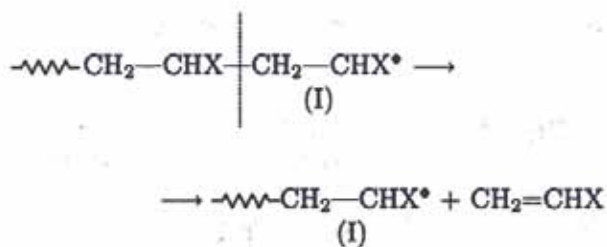


FIGURE 6: Propagation of the heat induced depolymerization through an *unzipping* mechanism that leads to the production of monomers [9].

The macroradicals produced according to the reaction depicted in figure 5 may also give rise to chain transfer reactions that foresee the extraction of hydrogen atoms situated in intra-chain or inter-chain position.

The reaction scheme concerning an inter-chain type of transfer is reported in figure 7.

First a macroradical (III) is formed then a chain scission in β position occurs with the production of the same macroradical (I) that started the reaction [4,9].

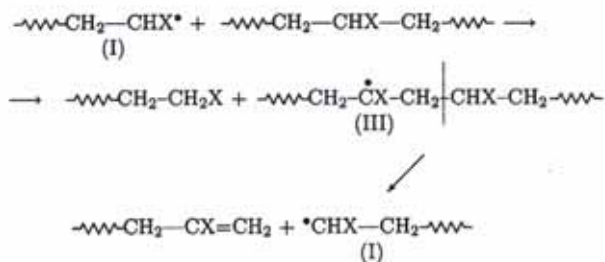


FIGURE 7: Transfer reaction through extraction of an intermolecular hydrogen atom [9].

In the case of an intramolecular transfer, as shown by the scheme in figure 8, the new formed macroradical by β chain scissions gives rise to the formation of volatile oligomer or chain fragments [4,9].

The reactions above depicted are named “*back biting*” or “*unbuttoning*” in contraposition to the one above presented and denominatet “*unzipping*”.

According to reference [10] the unzipping mechanism of degradation (depropagation) *< is characterized by rapid volatilization of products with little or no change in polymer molecular weight >*, see top curve in figure 9.

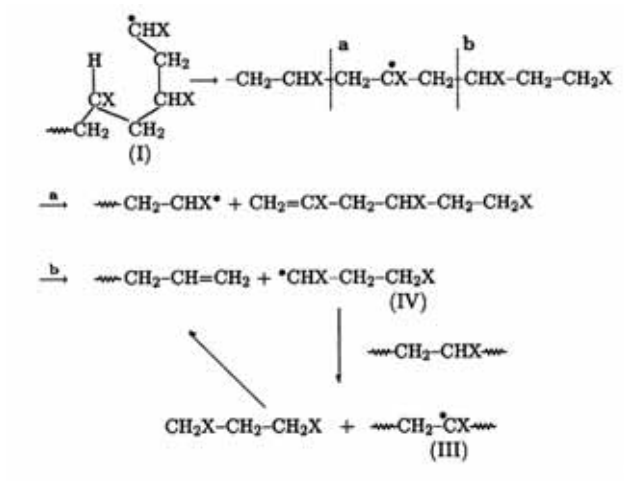


FIGURE 8: Chain transfer reaction through extraction of an intramolecular hydrogen [9].

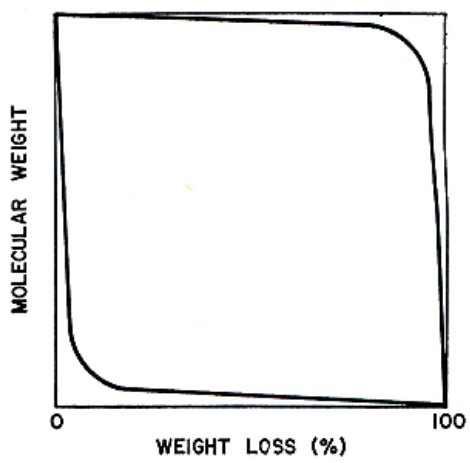


FIGURE 9: Schematic representation of molecular weight of degrading polymer as function of weight loss.

Top, following depropagation (unzipping mechanism of degradation).

Bottom, following chain random scission, see text [10].

On the contrary the peculiarities of degradation happening according to a “back biting” or “unbuttoning” mechanism (random chain scission) in reference [10] are described as follows:

< At high extent of reaction some of the molecules produced will volatilize, but the main characteristic of this type of degradation is a rapid fall of molecular weight with little or no weight loss. (see bottom curve in figure 9).

Practical polymers show all ranges of behaviour between the first and second types, consequently the molecular weight versus weight loss curves will fall between the two extremes sketched > [10].

In the reality the two possible process of depolymerization above described (depropagation and chain transfer) are in competition. When depropagation prevails then monomers are the main product of degradation. On the contrary if the intermolecular chain transfer reaction is prevalent then statistical scission of macromolecules is the prevailing mechanism. Finally in case of degradation occurring mainly through an intramolecular chain transfer mechanism the formation of chain fragments are the most probable events [9].

When the the rate of depropagation and chain transfer reactions are similar then the products of degradation are a mixture of monomers and macromolecule fragments [9].

The thermal degradation of the poly(methylmethacrylate) occurs prevalently according to depropagation mechanism in which < starting from a chain and or other weak point in the molecule, successive monomer units are lost to yield only one product, monomer > [10] (see figure 10).

An example of depolymerization occurring by chain transfer mechanism is given by polyolefins, polyethylene, polypropylene and polystyrene, (see mechanism in figure 11) [10].

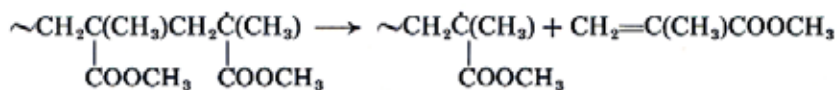


FIGURE 10: Thermal degradation of polymethylmethacrylate. Depolymerization step by unzipping mechanism [10].

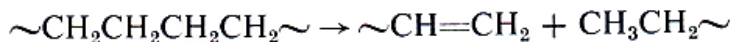


FIGURE 11: Heat depolymerization of polyethylene by chain transfer mechanism [9].

Termination of depolymerization

The termination of thermal depolymerization may occur by volatilization of low molecular mass radicals, or by combination of free radicals according to a coupling or disproportionation reaction (see figure 12) [9].

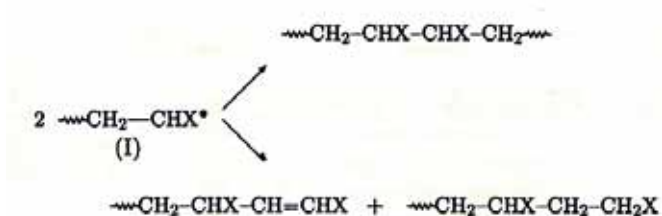


FIGURE 12: Termination step of the depolymerization reaction according to two different routes. Top: by reaction of coupling between two radicals. Bottom: by radical disproportionation reaction [9].

As shown by the data in table 2, in C-C polymers the prevailing mechanism of depolymerization process induced by thermal degradation is strongly dependent upon the molecular structure of the repeating units, and particularly by the reactivity of radical species and by the presence of mobile hydrogen atoms [9].

TABLE 2: The weight % of monomer obtained from thermal depolymerization for C-C chain polymers (100% of monomers means that the depolymerization occurs only by depropagation mechanism while 0% indicates that chain transfer is the prevailing mechanism, intermediate values are relative to a combination of the two depolymerization processes) [9, 11].

POLYMER	MONOMER %
Polymethylmethacrylate	100
Poly- α -methylstyrene	100
Polytetrafluoroethylene	100
Polymetha-methylstyrene	52
Polystyrene	42
polyisobutene	32
Polyisoprene (Natural rubber)	12
Polypropylene	2

The overall thermal degradation process of polymethylmethacrylate (PMMA) is described, with reference to the figure 13, as follows by I. C. McNeil [12]:

< *Depolymerization. This name can be applied to degradation processes in which the chain breaks at some point, leading to reactions in which the products all have the same composition as the repeat structure, but may consist of relatively small molecules such as monomer, dimer, trimer, or chain fragments.....The simplest reaction of this type involves chain homolysis, followed by depropagation, as in the case of PMMA. In PMMA, the depropagation proceeds rapidly along the chain once the initial break has occurred,.....Monomer is the only thermal degradation product from this polymer, obtained in up to 100% yield > [12] (see in figure 13).*

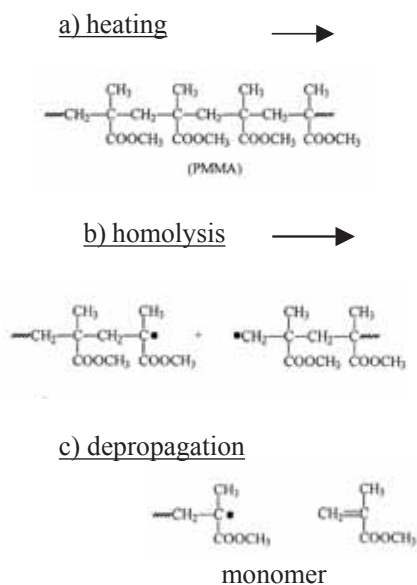


FIGURA 13: Thermal degradation of polymethylmethacrylate.

- a) PMMA: molecular structure before heating:
- b) Chain Homolysis with formation of two radicals.
- c) Following depropagation reaction monomer are formed [12].

Thermal degradation of polymers with intrachain functional groups

When along the macromolecules of a polymer material are present in intrachain position active functional groups then the mechanism of depolymerization depends upon the nature of those groups which usually under heating react at temperatures lower than those where C-C bond rupture occurs. Some relevant examples are hereafter presented [9,10,11].

I) Polyurethanes

This is a typical polymer obtained through a polyaddition polymerization. As shown by figure 14 following heating the equilibrium of the reaction is shifted to the right. Consequently polyurethanes decompose by forming essentially monomer units (glycol and isocyanate).

II) Polyester

Usually prepared by polycondensation reaction with elimination of small molecules (water, ammonia, ecc.). In such polymers following heating, the scission of the ester bonds leads to fragmentation of the macromolecular chains according to the mechanism described in figure 15.

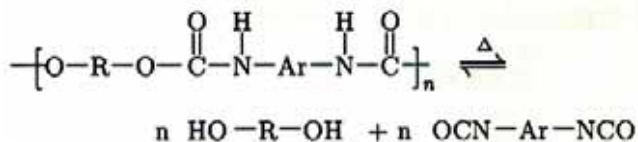


FIGURE 14: In the case of polyurethanes the heat induces a depolymerization reaction leading to the formation of monomers (glycol and isocyanate) [9].

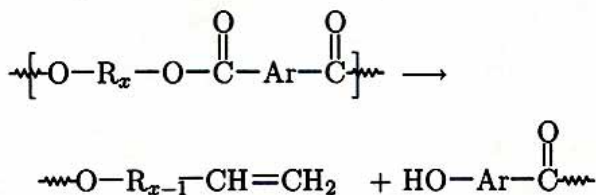
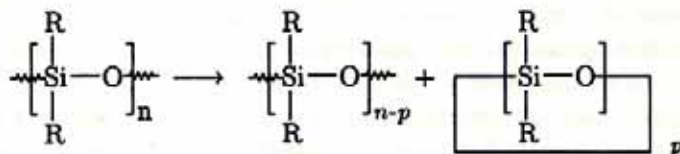


FIGURE 15: The heat induced depolymerization of polyester occurs by cleavage of the ester bonds with formation of chain fragments [9].



$$p = 3-13$$

FIGURE 16: The heat depolymerization of polysiloxanes may produce also cyclic monomer/oligomer products [9].

III) *Polysiloxanes*

In this polymers the depolymerization caused by heating may also lead to the formation of cyclic monomer or oligomer products (see mechanism in figure 16).

IV) *Polyoxymethylene (polyformaldehyde)*

As described by the reaction scheme in figure 17 in such a polymer depolymerization occurs mainly by a mechanism of depropagation from chain ends, activated by the presence of a reactive hydroxy end group, that gives rise to the formation of monomers [10].



FIGURE 17: Depropagation reaction from chain ends in the case of polyoxymethylene (polyformaldehyde). Monomer products are formed [9].

Thermal degradation involving Side Group reactions

The most common reactions involving the adjacent side groups present along macromolecular chains are essentially scission and cyclation.

a) Examples of reactions leading to the scission of side groups

Carbon chain polymers as polyvinylchloride (PVC) and polyvinylacetate (PVAC) by heating lose molecules of hydrochloric acid (HCl) and of acetic acid (CH₃COOH) respectively, as shown by the schemes in figure 18 and 19 [11].

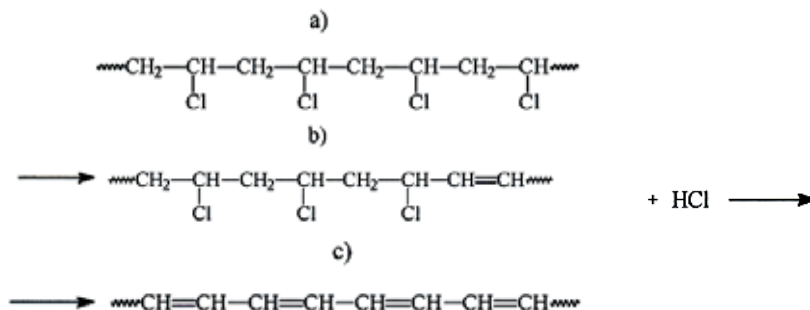


FIGURE 18: Mechanism describing as following heating PVC releases HCl molecules forming a polyene polymer [12].

In the case of PVC < *Once an acid molecule has been lost, the double bond so formed destabilises the next repeat unit, so that the reaction tends to proceed along the chain, which results in the formation of a conjugated polyene* (see molecular structure in figure 18-bottom) > [12].

The presence along the polyene macromolecules of sequences of conjugated double bonds is responsible for the discoloration process observed in PVC items following heating. The elimination of acetic acid molecules by PVAc chains may be easily perceived due to its intense and characteristic smell. The degraded PVAc material assumes a brown colouration.

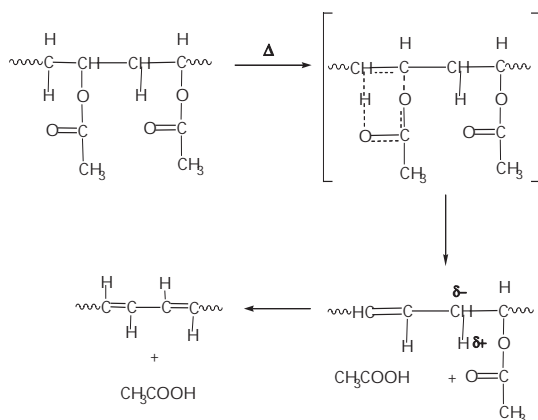


FIGURE 19: The PVAc, progressively heated in N₂ atmosphere, between 250-300°C lose acetic acid molecules by a molecular mechanism that sees the formation of an intermediate 6-centres transition state [5].

b) Examples of reactions leading to the cyclisation of side groups

In polymers having COOH side groups, as for polyacrylic acid, following heating the adjacent carboxyls react forming a cyclic anhydride structure (see scheme in figure 20) [12].

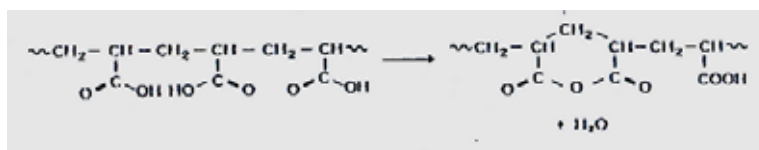


FIGURA 20: reaction, induced by heat, leading to the cyclisation of COOH side groups in the case of polyacrylic acid [12].

Thermal cyclisation of side $-\text{C}\equiv\text{N}$ groups is observed, at temperatures between 200-250°C, in the case of polyacrylonitrile (PAN). The reaction is highly exothermic thus a large amount of heat is emitted. As can be seen by figure 21, following the cyclisation a sequence of conjugated double bonds are formed [5,11].

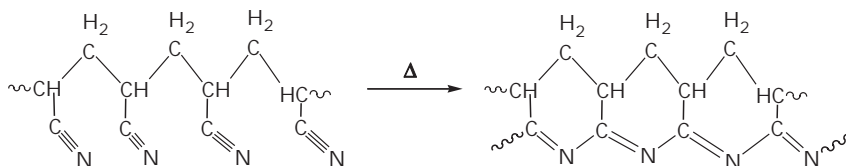


FIGURE 21: Thermal cyclisation of side $-\text{C}\equiv\text{N}$ groups in polyacrylonitrile [5].

The main products of thermal degradation for some carbon chain polymers are listed in table 3 [12].

TABLE 3: Thermal degradation products for some addition polymers.
(The polymer samples were heated slowly up to 500°C)[12]

POLYMER	DEGRADATION PRODUCTS
Polyethylene, polypropylene	Chain fragments, small amount of volatile saturated, unsaturated hydrocarbons
Polystyrene	50% yield of styrene monomer, dimer and short chain fragments
Natural rubber	Isoprene, dipentene, short chain fragments, some cyclised structure
Polyvinylchloride	Quantitative yield of HCl, small amounts of benzene, coloured tars, carbonaceous residue
Polyvinylalcohol	H ₂ O, coloured tars, carbonaceous residue
Polymethylmethacrylate	Quantitative yield of monomer
Polymethylacrylate	Short chain fragments as main products, CH ₃ OH, CO ₂
Polyvinylacetate	Quantitative yield of CH ₃ COOH, small amount of benzene, coloured tars, carbonaceous residue

The usefulness of knowing the thermal degradation products of polymer materials it is important as from their nature and reactivity depend most of the plans to be adopted for the conservation of many types of objects made in plastics.

By thermogravimetry it has been possible to elaborate a relative stability diagram for several kind of carbon chain polymers. The results are summarised by the diagram in figure 22 where, for each of the polymers investigated, the temperature at which the materials lose the 15% of their weight (in nitrogen atmosphere and with a rate of heating of 10°C/min.) are indicated [12]. From such a diagram it emerges that PVC, PVA and PMMA, between those examined, are the polymers with the lower relative thermal stability [12].

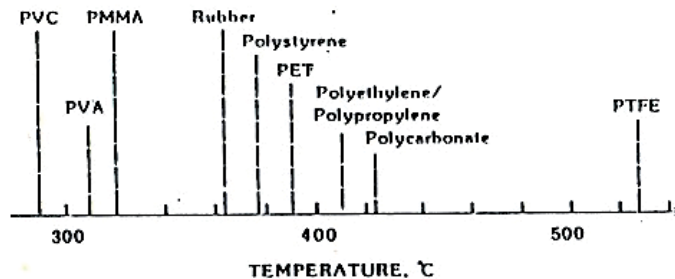


FIGURE 22: Relative thermal stability of some polymers. In the diagram are shown the temperatures corresponding to the 15% of weight loss in N₂ at 10°C/min. [12].

The chemical reactions involved in thermal degradation lead to physical and optical property changes relative to the initially specified properties. Thermal degradation generally involves changes to the molecular weight (and molecular weight distribution) of the polymer and typical property changes include reduced ductility and embrittlement, chalking, color changes, cracking, general reduction in most other desirable physical properties.

2.2) Photodegradation (Photochemical degradation) of polymers

The electromagnetic spectrum is constituted by radiations having a wide range of wavelengths (gamma ray, X-rays, visible light, microwaves and radio frequencies).

The visible light, that is the fraction of the electromagnetic spectrum that we can detect with our eyes, as can be seen by figure 23, includes radiations in the range of 400 (violet) to 750 nm (red) wave length [13].

As represented in figure 24 an electromagnetic wave consists of vibrating electric (E) and magnetic (M) fields which move with the rate of the light (c). The electric vector (E) vibrates in a direction that is perpendicular to that of the a magnetic field (M) [14].

The wavelength, the distance between successive wave crests, indicated by the greek letter λ [expressed in metres (m) or nanometres (nm, 10^{-9} metres), micrometres (μm , 10^{-6} metres) or centimetres (cm, 10^{-2} metres)] and frequency, the number of cycles of a wave passing a fixed point per unit of time, represented by the letter ν [measured in hertz (Hz): one cycle per second], are related by the following formula:

$$c = \lambda \nu \quad (1)$$

Equation (1) indicates that, being λ inversely related to ν , radiations with shorter wavelength are characterized by higher frequency and viceversa.

The energy (E) of an electromagnetic radiation (expressed in eV (electron volts) or in joules) is related to its frequency by the well known equation:

$$E = h \nu \quad (2)$$

Where "h" is the Planck's constant.

Of great importance is also the intensity (I) of electromagnetic radiation that is given by the number of photons (or quanta) passing through a unit area in space per unit time; or equivalently, the number of photons incident on a unit area (surface) per unit time [15].

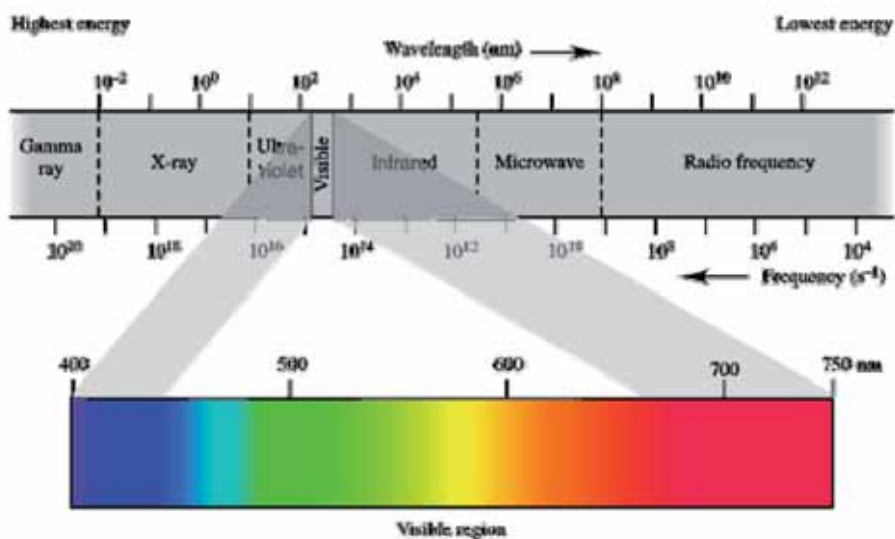


FIGURE 23: Electromagnetic spectrum. Wavelength are given in nanometers (nm), frequency in second⁻¹ (s⁻¹). The visible range of radiations is extrapolated from the top diagram [13].

The ultraviolet radiations (UV), λ in the range of 200-400 nm (140-75 Kcal/mol), are responsible of the primary processes that lead to photodegradation of polymers.

As shown by the data in table 4 UV radiations have enough energy to break most of chemical bonds present along the backbone of polymers. Thus in principle the absorption of UV should cause photodegradation process in polymer exposed to sun light.

The experimental observations in effect lead to the conclusion that the photodegradation of polymers occurs at a very low rate and the main reasons for that are hereafter listed :

- 1) The low rate of light absorbance by polymer materials;
- 2) The number of reacting molecules, per photon of light absorbed, are relatively low.

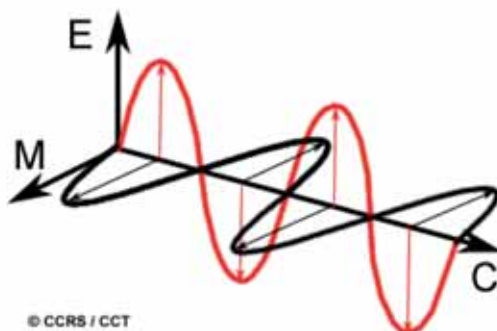
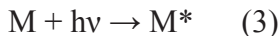


FIGURE 24: Representation of an electromagnetic radiation, traveling at the speed of light (c) along the C direction. The electrical field (E) vibrates in a direction perpendicular to that of the magnetic field (M) [14].

TABLE 4: Strength of some common chemical bonds. On the right side are reported the wave lengths of radiation with enough energy to break the corresponding bonds [16].

Chemical Bond	Bond Energy (kcal/mole)	Wavelength of Corresponding Energy (nm)
O—H	110.6	259
C—F	105.4	272
C—H	98.8	290
N—H	93.4	306
C—O	84.0	340
C—C	83.1	342
C—Cl	78.5	364
C—N	69.5	410

The absorption of UV or visible radiations by a generic molecule (M) is a two step process. First, M by reacting with a photon $h\nu$ transforms in the excited species M^* according to the following equation:



Second, being the life time of M^* very short (10^{-8} - 10^{-9} s) then such a species may dissipate energy through a *Photochemical process* that involving its decomposition gives rise to new products by means of different types of chemical reactions that include:

- Formation of free radicals;
- Photoionization;
- Cyclization; Intramolecular rearrangements;
- Fragmentation [16, 17,18].

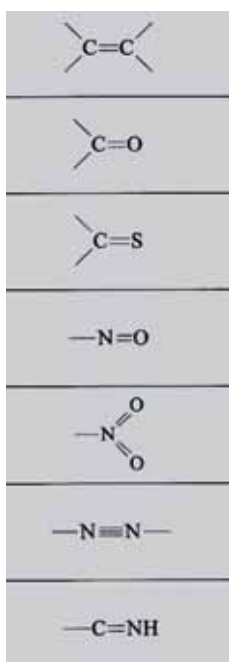


TABLE 5: Some common chromophore groups present in organic molecules and macromolecules. From top to down: Vinyl; Carbonyl; Tio-carbonyl; Nitroso; Nitro; Azo; Imino.

To have an effective *Photochemical process*, in absence of oxygen, polymers have to contain in their macromolecules groups able to interact specifically with radiations and by direct absorption of energy initiate fragmentation forming very reactive radical species. Such chemical groups are named “*Chromophores*”; the structure of some of them is represented in table 5 while the absorption characteristics of some common chromophores are reported in table 6 [17].

TABLE 6: Absorption characteristics of some common chromophores [17].

Chromophore	Example	Solvent	$\lambda_{\max}(\text{nm})$	ϵ_{\max}	Type of Transition
Alkene	$\text{C}_6\text{H}_{13}\text{CH}=\text{CH}_2$	<i>n</i> -Heptane	177	13,000	$\pi \rightarrow \pi^*$
Alkyne	$\text{C}_5\text{H}_{11}\text{C} \equiv \text{C}-\text{CH}_3$	<i>n</i> -Heptane	178	10,000	$\pi \rightarrow \pi^*$
			196	2,000	—
			225	160	—
Carbonyl	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CCH}_3 \end{array}$	<i>n</i> -Hexane	186	1,000	$n \rightarrow \sigma^*$
			280	16	$n \rightarrow \pi^*$
	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_3\text{CH} \end{array}$	<i>n</i> -Hexane	180	large	$n \rightarrow \sigma^*$
			293	12	$n \rightarrow \pi^*$
Carboxyl	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2\text{COH} \end{array}$	Ethanol	204	41	$n \rightarrow \pi^*$
Amido	$\begin{array}{c} \text{O} \\ \parallel \\ \text{CH}_2\text{CNH}_2 \end{array}$	Water	214	60	$n \rightarrow \pi^*$
Azo	$\text{CH}_3\text{N}=\text{NCH}_3$	Ethanol	339	5	$n \rightarrow \pi^*$
Nitro	CH_3NO_2	Isooctane	280	22	$n \rightarrow \pi^*$
Nitroso	$\text{C}_4\text{H}_9\text{NO}$	Ethyl ether	300	100	—
			665	20	$n \rightarrow \pi^*$
Nitrate	$\text{C}_2\text{H}_5\text{ONO}_2$	Dioxane	270	12	$n \rightarrow \pi^*$

Photochemical reactions are in competition with other types of radiative and non radiative relaxation processes by which the excited molecules dissipate the absorbed energy. Some of them are represented in figure 25 [16].

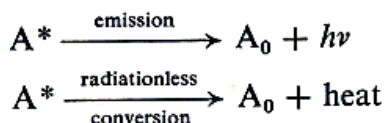


FIGURE 25: Radiative and non radiative relaxation processes by which the excited molecules dissipate the absorbed energy [16].

Polymers, characterized by repeat units containing groups UV-absorbent, are likely to be photochemically degraded by absorption radiations having suitable wavelengths. Polymers such as polystyrene and styrene copolymers, aromatic polyurethanes, polyesters and polyepoxides show this type of behaviour.

On the contrary, free from impurities polymers, such as polymethyl methacrylate, polyethylene or aliphatic polyesters are photochemically stable between 300 and 400 nm because they are intrinsically unable to absorb light. Nevertheless in case they contain impurities which absorb light (e.g. catalyst residues), additives, or oxidation products, may become sensitive to UV light, and then interested to photochemical reactions.

It can be said that in general the transformations induced in polymers by photodegradation are similar to those caused by thermodegradation (chain scissions, cross-linkings, formation of volatile products, ecc.). Nevertheless some polymers, due to several order of reasons, show some types of reactions specifically related to the absorption of radiations.

Some of this photochemically induced reactions, presented by commonly used polymers are hereafter described.

1) *Polystyrene*

Such a polymer on heating, following thermodegradation, decomposes forming styrene monomers and oligomers. On the contrary, under vacuum and at RT, exposed to the action of UV radiation (235nm) polystyrene, according to the reactions represented in figure 26, forms crosslinks and develops hydrogen. At the same time a yellowing process is observed [18].

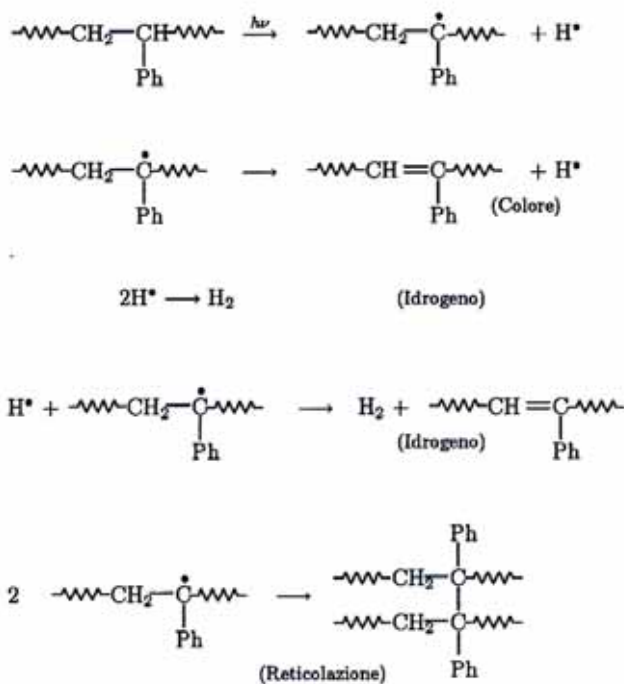


FIGURE 26: Chemistry of photochemical degradation of polystyrene (see text) [18].

2) *Polymethylmetacrylate (PMMA)*

PMMA, that on heating forms MMA monomers, by absorbing UV radiation (254nm), at RT and under vacuum, is photochemically degraded through decomposition of the ester groups followed by main chain scission and formation of gaseous products (CO, CO₂, CH₄) and CH₃OH and HC(=O)OCH₃ (see reaction scheme in figure 27) [18].

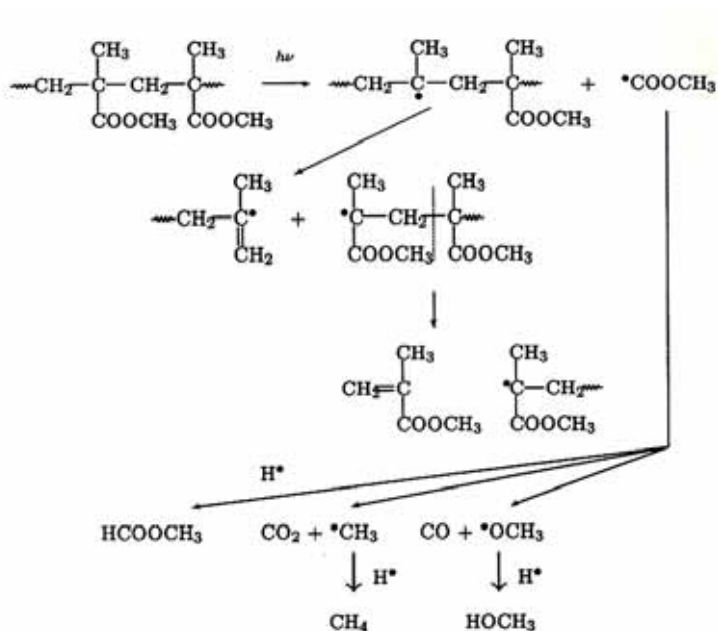


FIGURE 27: Photochemical degradation of polymethylmetacrylate (see text) [18].

3) *Ethylene-carbon monoxide copolymers*

Of great interest is the photochemical behaviour of polymers with keton groups along their chains. Such groups first absorb UV light (> 250nm) then from the excited state give rise to scission reactions, known as Norrish I (NI) and Norrish II (NII), together with reaction of extraction of hydrogen.

The photochemical decomposition of ethylene-carbon monoxide copolymers may occur according to NI and NII type of reaction as shown in figure 28 [18].

It can be seen that both NI and NII mechanisms lead to the scission of the macromolecules but in case of NI two macroradicals are formed with development of carbon monoxide, while with the NII reaction two de-activated macromolecules are obtained (see details in figure 28) [18].

4) *Poly (methyl vinyl ketone)*

Photochemical degradation with chain scission may occur also when the keto-groups are contained in side chain position. As shown by the schemes reported in figure 29 the NII reaction gives rise to chain scission while the NI process leads to the formation of low molecular weight products (methane, acetic aldehyde, CO) together with an active macroradical (IX in figure 29) [18].

Such macroradical may, as described in figure 29, decomposes through a chain scission in the C-C bond in β position or gives rise, by coupling mechanisms, to crosslinked products [18].

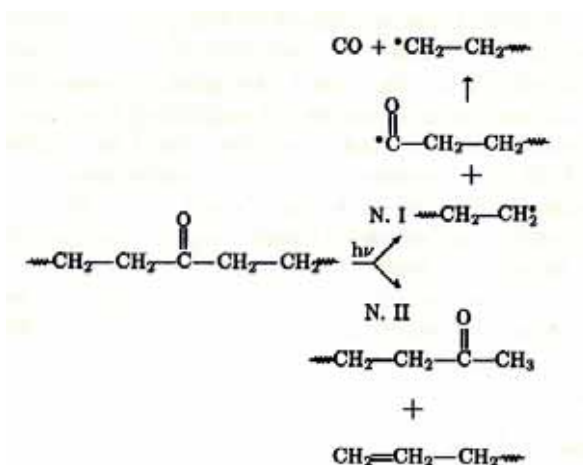


FIGURE 28: Photochemical degradation of ethylene-carbon monoxide copolymers according to Norrish I (top side) and Norrish II mechanism (bottom side) (see text) [18].

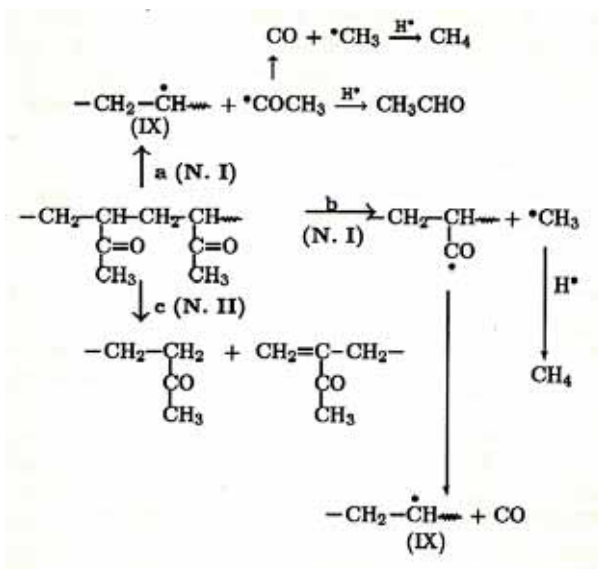


FIGURE 29: Photochemical degradation of Polymethylvinylketone according to Norrish I and Norrish II mechanisms (see text) [18].

2.3) Oxidative processes of Polymers (Thermo-oxidation(Factors: heat and oxygen), Photo-oxidation (Factors: light and oxygen)

The direct reaction between oxygen and organic polymers occurs at very low rate thus from a practical point of view such an event can be considered as negligible. On the contrary when in the mass of the polymers are present active radical species, produced by thermodegradation or photodegradation, then the rate of reaction between those radicals and oxygen is very high, consequently oxidative processes, are made possible.

Thus the most effective and common processes of oxidative degradation of polymers result from the synergic combined effects of oxidation, thermodegradation and photodegradation [12].

The exposure of plastic items to the action of UV radiation or heat in an oxygen-containing environment determines perceptible physical and chemical degradation effects (discoloration, surface cracking, embrittlement and drastic reduction in toughness and tensile strength and ultimately mechanical failure) [16].

The degree of changes in some of the above mentioned properties are often used as measure of the entity of damage occurred.

Oxidative processes induced by thermo-oxidation and photo-oxidation may lead to deep chemical transformations such as scission of macromolecular chains, crosslinks, formation of low molecular weight products and functional groups, along the chains, containing oxygen (ketones, carboxylic acid, peroxides and alcohols). The chemical changes induced in polyethylene by oxidative reactions can be easily detected by means of the infrared spectroscopy (see example in figure 30) [16].

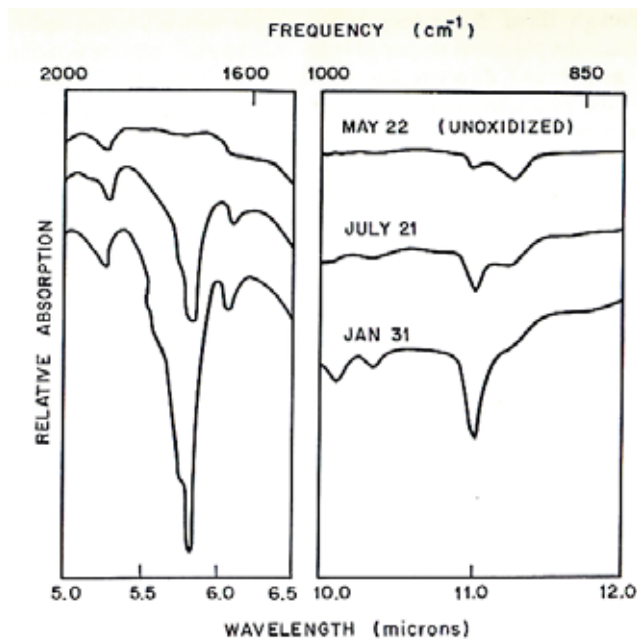


FIGURE 30: Development of carbonyl and vinyl bands in the infrared transmission spectrum of polyethylene following photo-oxidation process (outdoor exposure) [16].

The primary chemical changes induced by oxidation in polymer materials together with effects on properties and the measurement techniques suitable to quantify the entity of the damages are summarized by the scheme reported in reference [19] and reproduced in figure 31.

A typical case of discoloration phenomenon, due to environmental aging, observed in two plastic items is shown in figure 32 [20, 21].

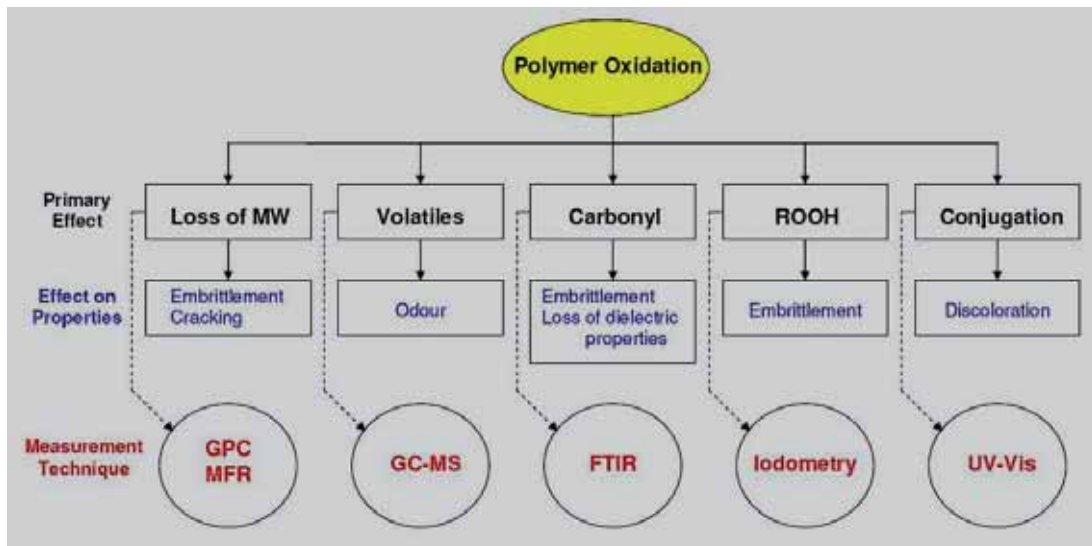


FIGURE 31: Scheme summarizing: the primary chemical effects induced by oxidation in polymer materials, the effects on properties and the techniques suitable to assess and measure the entity of the damages [19].

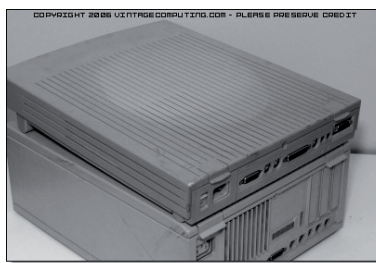
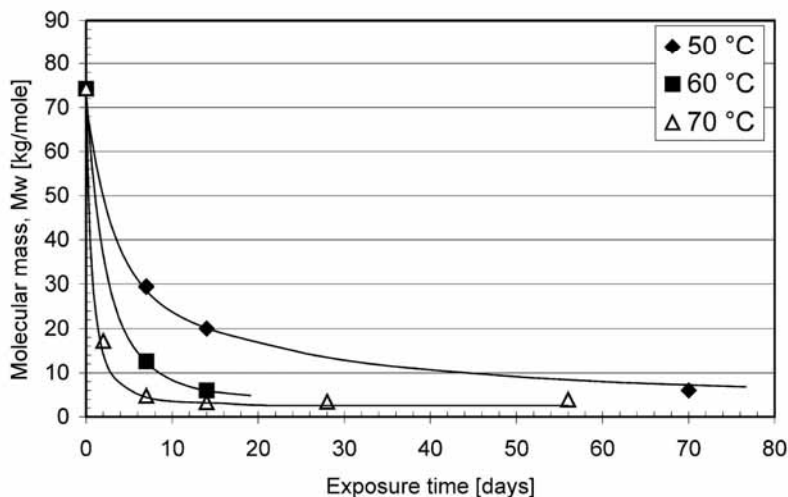


FIGURE 32: Example of a modern plastic item (computer parts) showing clear symptoms of discoloration due to photo-oxidation processes [21].

The dependence of the molecular mass of samples of polyethylene upon the exposure time to the oxidation (at different temperatures) is described through the diagrams of figure 33 [22]. The trend of the curves confirms that photo(thermo)-oxidation produces chain rupture. Moreover such an effect is more pronounced at higher temperature and longer exposure time.



FIGURES 33: Effect of photo(thermo)oxidation on molecular mass of polyethylene film containing pro-oxidation additives.

The molecular mass is reported against the exposure time at different temperatures [22].

The oxidation of polymers, essentially independent of the type of energy used to create primary radicals species in the initiation step (deriving from thermo or photo degradation), occurs through a chain radical mechanism whose different steps are schematically described in figure 34. In the scheme the symbols, PH, P*, POO*, POOH represent respectively: Polymer chain; Alkyl macroradical; Peroxy radical; Hydroperoxide [12,16,18,23]. The single steps, with reference to figure 34, are hereafter briefly discussed.

Initiation

The polymer macromolecules (PH) are converted into macroradicals (P*) (see scheme (1) in figure 34). The reaction is promoted by UV photons ($h\nu$) and by heat. Initiation, in photo-oxidation may be caused by interaction of UV radiations with impurities (i.e. catalyst residues) rather than by direct interaction with macromolecules. In case of thermo-oxidation initiation, being catalyzed by impurities, it may occur at pre-existing randomly distributed centers [24]. Thus for such step the presence of oxygen is not a relevant factor.

Propagation

The chain reaction is propagated by the macroradicals P* that first react with oxygen (O_2) forming peroxy POO* radicals which by reacting with a polymer chain (PH) give rise to a primary oxidative product, the hydroperoxide (POOH). The released macroradicals P* by reacting again with oxygen molecules contribute to the propagation of the reaction (see reaction (2) and (3) in figure 34).

The rate of the propagation step is determined by the reaction of extraction of hydrogen which is very slow in comparison with the reaction between the macroradical P* and the O_2 that is very fast.

Chain Branching

The hydroperoxides (POOH) being characterized by a PO – OH bond with a relatively low energy ($\approx 40\text{Kcal/mol}$) are sensible to rupture following photo/thermo-degradation. Thus according to an homolitic scission the hydroperoxides (POOH) form the two radical species PO^* and $^*\text{OH}$ (see (4) and (5) in figure 34).

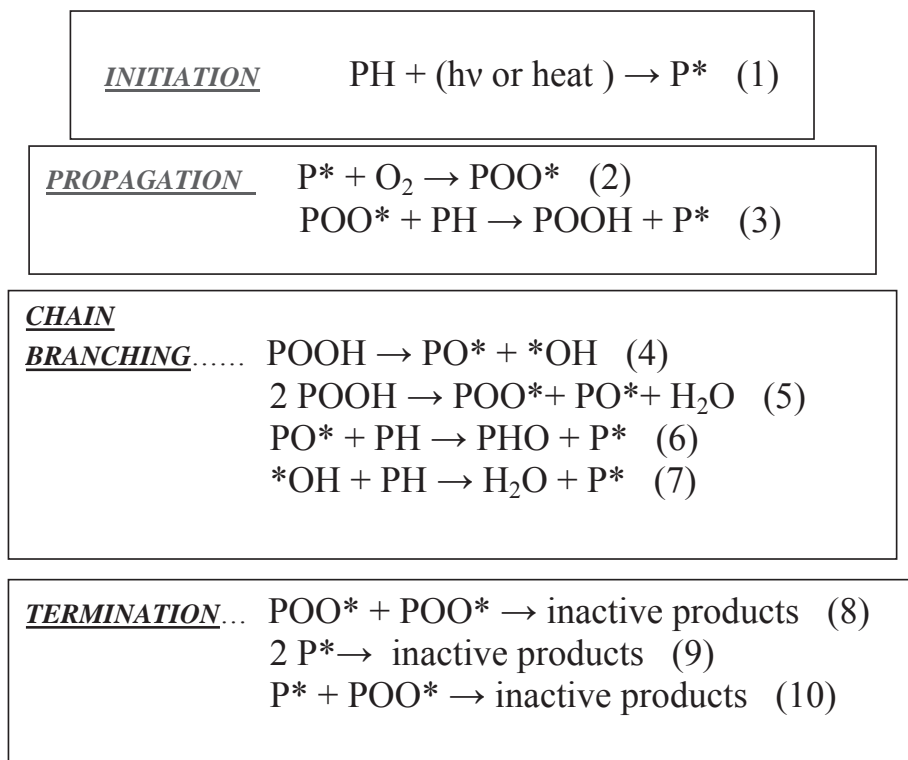


FIGURE 34: Scheme reporting the various steps of polymer thermo/photo-oxidation process (see text) [12,16,18,23,24,25].

Both radicals species PO^* and $^*\text{OH}$ have a high tendency in extracting hydrogen from polymer chains according to the schemes (6) and (7) of figure 34. Macroradicals P^* are produced capable to reiterate the propagation phase.

< As the photo-oxidation proceeds , the photolysis of the peroxides produced in the process becomes increasingly important as route of initiation and chain branching with respect to the role played by the photoactive impurities initially present > [25].

Termination

As described in the steps (8), (9) and (10) in figure 34, termination occurs by combination of the macroradicals produced during the chain process. According to reference [25] *< the most probable termination reaction is that involving peroxyradicals, because they are present in the highest concentration when oxygen is not depleted >*

From above it can be concluded that the oxidation of polymers, induced by photo or thermal mechanisms, is a very complex free-radical process whose nature as well as types of final products are strongly dependent on the chemical structure of polymer, its physical state and of course by the experimental conditions of aging (temperature, time, oxygen concentration ecc.). As already reported, in oxidative processes of polymers exposed to sun light an important role is played by pre-existing impurities, including chemical constitutional defects along the macromolecules. The list of some typical impurities as identified in common polymers is shown in figure 35 [26].

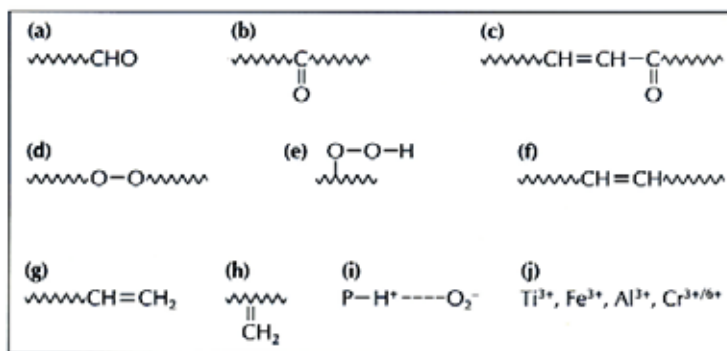


FIGURE 35: Impurities species found in many commercial polymers: (a) aldehyde, (b) ketone, (c) α , β -unsaturated ketone, (d) in-chain peroxide, (e) side-chain hydroperoxide, (f) in-chain vinyl, (g) end-chain vinyl, (h) vinylidene, (i) oxygen-polymer charge-transfer complex and (j) metal ions [26].

An example of how impurities based on transition metals may catalyse the reaction of decomposition of hydroperxyde to radicals is shown in figure 36 [18].

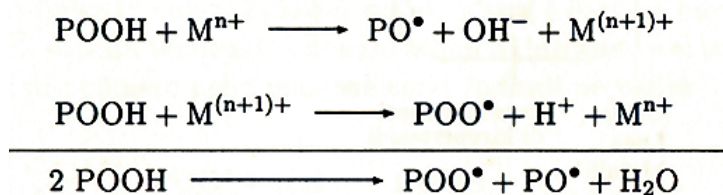


FIGURE 36: The reactions through which transition metals may catalyse the reaction of decomposition of hydroperxyde to radicals [18].

REFERENCES

- 1) E. Martuscelli, < *Plastics in Art (in Cultural Heritage)-Plastics for Art (for Cultural Heritage)* >, Lecture presented at Programma Giornata AIM on “Il restauro e la diagnostica degli oggetti d’arte e di design in plastica”, PLART, Napoli, 31/10/(2008).
- 2) E. Martuscelli, < *La Chimica Macromolecolare Applicata alla Conservazione dei Manufatti Lapidei* >, PAIDEIA, Firenze (2007).
- 3) N. Dintcheva, < *Degradazione e Stabilizzazione dei Polimeri* >, http://www.tmf.ukim.edu.mk/recapo/completed_files/Documents/Degradazione%20termica%20.pdf, (2009).
- 4) E. Martuscelli, < *Degradazione delle Fibre Naturali e dei Tessuti antichi* >, PAIDEIA, Firenze (2006).
- 5) < *Stabilization of Polymer Matrix* >, ADDCOMP, Polymer Additive Solutions, http://www.speautomotive.com/SPEA_CD/SPEA2006/pdf/f/f2.pdf, (2009).
- 6) Y. Shashoua, < *Conservation of Plastics* >, Elsevier, Amsterdam (2008).
- 7) <http://www.plastiquarian.com/deterio.htm>, (2009).
- 8) O. Chiantore < *Polymer Materials in Works of Art and in Design* >, Lecture presented at Programma Giornata AIM on “Il restauro e la diagnostica degli oggetti d’arte e di design in plastica”, PLART, Napoli, 31/10/(2008).
- 9) < *Fondamenti di Scienza dei Polimeri* >, a cura di M. Guaita et Al., pp. 849-912, Pacini Editore, Pisa (1998).
- 10) W. L. Hawkins, < *Polymer Stabilization* >, Wiley-Interscience, London (1972).
- 11) G. Camino, < *Reazioni di Degradazione* >, in < *Macromolecole, Scienza e Tecnica* >, a cura di F. Ciardelli et Al., Vol. I, pp. 442-457, Pacini Editore, Pisa (1983).
- 12) I. C. McNeil, < *Fundamental Aspects of Polymer Degradation* >, in “*Polymers in Conservation*”, Edt. by N. S. Allen, M. Edge, C. V. Horie, Royal Society of Chemistry, pp. 15-32, (1992).
- 13) www.mhhe.com/.../carey04oc/ch13/figures/1301.gif, (2009).
- 14) http://cct.mcan.gc.ca/resource/tutor/fundam/chapter1/02_e.php, (2009).
- 15) Canadian Space Agency, www.asc-csa.gc.ca, (2009).
- 16) A. M. Trozzolo, < *Stabilization against oxidative photodegradation* >, in “*Polymer Stabilization*”, Edited by W. L. Hawkins, pp. 159-214, Wiley-Interscience, New York, (1972).
- 17) D. A. Skoog, F. J. Holer, T. A. Nieman, < *Principles of Instrumental Analysis* >, Books/cCole, US, (1998).
- 18) < *Fondamenti di Scienza dei Polimeri* >, Editors: M. Guaita and others, Pacini Editore, Pisa (1998).
- 19) Bodycote Testing Ltd (PDL), United Kingdom Manchester (PDL), i265.photobucket.com/albums/ii220/bodycotepdl, (2009).
- 20) static.houseofnintendo.com/houseofnintendo.co, (2009).
- 21) www.vintagecomputing.com/wp-content/images/sn, (2009).
- 22) J. Jakubowicz, < *Polymer degradation and stability* >, **80**, 39 (2003). <http://degradableplasticbag.files.wordpress.com/2009/03/jt-dcc-e-evaluation-of-biodegradable-polyethylene-3.jpg>, (2009).
- 23) C. Puglisi, < *Degradazione Ossidativa delle Materie Plastiche* >, Lecture presented at Programma Giornata AIM on “Il restauro e la diagnostica degli oggetti d’arte e di design in plastica”, PLART, Napoli, 31/10/(2008).

- 24) J. R. White, < *Stress effects on polymer durability in the oxidative environment* >, in “*Trends in Polymer Science*”, pp. 197-202, **Vol.2**, No 11, Nov. (1994).
- 25) A. Faucitano and others, < *Photo-oxidation and stabilization of polymers* >, in “*Trends in Polymer Science*”, pp. 93-98, **Vol.4**, No 3, March (1996).
- 26) N. S. Allen, < *Why do polymer degrade in sun light?* >, in “*Trends in Polymer Science*”, pp. 366-375, **Vol.2**, No 11, Nov. (1994).

SECTION-1

FOURTH CHAPTER (PART-2)

DEGRADATION OF PLASTIC ARTEFACTS IN RELATION TO MOLECULAR STRUCTURE OF POLYMER CONSTITUENT, NATURE AND FUNCTION OF ADDITIVES, COMPOSITION AND PROCESSING CONDITIONS.

Photo-oxidative phenomena and mechanisms observed in some common polymers

The complexity of photo-oxidation processes in polymers comes out clearly by the description of some interesting real examples hereafter illustrated.

Together with the main mechanism of degradation pattern the most effective stabilisers against photo-oxidation are also indicated.

i) Polypropylene (PP)

The processes leading to the formation of radical species in the initiation step of photo-oxidation of PP in the air are described in figure 1 [1].

The radical species $-\text{CH}_2^*$ and CH_3^* , according to figure 1, are produced by Norrish I cleavage of the ketones and by photolysis of tertiary hydroperoxides [1].

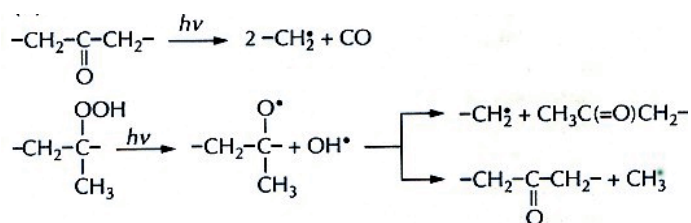


FIGURE 1: The two most effective reactions leading to the production of radicals in the initiation step of photo-oxidation of polypropylene.

Top, formation of $-\text{CH}_2^*$ radicals.

Bottom, formation of CH_3^* radicals [1].

The most effective propagation cycle of PP oxidation, represented by the reaction scheme of figure 2, seems to be < driven by the H abstraction of the peroxyradicals at the tertiary C-H bonds, which gives the tertiary hydroperoxides. Tertiary peroxyradicals and hydroperoxides lead in turn to tertiary alkoxy group that, by β scission, yield tertiary alcohols and terminal and intra-chain ketones > [1].

IR-Spectroscopy, as evidenced in figure 3, turns to be a very effective technique to assess, qualitatively and quantitatively, the chemical changes induced by oxidation in air of PP [2, 3].

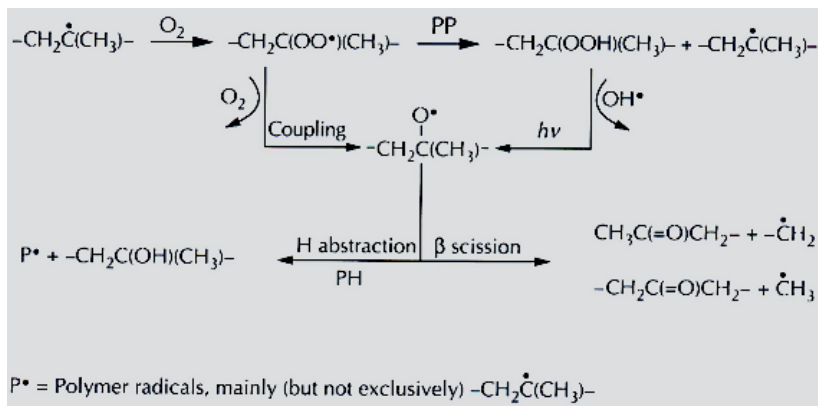


FIGURE 2: The most effective propagation cycles based on peroxy and alkoxy radicals in the case of photo-oxidation of polypropylene [1].

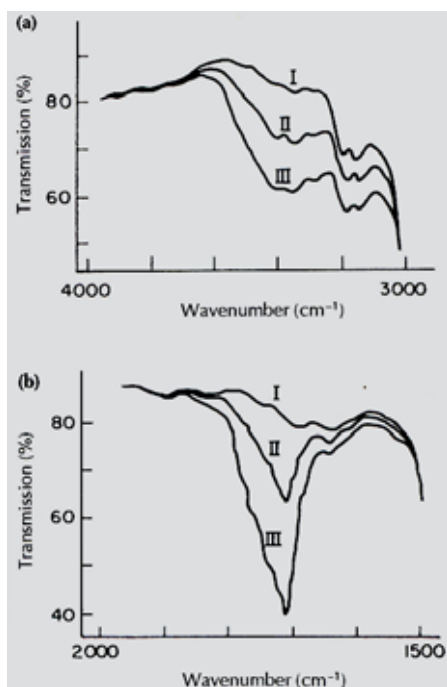


FIGURE 3: Infra-red spectrograms of samples of polypropylene exposed to the action of radiation for different times. The source of light is a 500W high pressure mercury arc. Time: I, 1h; II, 6h; III, 110h. Top (a), the hydroxyl region. Bottom (b), the carbonyl region [2].

The deep effects of degradation induced by exposition to sun light, in air, on samples of polypropylene fibers are clearly evidenced through the scanning electron micrographs showed in figure 4 [4].



FIGURE 4: Scanning electron micrographs of polypropylene fibers before (left) and after (right) exposition to sun radiations in air [4].

The deterioration in the mechanical properties of polypropylene following oxidation is exemplified in figure 5 where the values of elongation at break of film are reported against oxygen uptake. From the trend of the curve it emerges that with the increase of oxidation degree the material becoming brittle loses completely its mechanical resistance [5, 6].

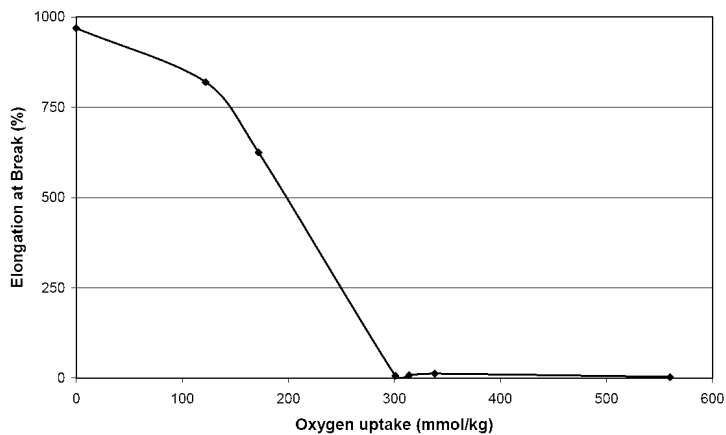


FIGURE 5: Relation between drop in elongation at break and oxygen uptake of PP films at 65 °C [5].

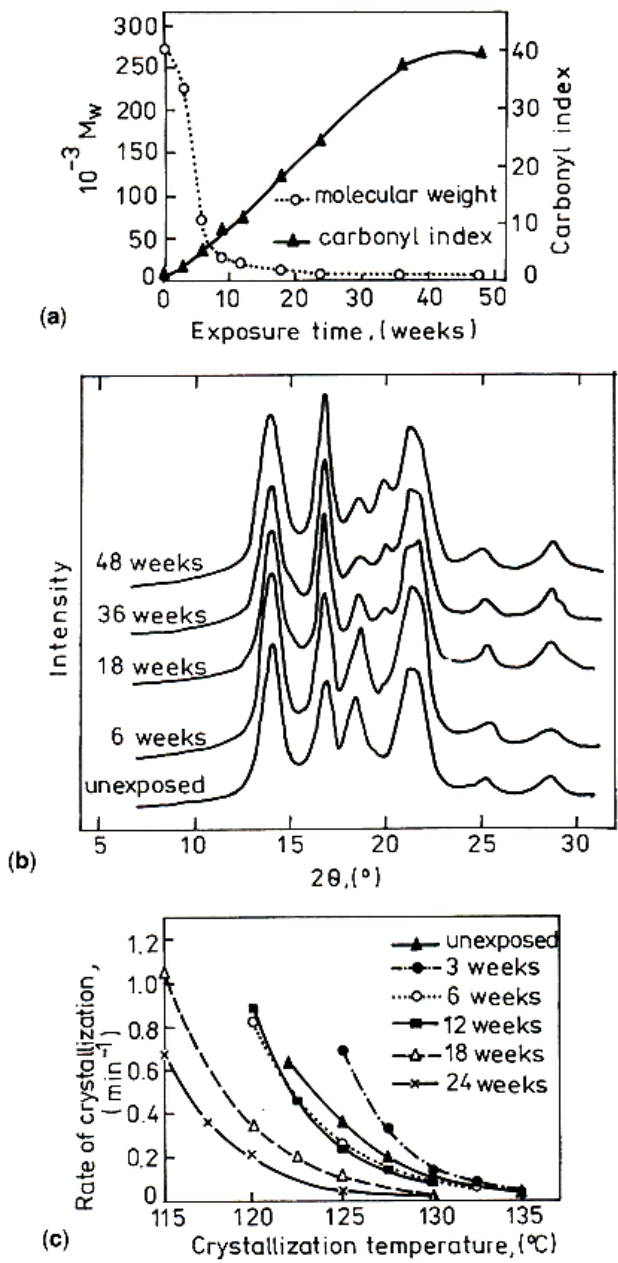


FIGURE 6: Polypropylene photo-oxidation behaviour.
 a) Variation of molecular weight (M_w), and carbonyl index with exposure time.
 b) X-Ray diffraction patterns of re-crystallized degraded samples at different time exposure.
 c) Rate of crystallization of samples after degradation [7].

The main effects of photo-oxidation of polypropylene, the reduction in the molecular weight and the formation of carbonyl groups, are documented in figure 6-a) where plots of Mw and of CI (carbonyl index) against exposure time are reported [7].

From figure 6-b) one observes that the crystallization of degraded samples leads to samples with an higher content of the γ solid PP-phase.

It is also interesting to point out that at a given crystallization temperature the degraded samples seem to show, with some exception, lower values of the rate of crystallization [7].

To mitigate the sensitivity of PP to photo-aging *Hindered Amine Light Stabilizers* (HALS) are used.

ii) Polyethylene (PE)

Polyethylene is more resistant than polypropylene to photo-oxidation nevertheless when exposed to UV-radiations in air undergoes deep chemical changes (see figure 7) [3].

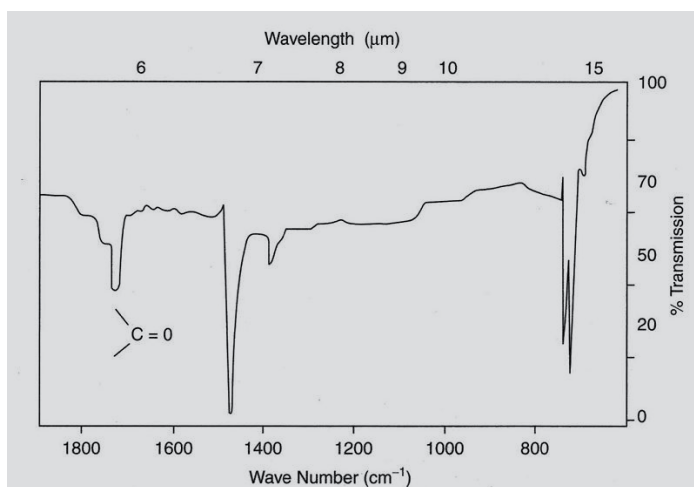


FIGURE 7: IR spectrum showing carbonyl absorption indicative of oxidative degradation of polyethylene [3].

The oxidation mechanism of polyethylene is basically the same of PP. Nevertheless it differs from that of polypropylene as far as initiation step is concerned that occurs essentially via the formation of an olefin-oxygen excited complex. As shown in figure 8 the reaction produces H₂O₂, which following photolysis gives OH* radicals [1].

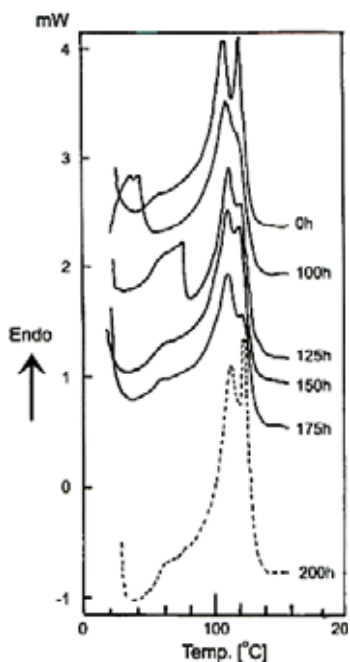


FIGURE 10: Differential scanning calorimetry thermograms of samples of low-density polyethylene as function of exposure time to photo-oxidation [6].

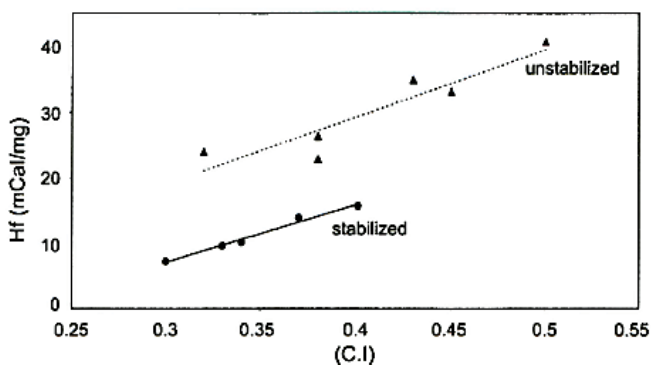


FIGURE 11: Relationship between the apparent heat of fusion, as measured from DSC, and carbonyl index CI for unstabilized and stabilized of samples of low-density polyethylene [6].

A similar behaviour was found also for samples of LLDPE as cited in reference [7], where a plot of crystallinity versus exposure time was reported (see figure 12).

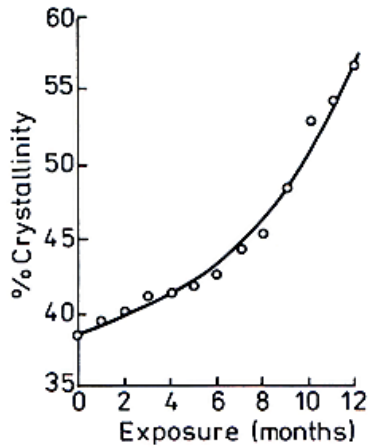


FIGURE 12: The dependence of crystallinity (%) of samples of LLDPE from the time of exposure to photo-oxidation [7].

The finding that for LLDPE the crystallinity increases from 39% for unweathered sample to 55% for degraded sample it is accounted for by assuming that following degradation:

- i) Strong interaction between new polar groups are formed;
- ii) The scission of constrained parts of chains in the amorphous regions favours the creation of new crystallization sites [30].

The lost of ductility of polyethylene samples, following photo-oxidation, is documented through the diagram in figure 13 where the elongation at break versus exposure time is represented [5].

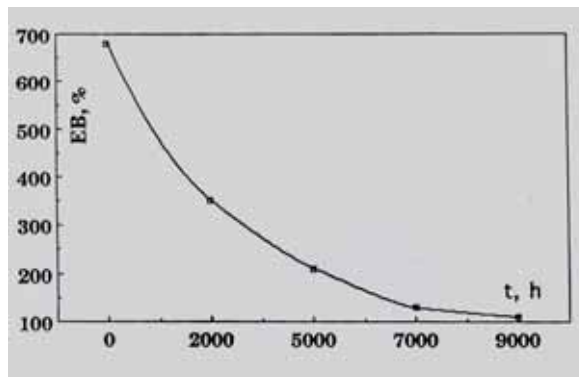
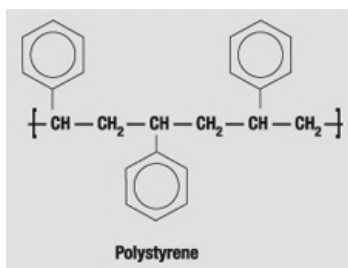


FIGURE 13: Elongation at break (EB%) of polyethylene samples versus exposure time to photo-oxidation [5].

iii) Polystyrene

In the case of polystyrene, whose molecular structure is below depicted,



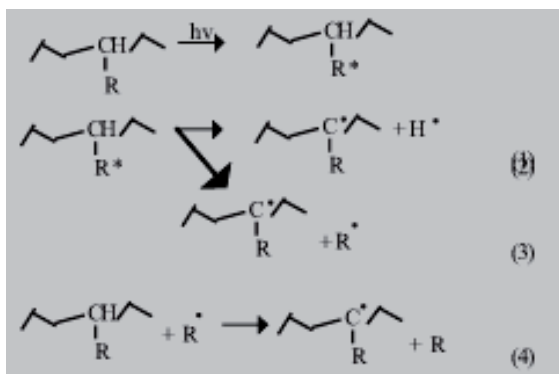
the photo-degradation seems to be essentially initiated by ketones of the acetophenone type produced in the course of the high temperature transformation processes.

< Triplet-state ketones can abstract benzyl hydrogens and decompose the hydroperoxides by energy transfer. A major propagation route in the photo-oxidation is the hydroperoxidation based on the H abstraction at the carbon adjacent to the aromatic ring, leading to tertiary hydroperoxides, tertiary alcohols and acetophenone residues > [1].

According to the below scheme, reported in reference [8], in the case of polystyrene the absorption of light of wavelength less than 300nm may give rise to the formation of the excited singlets state of the phenyl groups capable to dissociates into polystyryl radical (I) and phenyl radical (II) .



The phenyl radical, as depicted by the underneath reactions, may abstract hydrogen atoms from adjacent polymer molecules to form polystyryl radicals which represent the important precursors of photo induced chain scission, cross linking and the formation of unsaturation (yellowing) [8].



The photo-degradation of polystyrene exposed to the action of UV radiation with wavelength of 320nm in the presence of air, results in 90% chain scission, 10% cross-linking and discoloration phenomena. Such a behaviour, taking into consideration that:

- Oxygen penetrates into PS and the rate of penetration becomes slower in the interior of the PS;
 - The viscosity average molecular weight M_v decreases with the radiation time;
 - This decrease is complementary with the increase of peroxy radical formation,
- can be explained, according to reference [8], by the mechanism represented in figure 14.

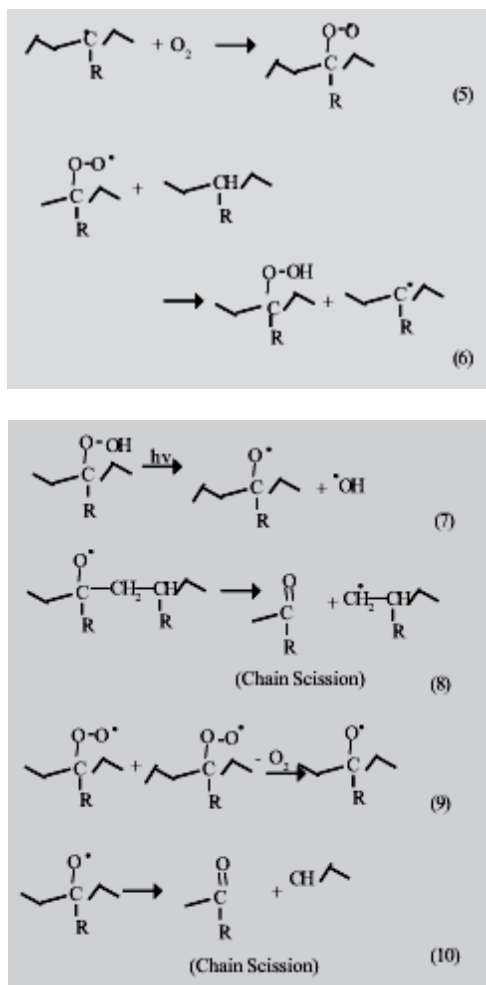
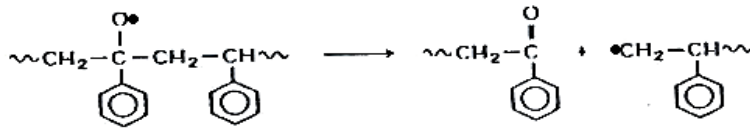


FIGURE 14: The chemistry of the mechanism of the photo oxidation process occurring in polystyrene when exposed, in air, to UV radiation with wavelength of 320nm [8].

From the scheme of figure 14 it follows < that the degradation reaction may proceed via peroxide intermediate and result in the main chain scission of PS leading to the formation of carboxyl compounds. The rate of oxygen attack to polystyryl radical formed by photo irradiation on the surface of the film is much faster than that in the interior. As a result chain scission takes place mostly on the surface of the film while a little cross-linkage can be observed in the interior when there is no oxygen >[8].

In the case of polystyrene it has been demonstrated that following the photo-induced decomposition of hydroperoxides ROOH, the primary oxidation products, two radical species RO* and *OH are produced.

The alkoxy *OH radicals by abstracting an H atom from the tertiary carbon along the chain form the macroradical that by chain scission generates a shorter chain and another macroradical which continues the chain process (see below reaction). This mechanism seems to be very effective in determining the photo-oxidation of polystyrene [12].



The melt flow index (MFI) of polystyrene samples aged in a air oven at 71°C is reported versus the ageing time in figure 15 [9].

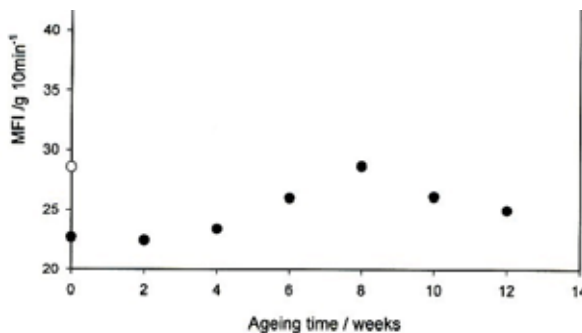


FIGURE 15: Melt flow index of polystyrene samples aged in air oven at 71°C versus the ageing time (see text) [9].

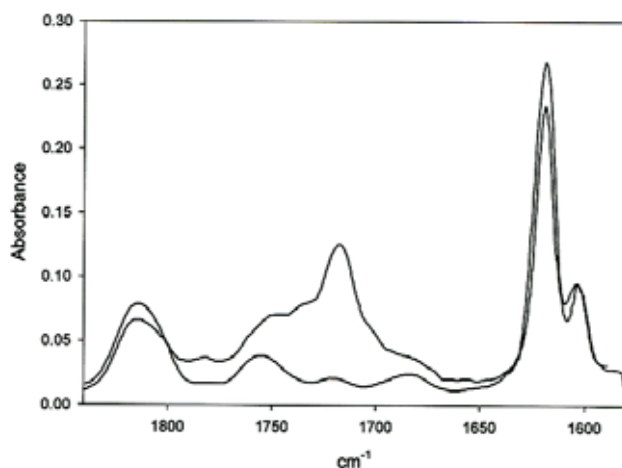


FIGURE 16: FTIR spectra of high impact polystyrene samples, carbonyl region, following air oven aging. Upper curve, highly degraded sample containing totally degradable plastic additives. Lower curve, sample without additive [9].

It can be seen that initially MFI increases with the time of ageing thus indicating, as expected, a reduction in the molecular weight caused by chain ruptures. The decreasing trend observed in MFI for longer ageing times (> 8 weeks) is accounted for by assuming that the process gives rise to the production of interchain cross-links [9].

The formation of carbonyl containing groups along the photo-oxidated polystyrene macromolecules can be clearly evidenced, as shown in figure 16, through FTIR spectroscopy [9].

The stabilization of polystyrene including acrylonitrile-butadiene-styrene copolymers (ABS) is based on the use of a combination of stabilizers (i.e. benzotriazole-type UV absorbers coupled with hindered amine light stabilizers (HALS)) [1].

iv) Elastomers (natural rubber and Polybutadiene)

According to reference [1] the most effective mechanisms able to explain the photo-oxidation processes of natural rubber and polybutadiene are similar to those of polyolefins. The main products of degradation, identified by means of infrared spectroscopy and carbon nuclear magnetic resonance (see typical spectra in the case of natural rubber in figures 17 and 18 [10]) are: hydroperoxides, alcohols, carboxylic acids, esters, ketones and epoxides.

Double bonds along the polymer chains favour the abstraction of H, by peroxy and alkoxy radicals, at the allylic C-H bonds. Epoxides products are formed following the reaction of the peroxide radicals with double bonds [1].

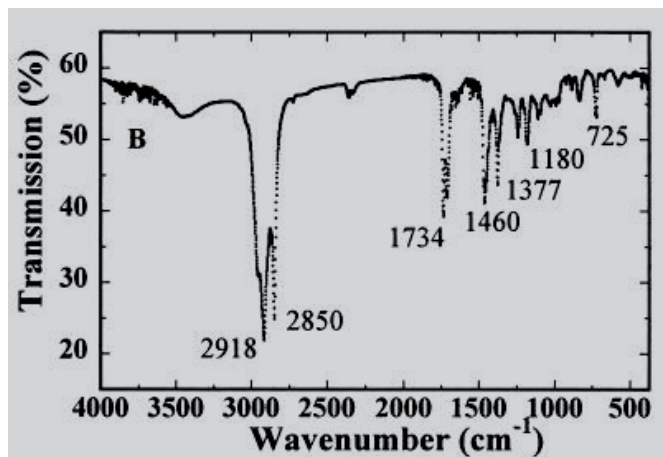


FIGURE 17: FTIR spectra of the rubber extracted from rubber tree (cis-1,4-polyisoprene) in potassium bromide disc, in the spectral range of 4,000 to 370 cm^{-1} at a resolution of 2 cm^{-1} [10].

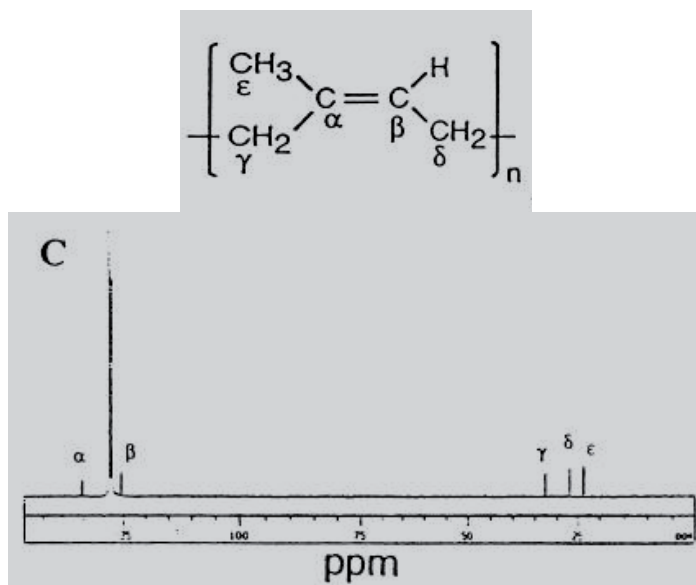
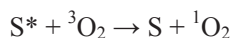


FIGURE 18: ^{13}C NMR spectra of the rubber extracted from rubber tree in C_6D_6 . Representative peaks for cis-1,4-polyisoprene are indicated as α through ϵ [10].

The finding of allylic peroxides is ascribed to the reaction of rubber molecules with oxygen in the singlet state that, unreactive towards saturated hydrocarbons chains, is capable to attack olefin groups [1].

The above type of degradation occurs when in the material a suitable photosensitiser (S) by absorbing UV radiations transforms in a radical species (S*) able to react with oxygen ($^3\text{O}_2$) giving rise to the formation of an excited singlet oxygen ($^1\text{O}_2$). The reactions are hereafter described [11].



It is interesting to point out that specific aminoacid residues present in proteins (i.e. tyrosine and tryptophane) act as photosensitisers. The $^1\text{O}_2$ formed by reacting with tryptophane forms hydroperoxides [11].

The basic properties requested to an elastomer (capability to be easily stretched and when released able to recover promptly most of its original length) are deeply affected by photo-oxidation, the samples becoming less flexible. Such a behaviour may be evidenced by means of uniaxially tensile test that allow to follow modifications on the stress/strain curve that, as shown in figure 19, in undegraded rubber assumes a characteristic S shaped form [12].

Unvulcanized rubber and polybutadiene are usually stabilized against photo-oxidation by using carotenoids, nickel(II) chelates and phenolic antioxidants [1].

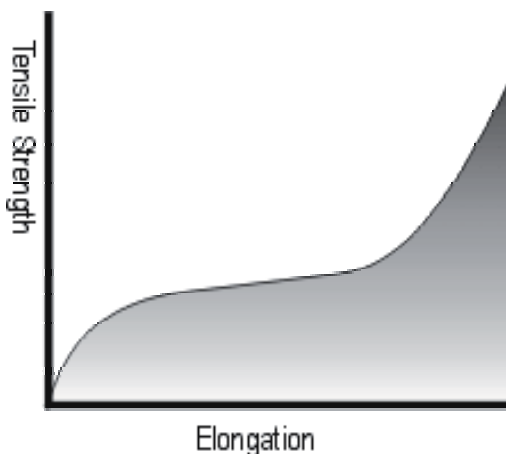


FIGURE 19: Tensile behaviour of an elastomer. Typical S shaped stress/strain curve [12].

v) Polyamides

It is well known that unstabilized polyamides, exposed at room temperature to the action of solar light, suffer discoloration and embrittlement due to photo-oxidation [13, 14].

A simplified scheme concerning the chemical mechanisms involved in the photo-oxidation of aliphatic polyamides is depicted in figure 20 [1].

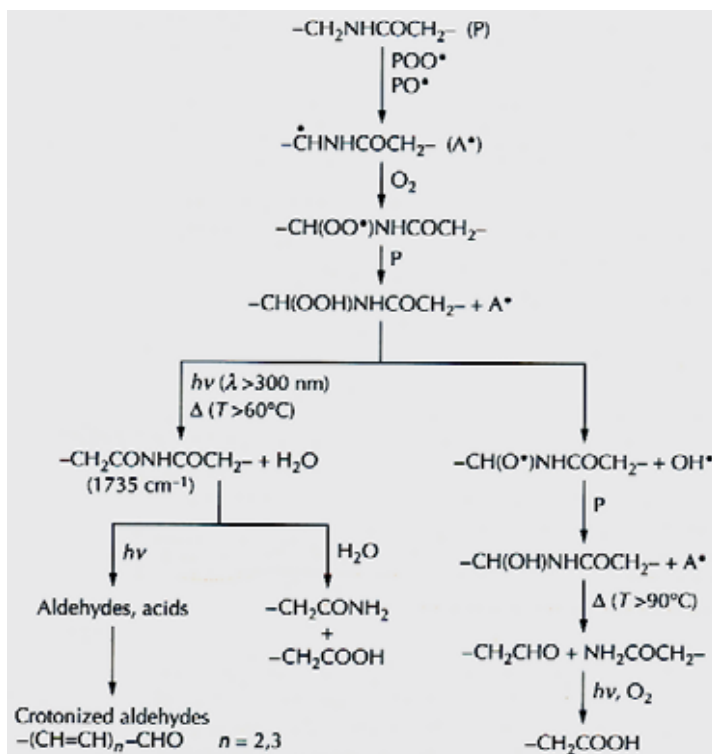


FIGURE 20: Scheme showing the main steps of photo-oxidation of aliphatic polyamides (see text) [1].

Such a scheme, as reported in reference [1], is based upon the following assumptions and experimental observations:

--- The photo-oxidation of nylons exposed to light with $\lambda > 340\text{nm}$ is sensitized by chromophore groups with an α -keto imide structure.

--- In nylons exposed to light with $\lambda < 340\text{nm}$ the cleavage of C-N is produced. This gives rise to the formation of radicals (for example acyl radicals, RCO^*).

--- In presence of O_2 the abstraction of H, following radicals attacks, occurs prevalently at the C-H bond in α to N atoms. This reaction leads to the generation of hydroperoxides, water and

new carbonyl and OH groups in the macromolecular chains.

--- The hydroperoxides find difficulties in acting as radical initiators of new oxidative chains, thus the most effective mode of decomposition leads to an imide ($-\text{CH}_2-\text{CO}-\text{NH}-\text{CO}-\text{CH}_2-$) and water.

--- The imides following hydrolysis produce chains with amides and carboxylic acids end groups [1].

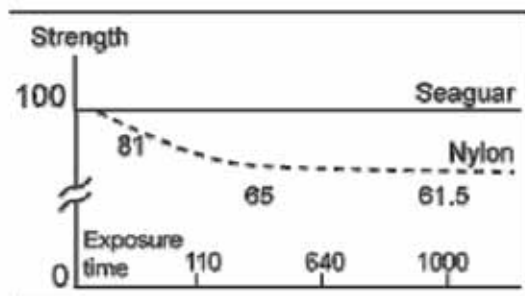


FIGURE 21: 1000 hour ultraviolet test to assess the influence of photo-oxidation on the mechanical properties of polyamides. The values of nylon strength is reported versus exposure time [15].

In the case of aromatic nylons the exposure to light with λ between 290-400nm determines the scission of the C-N bonds: aminyl and acyl-type radicals are formed. The photo-oxidation seems to produce essentially diaryl ketone derivatives [1].

Processes of photo-oxidation, as can be seen by the diagram reported in figure 21, where the strength of nylon samples is reported versus the exposure time to UV radiations, determine a clear adverse effects in the mechanical properties of such a polymer [15].

In the common practice the stabilization of polyamides is attained by using a mixture of phenolic antioxidants, HALS and benzotriazole UV absorbers [1].

vi) Polyvinylchloride (PVC)

The reaction scheme describing the photo-oxidation process of PVC, as published in reference [1], is shown in figure 22. The most relevant issues are hereafter summarized:

--- Sensitization due to polyenic structures seems to play an important role as far as the initiation step is concerned.

--- Peroxides and ketones, formed in the course of processing, may be also relevant for the initiation step.

--- The polyenic products are capable to transfer excitation energy to the allylic C-Cl bonds. This produces alkyl radicals and Cl atoms.

--- The formed radicals by abstracting the H atoms located on the secondary and tertiary C-H bonds produce peroxyradicals.

--- The most important products of photo-oxidation are: tertiary and primary hydroperoxides, ketones [$-\text{CH}(\text{Cl})\text{C}(=\text{O})\text{CH}(\text{Cl})-$], acyl chlorides [$-\text{CH}_2\text{C}(=\text{O})\text{Cl}$], carboxylic acid [$-\text{CH}_2\text{C}(=\text{O})\text{OH}$], and alcohols (figure 22) [1].

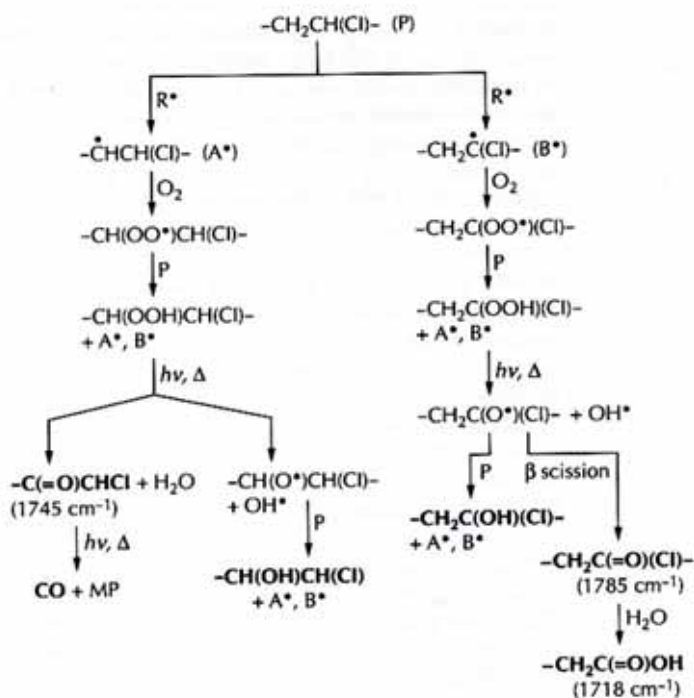


FIGURE 22: Scheme reporting the most effective reactions in the photo-oxidation process of polyvinylchloride. In such a scheme the products experimentally identified are in bold characters (see text) [1].

The formation of polyene, carbonyl, chloroketone and aliphatic ketone products in films of PVC exposed to the action of light with $\lambda = 313\text{nm}$ was recently confirmed by R. Rasheed and others, while assessing the photostabilization effectiveness of some compounds, by means of the FTIR spectroscopy [16].

As matter of fact, as can be seen in figure 23, in the FTIR spectra of exposed PVC samples new bands, at 1772 cm^{-1} and 1724 cm^{-1} , attributed to carbonyl groups belonging, respectively, to chloroketone and aliphatic ketone, and at 1604 cm^{-1} related to polyene group, were observed [16]. By applying the “band index method”, it was possible to follow the progress of photodegradation by correlating the values of the carbonyl (I_{co}), polyene (I_{po}) and hydroxyl (I_{oh}) indices with the irradiation time.

As shown in figure 24 the polyene index (I_{po}) of PVC samples increases with the exposure time [16]. This result is a clear evidence that photodegradation leads to the formation of such type of

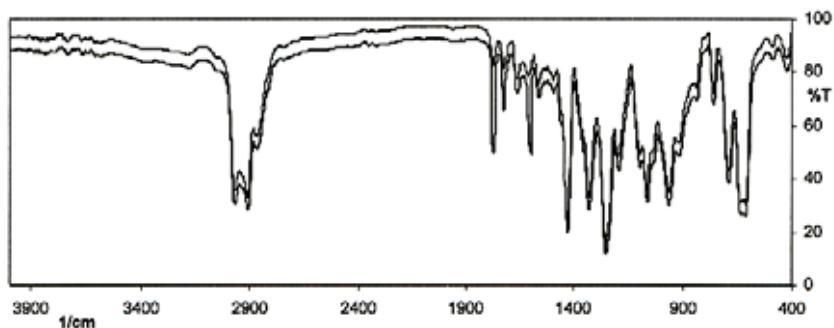


FIGURE 23: Comparison between the FTIR spectra of PVC samples (see text).

Top, unaged film.

Bottom, film after exposure (250hrs) to the action of light with $\lambda = 313\text{nm}$ [16].

compound which may have an important role also in the initiation step of photo-oxidation of PVC. The increase in the values of (Ipo) is accompanied, as expected, by a corresponding lowering in the values of the viscosity average molecular weight (Mv) (see figure 25) [16].

As can be deduced by the trends of the curves shown in the figures 24 and 25 some of the 2-(Aryl)-5-[4-(Aryloxy)-Phenyl]-1,3,4-Oxadiazole compounds, whose molecular structures are represented, in figure 26, seems to be, more or less, effective as photo-stabilisers [16].

According to R. Rasheed and others the 1,3,4-oxadiazole carboxylates compounds act as UV absorber following the mechanism suggested in figure 27.

< The UV light absorption by these additives containing 1,3,4- oxadiazole dissipates the UV energy to harmless heat energy scheme. Furthermore this ring play a role in resonating structures conjugation of radical in peroxide decomposer, which support these compounds as photostabilizer > [16].

The mechanism producing the photostability effectiveness, schematically represented in figure 28, is based on the presence in the compound molecules *< of two different atoms of different electronegativity such as nitrogen and oxygen atoms. The polarity of the compound explains the attraction between the stabilizer and PVC. This mechanism can lead to the conclusion that crosslinking take place upon UV irradiation, which may be correct for all compounds prepared >* [16].

The use of pigments (acting also as light protectors) and thermal stabilisers in PVC manufacturing quite often are sufficient in determine photo-oxidation stability. In transparent PVC hydrobenzophenones and benzotriazole compounds have been employed with success as light stabilisers [1].

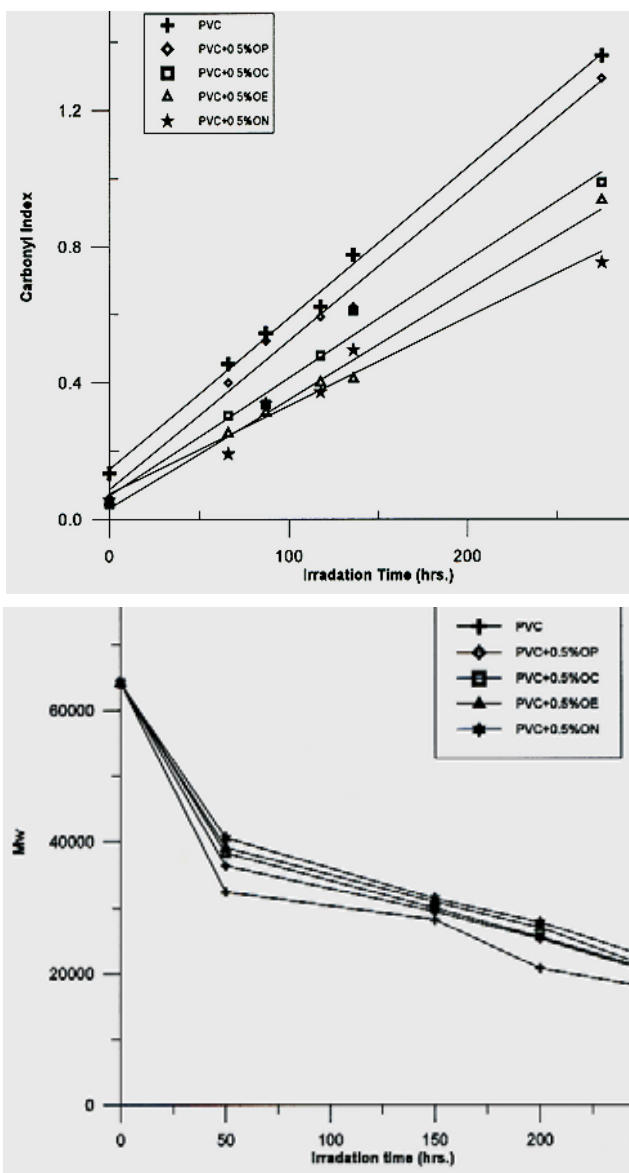


FIGURE 24, top: The relationship between the polyene index (I_{p0}) and irradiation time for unaged PVC films (30 μm thickness) and for films containing different photostabilisers additives (see figure 26), concentration of additives is fixed at 0.5% [16].

FIGURE 25, bottom: Changes in the viscosity average molecular weight (M_v) during irradiation of PVC films (30 μm) (control) and with 0.5 wt% of additives [16].

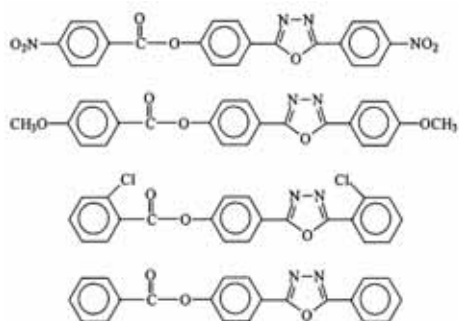


FIGURE 26: Molecular structures of compounds used as PVC photo-stabilisers. From top to bottom: 2-(4-nitro phenyl)-5-[4-(4-nitro benzoyloxy)-phenyl]-1,3,4-oxadiazole; 2-(4-methoxy phenyl)-5-[4-(4-methoxy benzoyloxy)-phenyl]-1,3,4-oxadiazole; 2-(2-chloro phenyl)-5-[4-(2-chlorobenzoyloxy)-phenyl]-1,3,4-oxadiazole; and 2-(phenyl)-5-[4-(benzoyloxy)-phenyl]-1,3,4-oxadiazole [16].

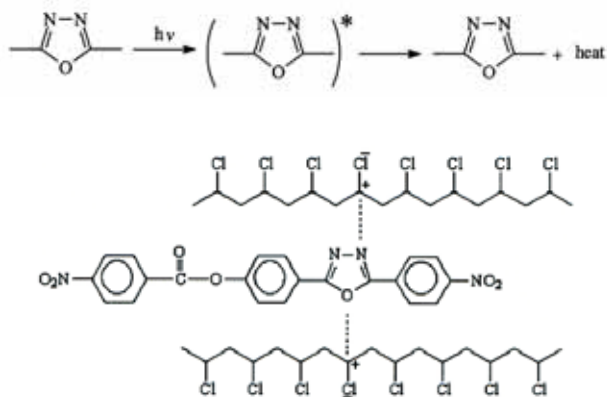


FIGURE 27, top: The suggested mechanism of photostabilization of 1,3,4-oxadiazole carboxylates compounds as UV absorbers [16].

FIGURE 28, bottom: The suggested mechanism of photostabilization of PVC through the interaction between PVC and oxadiazole compounds [16].

vii) **Polyesters**

--- Aromatic Polyesters: Polyethylene terephthalate (PET)

PET, whose molecular structure is represented in figure 29-(a), belongs to the family of aromatic polyesters, a wide class of polymers characterized by the presence of ester groups along the macromolecular chains.

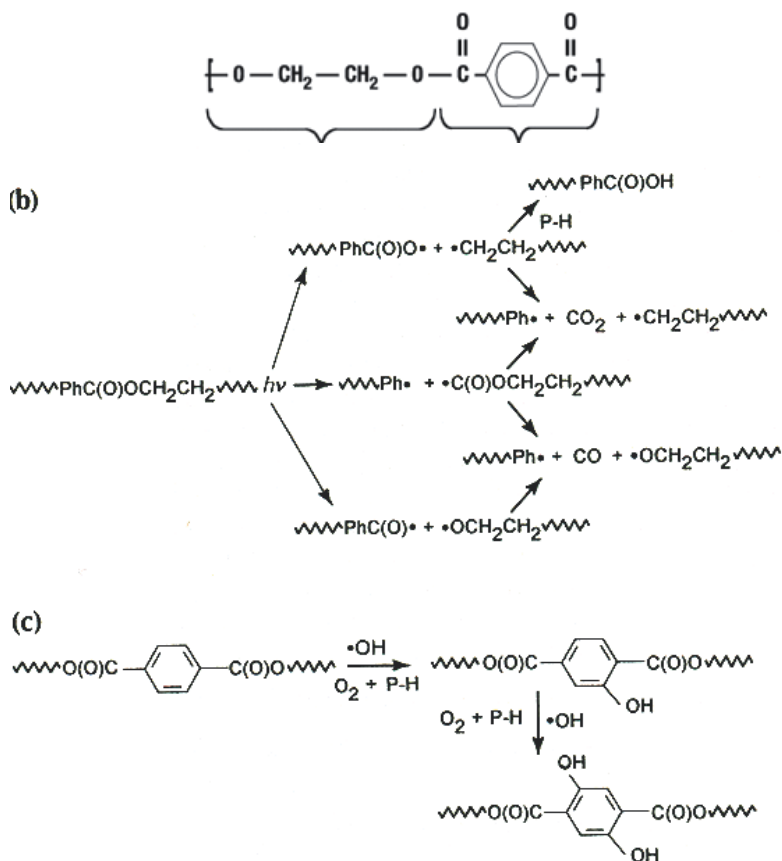


FIGURE 29: Photo-oxidation schemes of reactions of polyethyleneterephthalate (PET).

(top): Molecular structure of repeat unit of (PET).

(b): Photolyses of the ester groups in PET chains following exposure to near-UV solar radiations [2].

(c): PET photo-oxidation degradation following oxygen and hydroxyl radical attack giving rise to bis-hydroxylated phenyl units [2].

As reported in reference [2] PET exposed to sun light exhibits strong absorption of radiations in the near-UV region. Such a behaviour determines as main effect, according to the scheme depicted in figure 29 (b) photolyses of the ester groups. < Hydrogen atoms abstraction reactions by these radicals from the polymer backbone will also occur, giving rise to the formation of hydroperoxides and chain transfer reactions.

Oxygen and hydroxyl radical attack are another feature of polyester degradation reactions giving rise to bis-hydroxylated phenyl units as shown in scheme (c) (see figure 29 (c) > [2].

The photolysis of ester bonds following exposure of PET to light with $\lambda = 360\text{nm}$, with the formation of acyl and carboxyl radicals is mentioned in reference [1]. The main effective photo-oxidation steps are described as follows: < These species (acyl and carboxyl radicals) can lose CO and CO₂ yielding phenyl and alkyl radicals, or abstract hydrogens to give aldehydes and carboxylic acids. In the presence of oxygen, the hydroperoxidative chain gives rise to anhydrides and aldehydes, and to OH addition at the aromatic ring > [1].

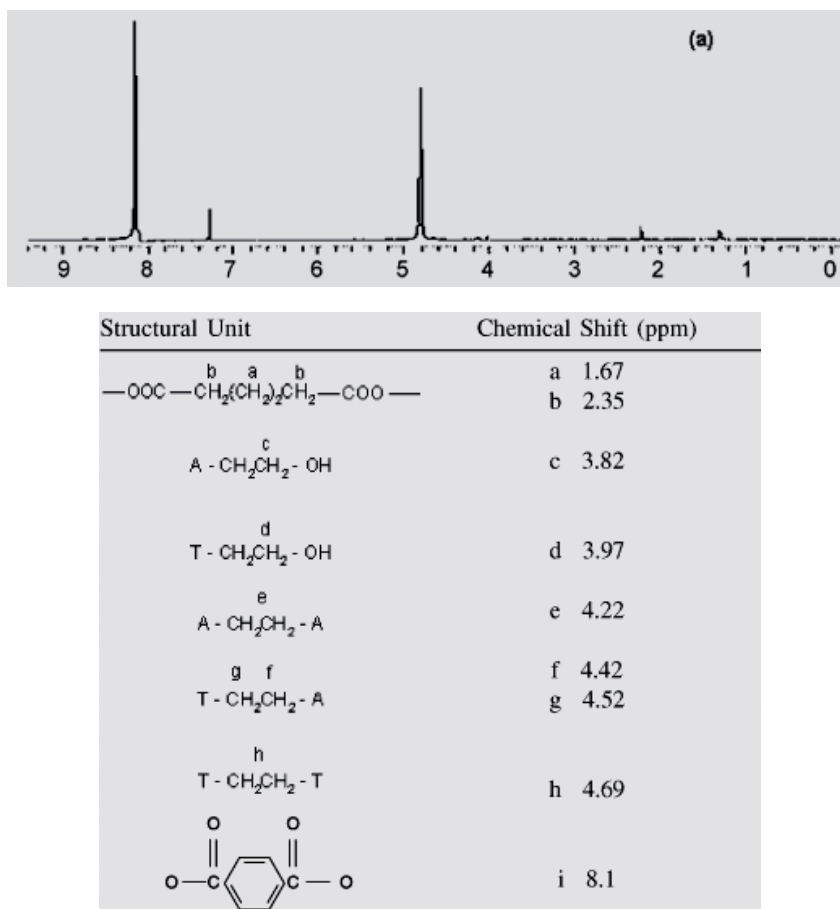


FIGURE 30: (Top): Proton NMR spectrum of PET. (Bottom): chemical shifts and assignment of proton signal showed in ¹H-NMR [17].

The degradation pattern of PET can be conveniently studied by means of Proton Nuclear Magnetic Resonance Spectroscopy ($^1\text{H-NMR}$) whose spectrum and typical chemical shifts assignment are shown in figure 30 [17]. FTIR analysis represents also an useful tool for studying the degree of damages induced to PET artefacts (see figure 31) [18].

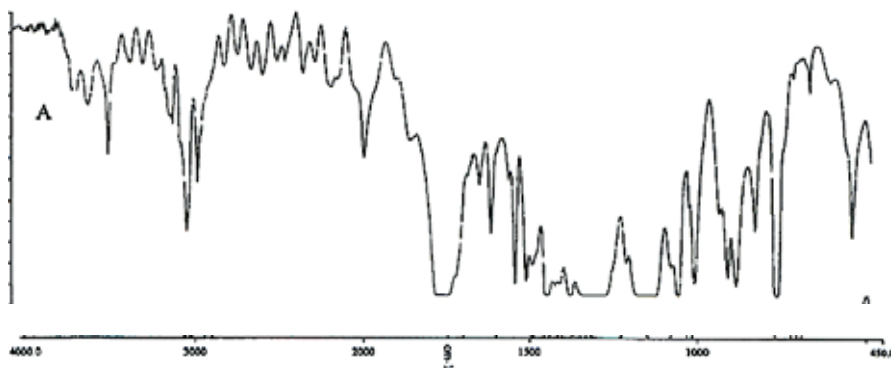
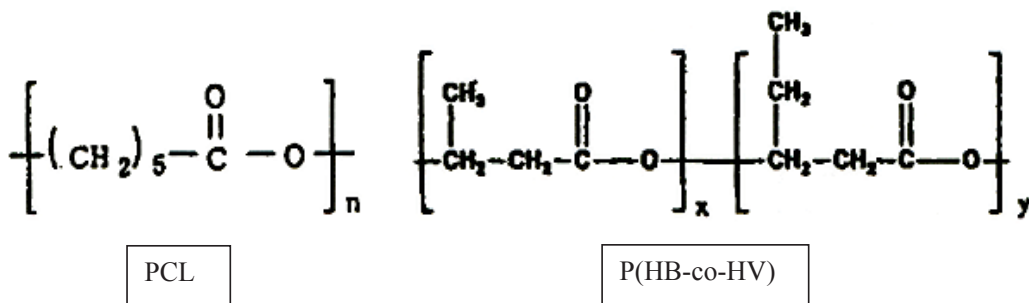


FIGURE 31: Typical FTIR spectrum of polyethyleneterephthalate in transmittance mode at ambient conditions in the range $500\text{-}4000\text{cm}^{-1}$ [18].

--- *Aliphatic polyesters*

The photodegradation behaviour of two aliphatic polyesters, namely a copolymer between hydroxybutyrate and hydroxyvalerate monomers, P(HB-co-HV), and the polycaprolactone (PCL), whose molecular structures of repeat units are below represented, have been studied by E. Ikada [19]. It was found that the two aliphatic polyesters, PCL and P(HB-co-HV), exposed to the radiations emitted by a Hg lamp, undergo a drastic reduction of the molecular mass. The process, as shown by figure 32, was monitored by plotting the limiting viscosity number of degraded samples against exposure time.



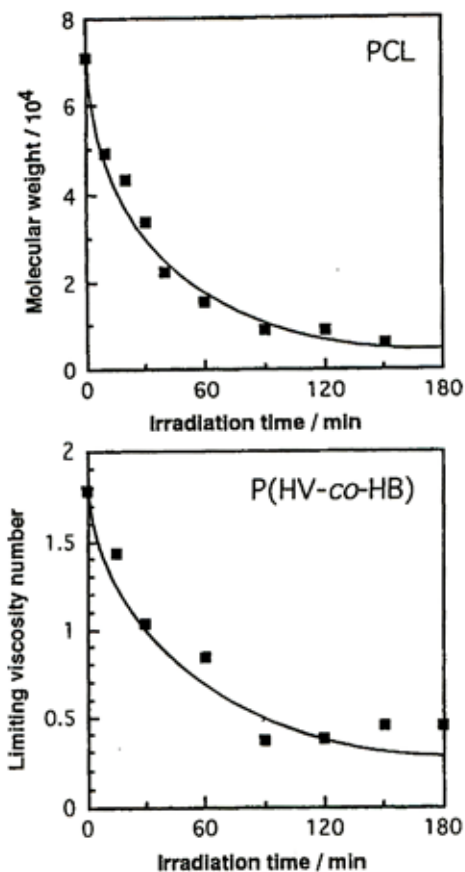


FIGURE 32: Photodecomposition rate of two aliphatic polyesters, PCL and P(HB-co-HV), as measured by the variation of the limiting viscosity number of samples exposed for different times to radiation emitted by a Hg lamp (see text) [19].

To correlate the values of the viscosity average molecular mass to the limiting viscosity number $[\eta]$ the hereafter reported equation of Mark-Houwink-Sakurada was used:

$$[\eta] = KM^a$$

Thus it can be concluded that viscosimetry turns to be an useful methodology to quantify the mass reduction following photo-oxidation processes in polymers.

Polymer with carbonyl groups along the chains, according to reference [19], are photochemically decomposed via the Norrish I or Norrish II type mechanisms.

The Norrish I mechanism, depicted in figure 33, foresees the formation of active radicals resulting from photo-rupture of C-C bonds adjacents to the carbonyl groups [19].

Norrish I type reaction

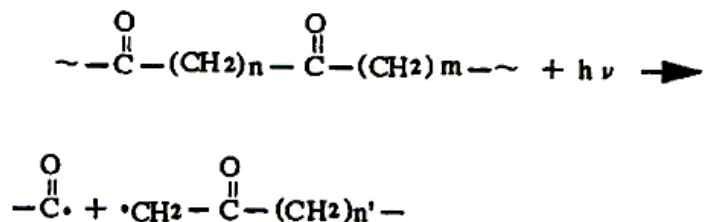


FIGURE 33: Photochemical mechanism of decomposition of a polymer with carbonyl groups along the chains via the Norrish I mechanism [19].

viii) *Polymethylmetacrylate (PMMA)*

Polyacrylates and polymethacrylates as PMMA, even being considered stable polymer nevertheless at relatively longer time of exposure to sun radiation may suffer severe effects of photo-oxidation (loss of molecular mass, yellowing ecc.).

The reactions leading to the degradation of PMMA are described in the scheme of figure 34 [2].

The most effective reactions leading to chains scission occur through the mechanism described in figure 34 as scheme (I). The other reactions refer essentially to various kind of side-chain processes [2].

< In the case of step (II) the acyl radical will abstract a hydrogen atom to form aldehydes, which along with unsaturation are the two main functionalities identifiable by IR spectroscopy > [2].

In reference [1] the main steps of PMMA photo-oxidation are described as follows:

< The initiation of the photo-oxidation of PMMA by sun light or artificial sources is mainly due to the direct photolysis of the ester groups between 300-330nm with scission of the C-C or C-O bonds leading to the predominant formation of tertiary-carbon-centred chain radicals, acyloxy and acyl radicals. In the presence of oxygen, the species act as initiators of the oxidative degradation propagated by peroxy and alkoxy radicals >.

As for other polymers Infra-red Spectroscopy and Proton Nuclear Magnetic Resonance Spectroscopy (¹H-NMR) turn to be suitable methodologies to assess degradation on PMMA objects by following the development in the spectra of new functionalities.

The FTIR spectrum of undegraded PMMA, as shown in figure 35, is characterized by a:

- Sharp intense peak at 1731 cm⁻¹ due to the stretching vibration of the ester carbonyl group.
- Broad peak between 1260-1000 cm⁻¹ accounted for by the C-O (ester bond) stretching vibration.

- Broad band from $950\text{-}650\text{ cm}^{-1}$ to be attributed to the bending of C-H.
- Broad peak from $3100\text{-}2900\text{ cm}^{-1}$ due to stretching vibration [20].

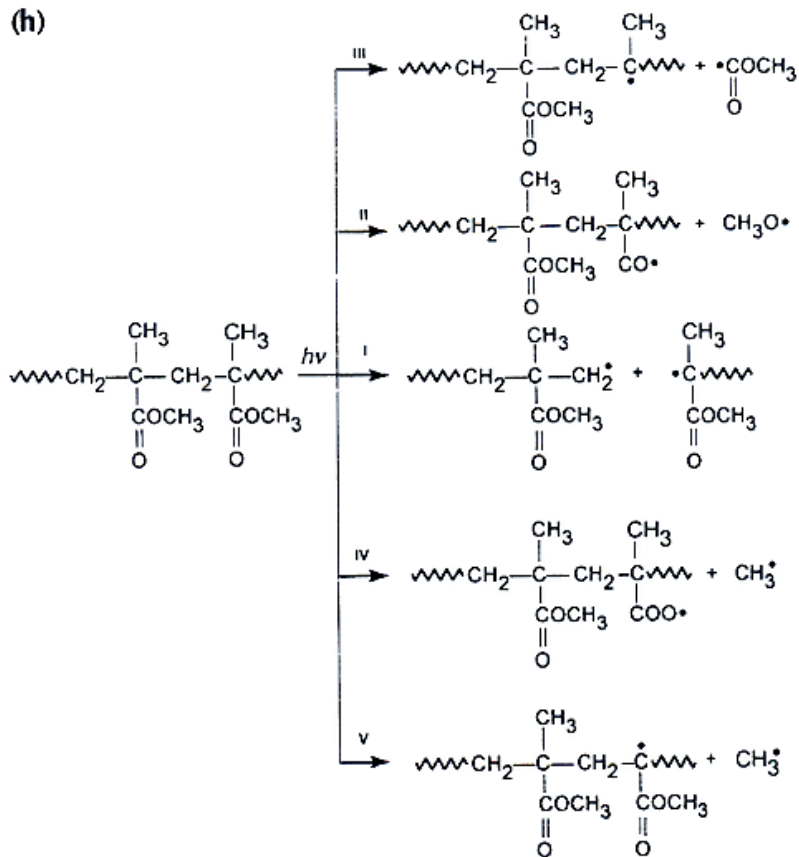


FIGURE 34: The most effective photodegradation mechanisms observed in polymethylmethacrylate (PMMA) [2].

The main features of the $^1\text{H-NMR}$ spectrum, reproduced in figure 36, is the peak corresponding to the methoxy carbon ($-\text{OCH}_3$) at $\delta=3.57\text{-}3.64$ [20].

For outdoors applications, especially when PMMA is compounded with dyes, photo-stabilization is accomplished by using benzotriazoles UV-absorbers and HALS [1].

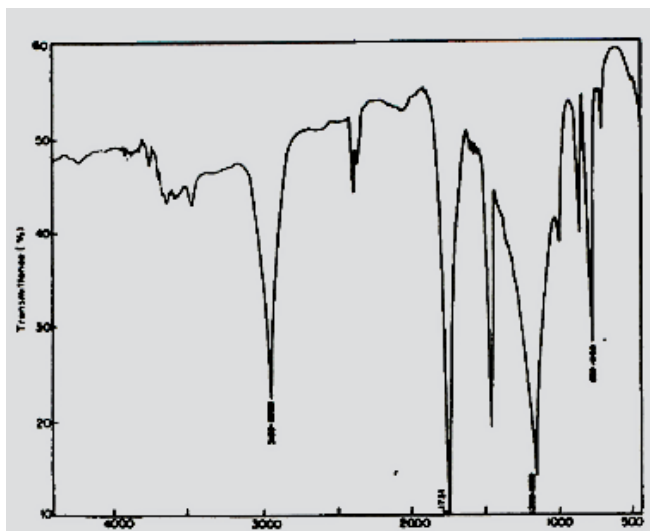


FIGURE 35: FTIR spectrum of undegraded polymethylmetacrylate (PMMA) [20].

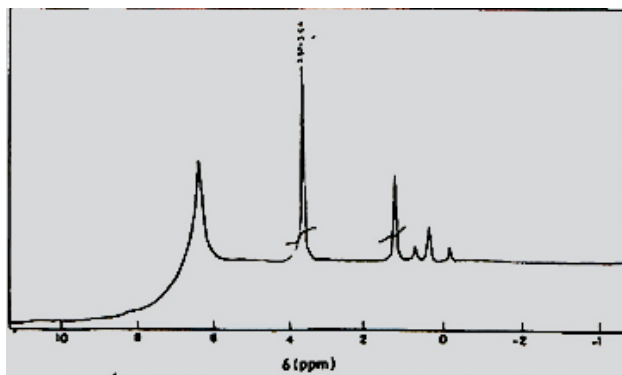


FIGURE 36: ^1H -NMR spectrum of undegraded polymethylmetacrylate (PMMA) [20].

ix) Polyurethanes (PU)

Polyurethanes (PU) are a family of polymers where, generally, soft and hard segments alternate along the chains. Such segmented polymers are prepared starting from three different types of molecules:

- Diisocyanate;
- Chain extender;
- Polyol.

The hard segments include the diisocyanate and the chain extender, while the soft ones derive from polyols that can be of polyester or polyether in nature (PU-PES and PU-PE types polyurethanes, see figure 37-top)).

The complex molecular structure of a special thermoplastic elastomeric- PU (it has both urea and urethane linkages in its backbone), commercialized by DuPont as “*Spandex*”, is represented in figure 37-centre, where the chemical nature of hard and soft blocks in its repeat unit are indicated [21].

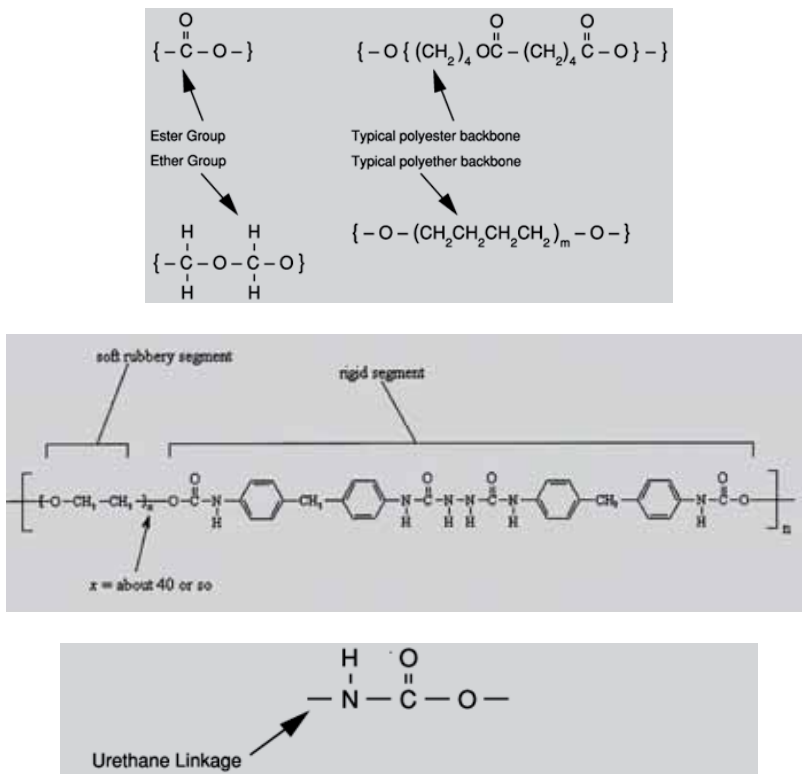


FIGURE 37: Top - Chemical structure of polyester polyurethane and polyether polyurethane. Centre - Soft and hard segment sequences in a thermoplastic elastomeric- PU with both urea and urethane linkages in its backbone, commercialized by Du-Pont as “*Spandex*”. Bottom – The typical urethane linkage [21].

In general the photodecomposition of PUs, as reported in figure 38, produces the scission of the N-C and C-O bonds part of urethane linkage as below indicated.

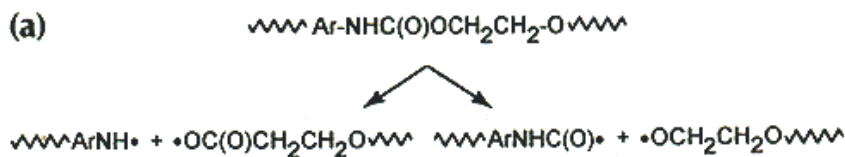


FIGURE 38: The mechanism concerning the photodecomposition of Polyurethanes [2].

The radical species formed, in presence of O₂ initiate the oxidative processes.

In reference [1] the process of photo-oxidation of PUs is described as follows:

< In the oxidation, the preferred sites of attack for the H abstraction are the activated C-H bonds α to the aromatic ring or α to the urethane moiety. An important contribution to the overall degradation of PUs also comes from the photo- and photo-thermal oxidation of the aliphatic section of the polymer chains, the preferred sites of attack being the C-H bonds activated by adjacent ether and carboxylate groups > [1].

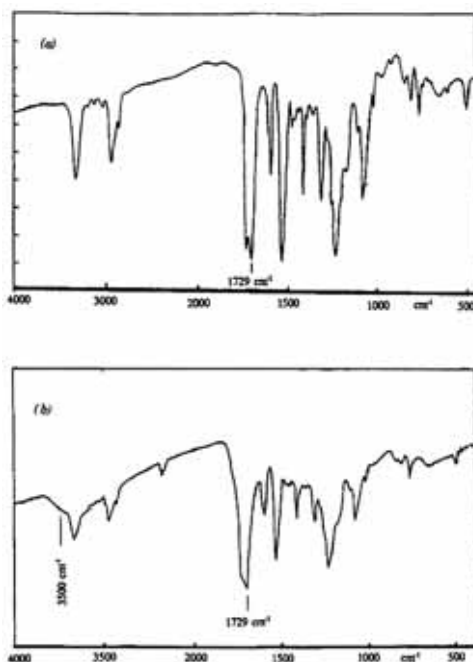


FIGURE 39: FTIR spectra of aromatic isocyanate-based polyurethane elastomer. (a) before and (b) after UV irradiation [22].

In the case of 4,4'-diphenylmethanediisocyanate based PU, quite unstable polymers, the oxidation seems to be caused mainly by presence of benzophenone-type chromophores [2].

< On irradiation, quinone-imide structures are responsible for the observed photoyellowing > [2].

The effects caused by photo-oxidative degradation on the properties of PUs are strongly dependent upon the molecular structure of their repeat units (i.e. chemical structure of the diisocyanates and the hard/soft segment ratio), and, as shown by figures 39, they may be followed by FTIR spectroscopy [22].

As far as stabilization of PU is concerned usually it is accomplished by using formulations containing benzotriazole-UV-absorbers, phenolic antioxidants and HALS [2].

x) Polycarbonates (PC)

From a commercially point of view the Bisphenol A Polycarbonate (PC-A), whose synthetic pathway is described in figure 40, represents far the most important polycarbonate.

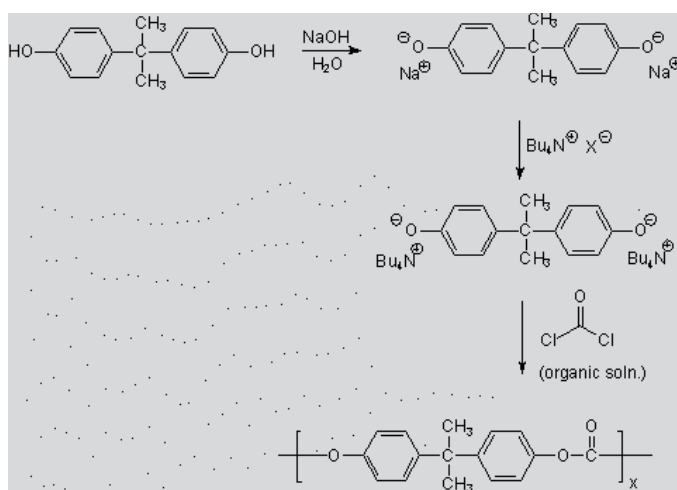


FIGURE 40: Main steps in the *interfacial polymerization* of Bisphenol A Polycarbonate (see text) [23].

< polycarbonates are made from phosgene, ClC(=O)Cl, in a two phase reaction(i.e., water + immiscible organic solvent). The Bu₄N⁺ is a phase transfer catalyst, which improves the solubility of the phenolate in the organic phase, and greatly speeds reaction > (see figure 40) [23].

< It has good optical clarity, reasonable resistance to heat, and spectacular impact resistance. It is used as a substitute for window glass, for plastic parts in all kinds of household appliances, for spectacles (especially safety glasses), sporting goods, automobile bumpers, compact disks, and many other applications > [23].

Polycarbonate find applications that quite often foresee exposure to light in air. Thus their stability to photo-oxidative degradation is of great importance.

The exposure to light and oxygen may cause chain scission and crosslinks in PC-A according to scheme depicted in figure 41 [2]. The main reactions are hereafter described.

1) The initial step consists in the chain scission at the C-O carbonate bonds determined by absorption of light.

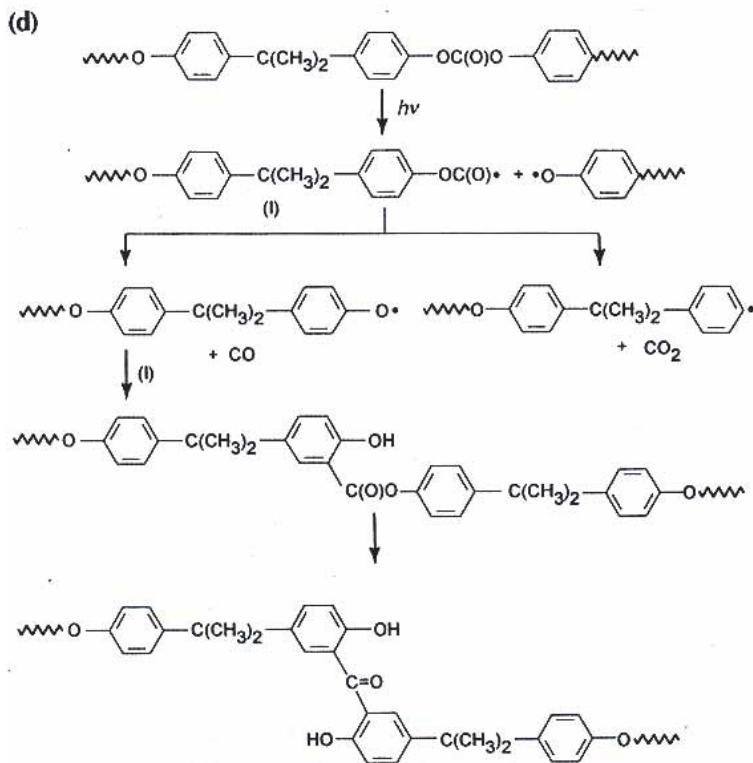
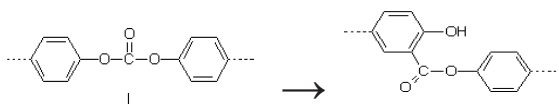


FIGURE 41: Photodegradation mechanism for polycarbonate (Bisphenol A Polycarbonate) [2].

2) In the next step decarboxylation occurs: CO and CO₂ molecules, together with phenyl and phenoxy radicals are formed.

3) The ester radicals (I) via a *photo-Fries* reaction rearrange to the ortho position (see below) [24].



Then the phenoxy radicals react with ester radicals forming a phenyl ester.

4) The phenyl ester following further rearrangement transforms in a 2-hydroxybenzophenone. Such a product is stable and being able to absorb sun radiations in the near-UV may act as light stabiliser (self-protective mechanism) [2].

In reference [1] the mechanism of photo-oxidation of polycarbonates is described as follows:

< The direct photolysis of the carbonate moiety takes place with photo-Fries rearrangements at c. 360nm, and leads to the formation of products absorbing in the visible region. Under oxygen atmosphere, both direct photolysis and radical photo-oxidation take place, leading to the formation of carboxylic acids, phenols, esters, anhydrides and ketones. In bisphenol-A-polycarbonates the favoured sites for radical attack are the methyl C-H bonds > [1].

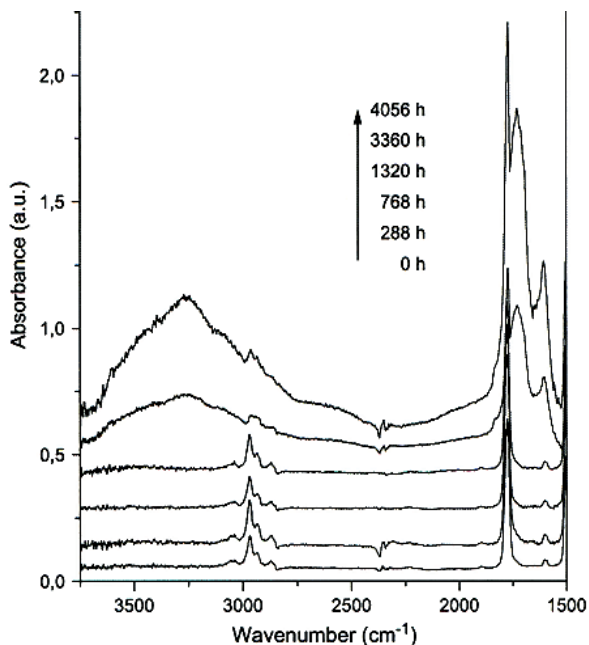


FIGURE 42: Infrared spectra after different photochemical aging times of film samples of polycarbonate [25].

As shown by figure 42 FTIR-spectroscopy is a suitable technique to evaluate the chemical modifications induced by photo-oxidation in samples of PC-A exposed to artificial aging.

From the examination of the Infrared spectra it can be deduced that:

--- The intensity of the carbonyl and hydroxyl absorption bands, at 1770cm^{-1} and 3200 cm^{-1} respectively, increase with exposure time [25].

Thus the degree of degradation can easily be followed and quantified by measuring the intensity of the above bands as function of the time of exposure to radiations.

Following photo-oxidation objects in PC-A become yellow in color and more brittle, thus especially for outdoor prolonged applications, benzotriazole UV-absorbers, phosphite or phenolic antioxidants are added to commercial polycarbonates to inhibit such degradation process [1].

CONCLUDING REMARKS CONCERNING THERMO AND PHOTO-OXIDATION OF POLYMERS

Some general conclusions concerning the mechanisms of thermo and photo-oxidation of polymers are hereafter summarized also with reference to the diagram shown in figure 43 where some of the main steps of the overall process of degradation are schematically represented [25].

1) The thermo and photodegradation processes of polymers (PH) are initiated by absorption of energy (of thermal or electromagnetic nature) followed by the formation in the material of highly reactive chemical species, especially free radicals (P*).

2) The free radicals P* reacting with oxygen, give rise to a series of chemical reactions, which represent the effective degradation steps of the polymer.

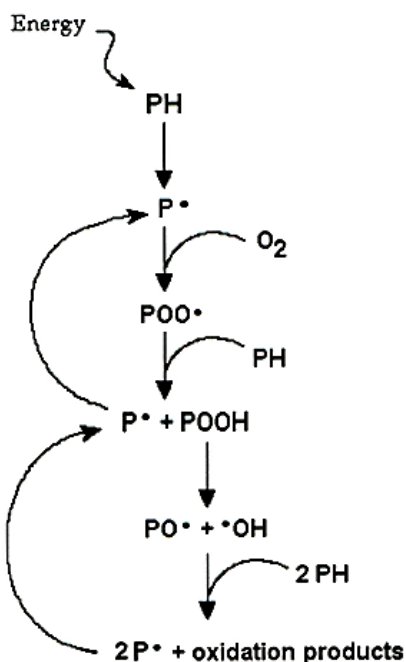


FIGURE 43: Photo-oxidation mechanism of polymers leading to their total degradation (see text) [25].

3) As shown in figure 43, P* radicals by reacting with O₂ molecules generate highly reactive peroxy radicals (POO*) which by reacting with other polymeric chains (PH) produce hydroperoxide structures (POOH) and new free radicals P*. With such step the cycle of degradative reactions practically starts.

4) POOH hydroperoxides, through the rupture of the oxygen-oxygen bond give rise to the formation of hydroxy and alkoxy free radicals (*OH and PO* respectively).

5) All free radicals species formed can react with other polymeric chains, catalyzing new degradative cycles. Meanwhile the production of stable oxidation products is observed.

The net effects of photo and thermo-oxidation of polymers, essentially the same, are: formation of backbone carbonyls, chain rupture, formation of CO, H₂O, CO₂ and other small size molecules.

In general it can be said that polymers susceptible to thermal oxidation are also sensitive to photo-oxidation.

Finally it must be underlined that photo-oxidation occurs essentially at the surface due to the combination of factors such as oxygen diffusion and the opacity of polymers to radiations [26].

The photo-oxidation behaviour of polymers is influenced by many internal factors. Some of them are below listed and discussed.

--- The intrinsic stability of the polymer chains determined by their molecular structure (molecular weight or molecular weight distribution, degree of branching, composition ecc.) and by the structure in the solid state (i.e. crystallinity content and consistency of the amorphous state (glassy or rubbery)).

--- The presence of residual catalyst, metallic contaminants and other impurities which acting as chromophores may accelerate photodegradation processes.

--- Additives incorporated in the polymer which can also act as chromophores, sensitizing the polymer to degradation.

Colourants and dyes may play an important role on the photo-oxidation behaviour of polymers.

According to what reported in references [25, 27] the action of dyes and pigments may influence the processes of photo-oxidation following two distinct pathways (see scheme in figure 44).

Pathway A, < dyes and pigments after absorbing light in the presence of O₂, produce chemical species such as singlet oxygen (¹O₂) and superoxide anion (O₂⁻). O₂ can also participate directly in the oxidation-reduction reactions with the polymer. The reactive chemical species, as well as oxidation-reduction, accelerate polymer degradation > [25].

Pathway B, < colorant, after absorbing light, reaches excited singlet (S₁, S₂) and triplet (T₂, T₁) states. The energy absorbed by the colorant is transferred to the chemical groups in the polymeric chain by intermolecular energy transference. The energetic excitation of polymer by colorant increases the potential formation of free radicals (P*) > [25].

It has been found that the efficacy of a colorant in influencing the degradation of polymers will depend on its intrinsic properties and on the colorant-polymer molecular interactions.

As shown by the scheme of figure 45 the addition to polymers of compounds able to act as *H-donors*, *radical scavengers* and *hydroperoxides decomposers* in many cases results to be essential to interrupt the oxidation interlocking cycle of reactions leading to the photo-oxidation of polymers [28].

In considering the thermo-photo-oxidation of polymers the concomitant degradative action of very reactive chemical substances (nitrogen and sulphur oxides, ozone, ecc.) present in the atmosphere as pollutants should be taken also into consideration. In such a case the overall mechanisms of degradation result to be still much more complex than those so far examined.

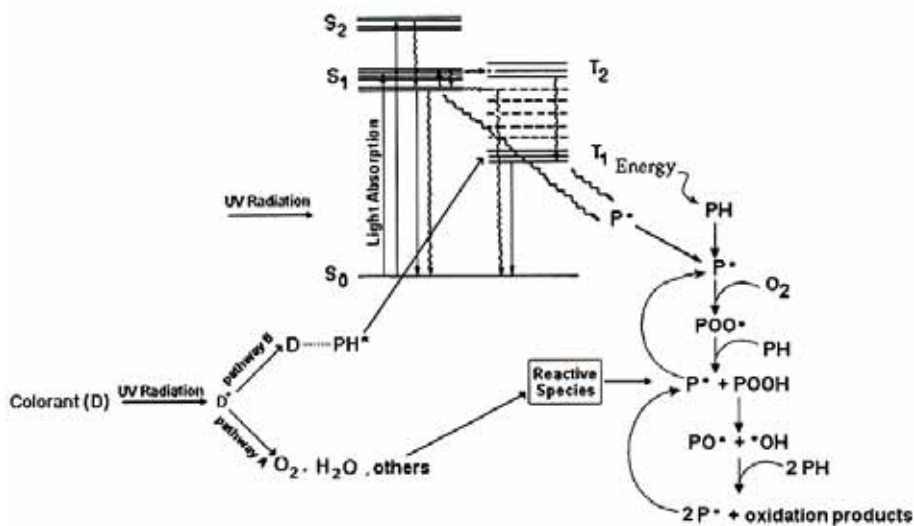


FIGURE 44: Schematic representation of the two possible pathway according to which colorants interfere with the photo-oxidation mechanism of polymers [25,27].

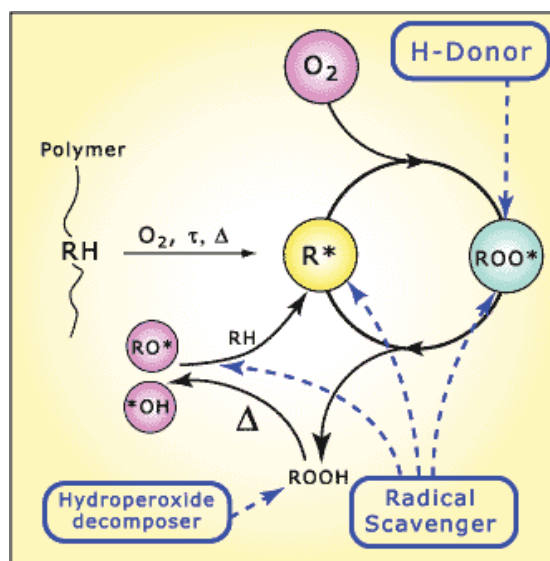


FIGURE 45: the addition of H-donors, radical scavengers and hydroperoxides decomposers results to be essential to interrupt the oxidation interlocking cycle of reactions leading to the photo-oxidation of polymers [27].

REFERENCES

- 1) A. Faucitano and others, < *Photo-oxidation and stabilization of polymers* >, in “*Trends in Polymer Science*”, pp. 93-98, **Vol.4**, No 3, March (1996).
- 2) N. S. Allen, < *Why do polymer degrade in sun light?* >, in “*Trends in Polymer Science*”, pp. 366-375, **Vol.2**, No 11, Nov. (1994).
- 3) en.wikipedia.org/wiki/Forensic_polymer_engine..., (2009).
- 4) 28) P. Maltese, < *Materie Plastiche ed Elastomeri* >, pp. 728-735 Nov. Dic. (2002).
- 5) C. Puglisi, < *Degradazione Ossidativa delle Materie Plastiche* >, Lecture presented at Programma Giornata AIM on “Il restauro e la diagnostica degli oggetti d’arte e di design inplastica”, PLART, Napoli, 31/10/(2008).
- 6) M. A. Salem, H. Farouk, I. Kashif, < *Macromolecular Research* >, **10**, 168 (2002).
- 7) C. Vasile, < *Degradation and Decomposition* >, in “*Handbook of Polyolefins*”, Edited by C. Vasile, M. Dekker, USA, (2000).
- 8) Y. Eric, < *Photodegradation of Polystyrene* >, “*The extruder*”, December (2007) <http://www.spe-stx.org/Newsletters/Dec07ExtruderOnline/index.htm>, (2009).
- 9) N. C. Billingham and others, < *Controlled-life time environmentally degradable plastics based conventional polymers* >, NCB, Pisa Paper, (2002). EPI, Environmental Technologies Inc., (2009).
- 10) Hunseung Kang, Min Young Kang, and Kyung-Hwan Han, < *Identification of Natural Rubber and Characterization of Rubber Biosynthetic Activity in Fig Tree* >, *Plant Physiol.*; **123(3)**: 1133–1142 July (2000).
- 11) I. C. McNeil, < *Fundamental Aspects of Polymer Degradation* >, in “*Polymers in Conservation*”, Edt. by N. S. Allen, M. Edge, C. V. Horie, Royal Society of Chemistry, pp. 15-32 (1992).
- 12) www.nps.k12.nj.us/.../ChemSite/degredation.h, (2009).
- 13) M. I. Kohan, < *Preparation and chemistry of nylons* >, in “*Nylon Plastics*”, edited by M. I. Kohan, John Wiley & Sons, New York (1973).
- 14) A. Ciaperoni, A. Mula, < *Chimica e tecnologia delle poliammidi* >, Pacini editore, Pisa, (2001).
- 15) www.seaguar.co.uk/about%20seaguar.html, (2009).
- 16) R. Rasheed, H. Mansoor, E. Yousif, A. Hameed, Y. Farina, A. Graisa, < *European Journal of Scientific Research* >, **Vol.30 No.3**, 464, (2009).
- 17) A. F. Baldissera; C. E. S. Valério; N.. R. de S. Basso; F. Guaragna; S. Einloft, M. Tessier, A. Fradet, < *Quim. Nova* >, **vol.28, no.2**, São Paulo, Mar./Apr. (2005). www.scielo.br/scielo.php?script=sci_arttext..., (2009)
- 18) Mohamed Mahmoud Nasef, < *Journal of Applied Polymer Science* >, **Vol. 84**, 1949 (2002)
- 19) E. Ikada, < *J. of Photopolymer Science and Technology* >, **12**, 251 (1999).
- 20) A. Balamurugan, S. Kannan, V. Selvaraj, S. Rajeswari, < *Trends Biomater. Artif. Organs* >, **Vol 18 (1)**, 41, (2004), <http://www.sbaoi.org>, (2009).
- 21) pslc.ws/macrogcss/urethane.html, (2009).
< *Urethane Primer. An Introduction and Glossary of Key Terms* >, www.extrapackaging.com/polyurethane/whatispol...
- 22) V. Rek, E. Govorcin, A. Sendijarevic, V. Sendijarevic, K.C. Frisch, < *Journal of Elastomers and Plastics* >, **26**, 143 (1994).
- 23) www.chem.rochester.edu/~chem424/pcsynth.htm, (2009)
- 24) A. Factor, < *ACS Adv. in Chem. Ser.* >, **249**, 59, (1996).
- 25) C. Saron, F. Zulli, M. Giordano, M. I. Felisberti, < *Polymer Degradation and Stability* >, **91** 3301, (2006)
- 26) D. L. Allara < *Environmental Health Perspectives* >, **11**, 29 (1975).

27) E. I. Sanchez, M. Calderon, M. I. Gutierrez. < *Polym Bull* >, **51**, 271, (2004).
- N. S. Allen.< *Polym Degrad Stab*>, **44**:357 (1994).
28) UV/Light Stabilizers Center (CIBA).
<http://www.specialchem4polymers.com/tc/UV-Light-Stabilizers/?id=2258>, (2009).

SECTION-1

FIFTH-CHAPTER-

THE DEGRADATION OF PLASTIC ARTEFACTS INDUCED BY ENVIRONMENTAL CHEMICAL AGENTS

The overall process of degradation of plastics in outdoor environment is the resultant of the concomitant action of different factors.

For example, as shown in figure 1, the effects of the photo-oxidation of samples of polycarbonate, measured by the elongation at break, are dramatically enhanced, for the same time of exposition to sun radiations, when the temperature of experiments is increased (compare upper curve with lower one) [1].

Aggressive chemical pollutants in the outdoor or indoor environments together with humidity may be very active in producing degradation phenomena in polymer based artefacts (see the schematic representation in figure 2 where the influence of such factors on the photo-oxidation process is qualitatively indicated) [1,2,3].

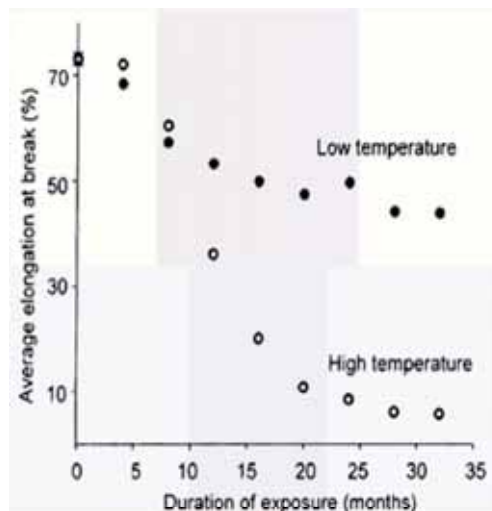


FIGURE 1: The photo-oxidation of samples of polycarbonate, measured by the elongation at break, is enhanced when the temperature of experiments is increased (compare upper curve with lower one) [1,3].

The most effective outdoor atmospheric pollutants include: Sulfur dioxide (SO_2); Nitrogen dioxide (NO_2) and Ozone (O_3). Sulfur dioxide and nitrogen dioxide reacting with water in presence of oxygen form strong acids (H_2SO_4 and HNO_3 respectively).

Many plastics in presence of the above reactants may give rise to specific degradation processes whose mechanisms will depend essentially on the functionalities present in their repeat units and as well as on their physical state. Some examples are hereafter described.

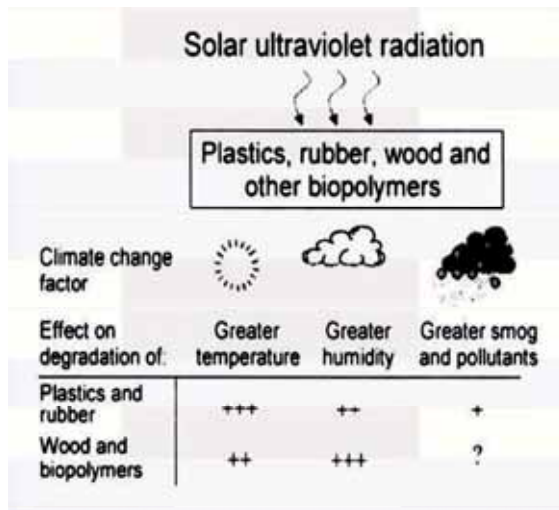


FIGURA 2: The photo-oxidation of plastics is implemented by the presence in the environment of aggressive chemical pollutants and by humidity and also by the temperature (+++ very high effect; ++ high effect; + moderate effect) [1,3].

1) Degradation of polyamides and polyurethanes by nitrogen oxides (NOx)

It is widely documented by literature that polyamides and polyurethanes exposed to the action of NO₂ undergo reactions of chain scission and cross-link, the former being the main degradation pathway. The scheme of the reaction leading to chain scission is represented in in figure 3 [4]. It can be seen that in the initial step the NO₂ abstracts an H atom from the NH group and this gives rise to the formation of a highly reactive radical species that are able to start the propagation step of degradation.

2) Degradation of rubbers and unsaturated polymers by ozone(Ozonolysis)

Rubber and many different elastomers and polymers containing along the backbone double bonds easily undergo ozonolysis, a degradation process that leads to the rupture of macromolecular chains due to ozone attack. The ozone molecules are able to react with alkene double bonds, present in unsaturated polymers, forming a five atom cycle, named ozonide, where the previously doubly bonded carbons are linked to two oxygens. The ozonides are very unstable structures.

Their decomposition is followed by scission of the macromolecular backbone according to the scheme depicted in figure 4 for natural rubber [4].

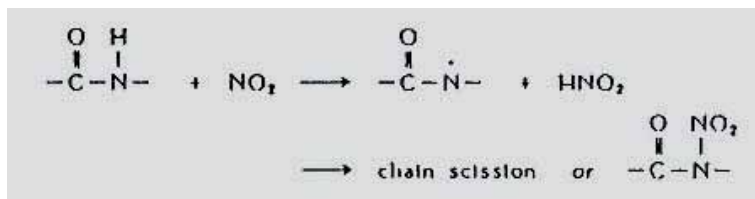


FIGURA 3: Initial step of the process of degradation of polyamides and polyurethanes induced by the attack of nitrogen oxide [4].

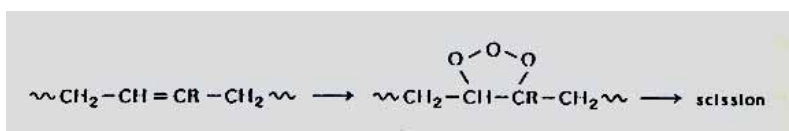


FIGURA 4: Initial step of ozonolysis of natural rubber (see text) [4].

The products of ozonolysis of natural rubber are < a shorter chain with an aldehydic end and either a poly-peroxide or an iso-ozonide which can undergo further degradation reactions. The oxidised structures are effective chromophores for degradation by photo-oxidation > [4].

The reaction of ozonolysis, according to the scheme in figure 5, is favoured by the presence of water and zinc. In such a respect in reference [5] is textually written:

< When ozonide is in the presence zinc (Zn) and water (H₂O), bonds between the carbon and oxygen are broken; the oxygen that separates from the ozonide combines with water to form hydrogen peroxide (H₂O₂). The result is that the original alkene molecule is split, with the carbon forming a double bond with the oxygen in each case > [5].

The degradation effects produced by the ozone attack on single crystals (see figure 6), grown from solution, of *trans*-1,4-polyisoprene (TPI), a natural unsaturated polymers commonly named as “Guttapercha”, were qualitatively and quantitatively followed by Keller and Martuscelli by using infra-red spectroscopy, gel-permeation chromatography (GPC) and differential scanning calorimetry (DSC) [6].

From the examination of the IR spectrograms of TPI, reported in figure 7, taken at different times of exposition to the O₃ at RT, the following results emerges [6]:

--- The bands of the -CH₂- and -CH₃ groups are practically unaffected.

--- The intensity of the peaks characteristics of the *trans* double bond -C(CH₃)=CH-, between 750-960cm⁻¹, drops rapidly at the early stage of exposure (see figure 9) thereafter it keeps constant.

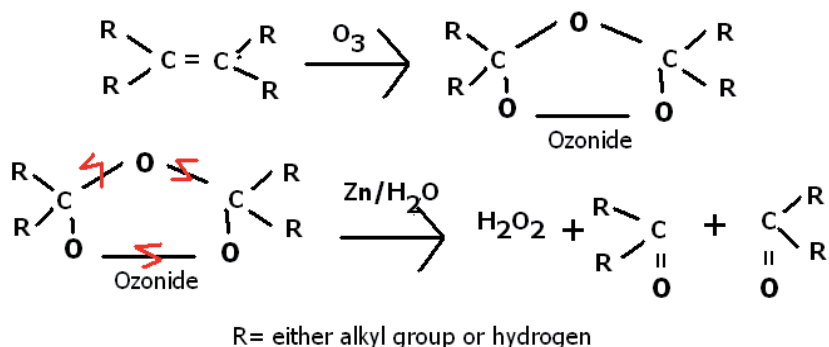


FIGURE 5: Ozonolysis reaction of rubber-like macromolecules leading to chain rupture in presence of water and metallic zinc (see text) [5].

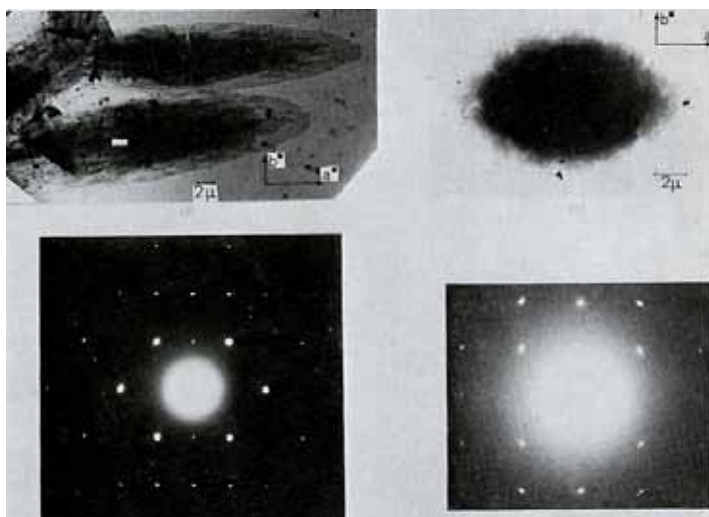


FIGURE 6: Electron micrographs (above) and corresponding electron diffraction patterns (below) of two solution grown single crystal polymorphs of *trans*-1,4-polyisoprene, “Guttapercha”.
Left, low melting form. Right, high melting form [6].

It was possible to calculate that $\approx 20\%$ of double bonds are left uncutted in the material.

--- The intensity of the carbonyl band at 1712cm^{-1} , as expected behaves in a complementary manner than that of double bonds as can be followed by the trend of the plot in figure 10. For low values of exposure it increases very fast then a sensible reduction in the rate of degradation is observed.

Thus it can be concluded that meanwhile double bonds are preferentially destroyed at the same time molecular species with carbonyl groups are formed [6].

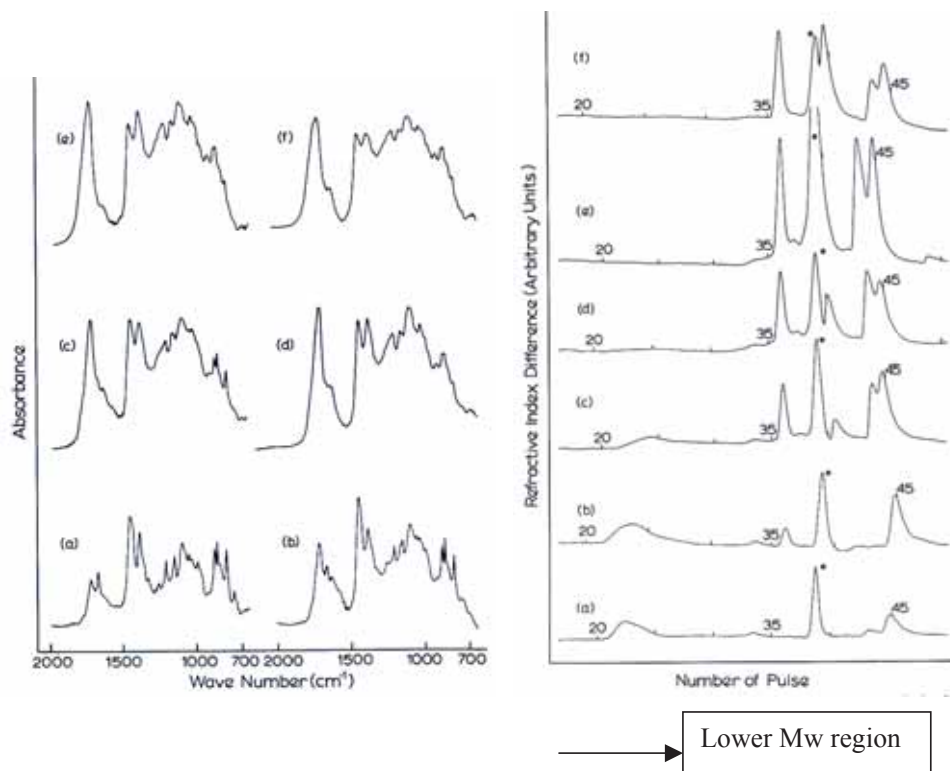


FIGURE 7-Left: Infra-red spectra of samples of *trans*-1,4-polyisoprene single crystals exposed to O₃ at RT: (a) Untreated; (b) exposed for 2 min; (c) 5 min; (d) 36 min, (e) 2h 44min; (f) 5h 38min [6].

FIGURE 8-right: Gel permeation chromatograms of samples of *trans*-1,4-polyisoprene single crystals after exposition to O₃ at RT: (a) Untreated; (b) exposed for 1 min 10sec; (c) 5 min; (d) 18 min; (e) 3h 50min; (f) 15h. The peak labeled with * is an impurity peak serving as reference [6].

--- The strong band observed at 1115cm⁻¹ was accounted for by assuming the production of unstable peroxidic or ozonide structures [7].

The effects of exposure to O₃ attack on the molecular mass of TPI and its distribution, were quantified through GPC measurements (see results in figure 8).

It can be seen that the initial peak at the high molecular weight region of the chromatograms rapidly shifts towards larger elution volume region (lower molecular mass). As the time of attack increases its intensity is reduced and after 36 minutes the peak practically disappears.

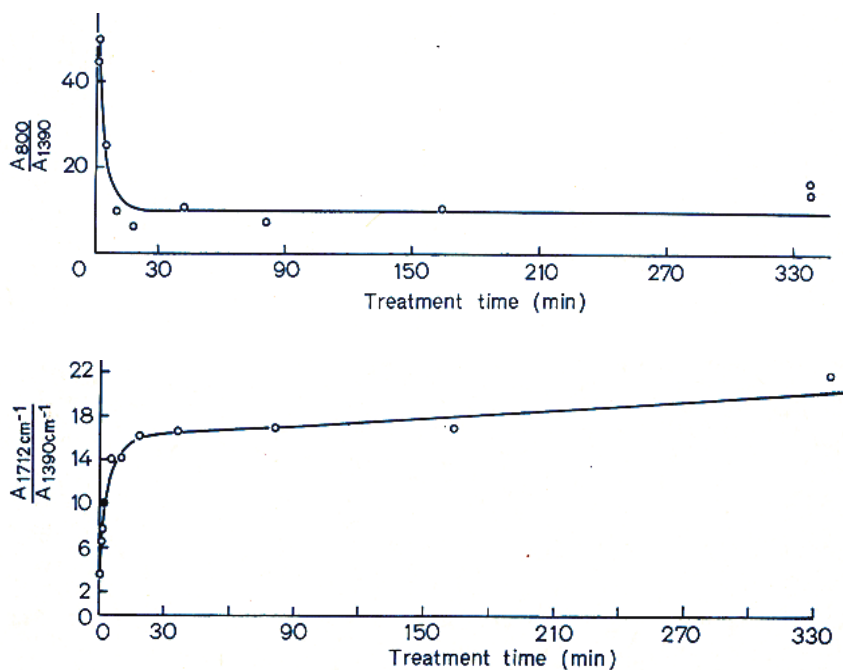
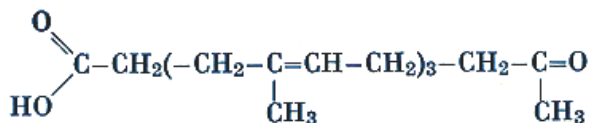


FIGURE 9, top: Intensity of the IR trans double bond peak at 800cm^{-1} normalized with respect to the 1390cm^{-1} band as function of exposition time to O_3 for samples of *trans*-1,4-polyisoprene single crystals [6].

FIGURE 10, bottom: Intensity of the IR carbonyl band at 1717cm^{-1} normalized with respect to the 1390cm^{-1} band as function of exposition time to O_3 for samples of *trans*-1,4-polyisoprene single crystals [6].

Contemporaneously in the chromatograms a series of discrete, and strong in intensity, peaks are observed in the low molecular weight region (larger elution volume). The strong peak found at 3.62 pulses, produced by the degradation suggests that the TPI macromolecules are broken down into a sharply defined fragment length which was identified as a trimer or tetramer with carboxylic and carbonylic termination whose suggested molecular structure is below represented [6].



The observed reduction in the melting temperature of crystals with the exposure time (see figure 11) was accounted for by assuming that the degradation proceeds preferentially from the surface toward the internal part of the crystals thus reducing their thickness (L) and this in agreement with the hereafter relationships

$$\sigma_e = \frac{L\Delta H_{\mu} (T_m^0 - T_m)}{2 T_m^0}$$

that correlates the thickness of crystals (L), melting temperature (T_m), heat of fusion (ΔH_{μ} , cal mol⁻¹ of repeating unit), melting temperature of an infinite thick crystal (T_m^0) and the interfacial free energy associated with the surface the crystal (σ_e) [6].

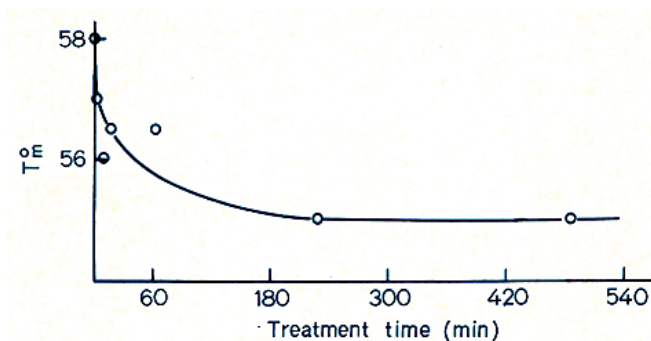


FIGURE 11: melting temperature of *trans*-1,4-polyisoprene single crystals as function of exposure time to O₃ at RT [6].



FIGURE 12: Development of cracking structures produced in natural rubber tubing by the exposure to ozone [8].

In the case of rubber it has been found that chain scission as well as cross linking and side branch formations are implemented by the presence of active hydrogen molecules such as in water, acids and alcohols. The degradation process induced by ozonolysis make the rubber material more brittle: *< cracks form in areas of high stress... As propagation of these cracks increases, new surfaces are opened for degradation to occur >* (see figure 12) [8].

3) Degradation of polyethylene by ozone

Polyethylene reacts with ozone even though, in normal conditions, the rate of the process is relatively low. The mechanism of degradation depicted in figure 13 was suggested by I. C. McNeil [4].

< ..after initial attack by ozone, the oxidation chain can be established and chromophores for absorbtion of UV light are formed > [4].

The possibility to cut polyethylene macromolecules by exposure to ozone was clearly demonstrated by the studies performed by Keller, Martuscelli, Priest and Udagawa on single crystals grown from solution (see micrograph in figure 14) [9,10].

The progress of degradation of polyethylene chains as well as the evolution of the molecular mass distribution was followed by GPC. The trend of the chromatograms, performed on samples exposed to ozone at increasing times, some of them shown in figure 15, leads to the conclusion that essentially the ozone react preferentially with part of chains, with a more irregular or amorphous structure, located at the surfaces of the crystals according to the simplified picture of figure 16 [10].

The distinct peaks developed in the course of the ozone attack (see figure 15) was accounted for by assuming that the peak at the lowest molecular weight (peak-1) corresponds to a chain fragments with a length that is only few angstroms lower that the thickness of the crystals (single chain traverse).

The second peak (peak-2) it is assumed to be related with the length of a double traverse fragment of a chain folded structure of single crystals

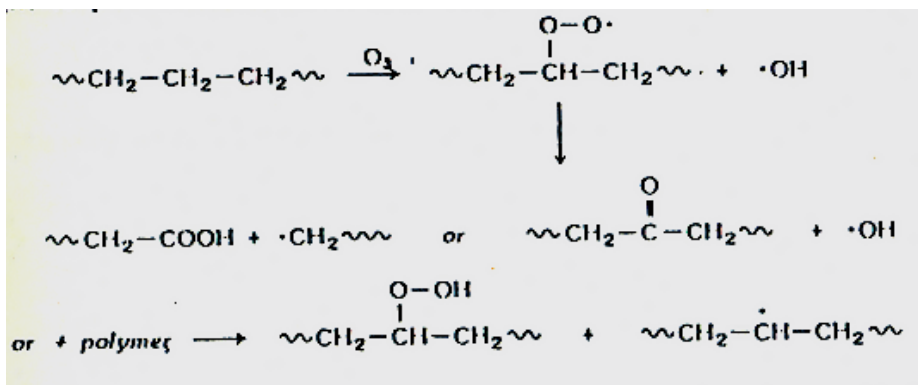


FIGURE 13: Suggested mechanism for the degradation of polyethylene induced by exposure to ozone [4].

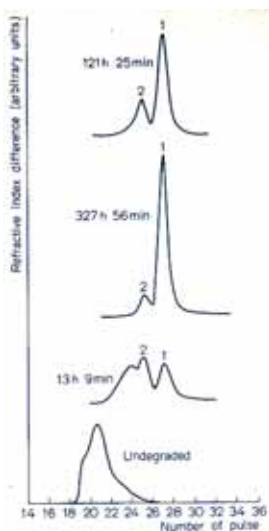
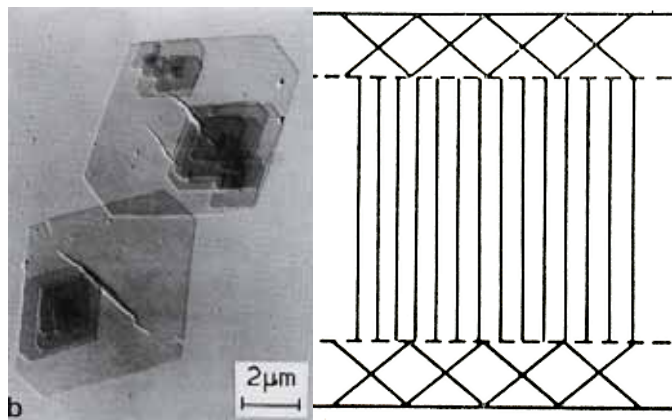


FIGURE 14, top-left: Electron micrograph showing the typical morphology of solution grown single crystal of polyethylene [9].

FIGURE 16, top-right: Schematic representation of single crystal structure of polyethylene grown from solution. The central part, the crystalline core, is bordered by two surface regions with disordered structured part of chains that are preferentially degraded by ozone [10].

FIGURE 15, bottom: Gel permeation chromatograms of ozone-degraded single crystals of polyethylene. Increasing number of pulse corresponds to increasing elution volume, hence to decreasing molecular weight [10].

The characterization of degraded samples by Infra-red spectroscopy (see examples in figure 17) confirmed the capability of ozone to cut the C-C bonds present along the backbone of polyethylene chains [11]. As shown by the evolution of the IR spectra in figure 17, following degradation the intensity of the carbonyl band at 1715cm^{-1} increases in the course of the reaction indicating that the rupture of chains occurring through the formation of fragments containing the carbonyl C=O group [10,11].

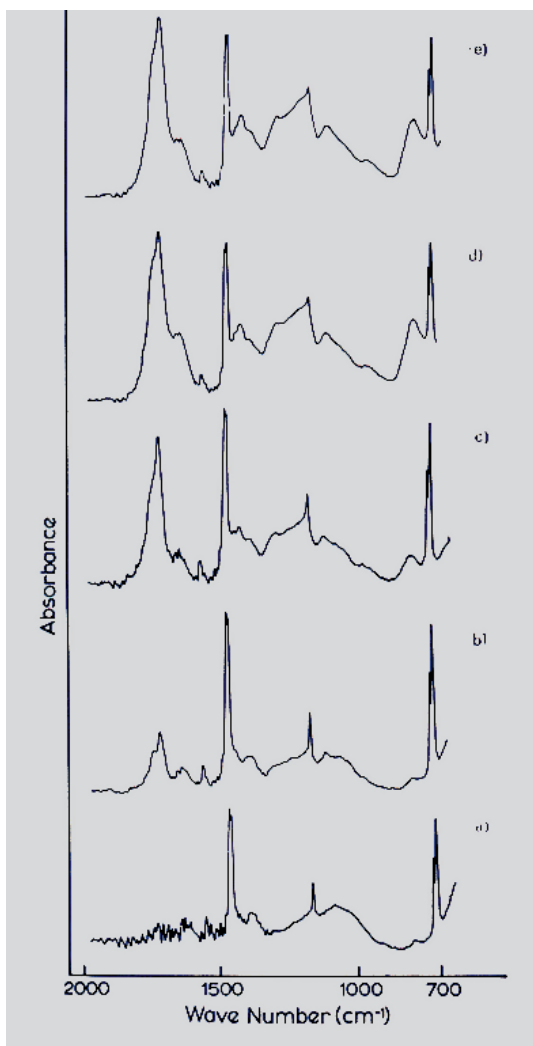


FIGURE 17: Infra-red spectra of short aliphatic chain crystal, grown from solution, degraded with ozone at RT for different time exposure. From bottom to top: (a) untreated; (b) treated for 2hr; (c) 15hr; (d) 99hr (e) 151hr. The figure refers to I_2 terminated chains [11].

4) Degradation of polyethylene and aliphatic chain polymers induced by nitric acid

Keller and Others demonstrated the capability of concentrated nitric acid to degrade polyethylene macromolecules in single crystals grown from diluted solution. The evolution of the reaction, followed by GPC and IR techniques, showed that HNO_3 preferentially cuts intra-chain C-C bonds belonging to disordered part of macromolecules on the surface of the crystals leaving the more compact crystal core practically unaffected. Such behaviour is accounted for by the sequence of GPC chromatograms shown in figure 18 [10].

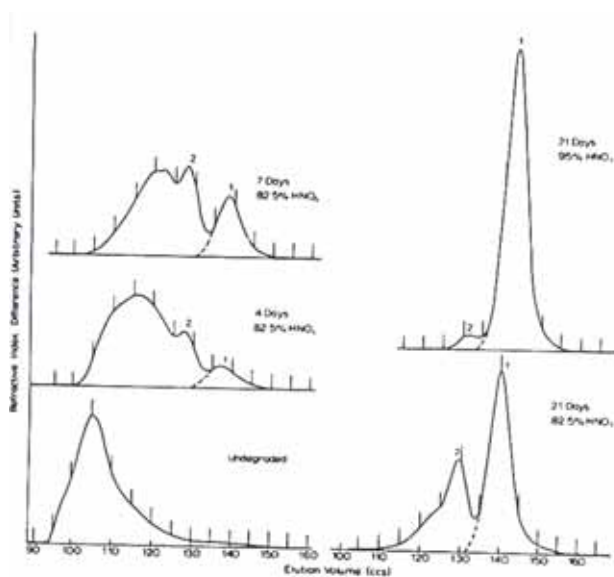


FIGURE 18: GPC chromatograms of HNO_3 -degraded single crystals of polyethylene grown from solution at various stage of treatment time (Increasing volume correspond to decreasing molecular weight). Single and double traverse peaks are marked by 1 and 2 respectively [10].

5) Solvolysis in polyvinylchloride(PVC)

In PVC the C-Cl bonds are easily broken under the action of acid species. The process releases in the environment hydrochloric acid molecules (HCl) which may cause dechlorination of adjacent carbon atoms leading to the formation of intrachain double bonds. Such unsaturated bonds as happen in the case of rubber-like macromolecules can be broken by ozone according to the mechanism of degradation described above [12].

6) Hydrolytic degradation of polymers

Hydrolytic degradation occurs essentially in polymers characterized by the presence along the backbone-chain of functional groups like esters, amides, urethanes and acetals as well as in polysaccharides. In the cases of amides and esters the groups reacting with water give rise to the formation of the parent acid or aldehyde group and the corresponding alcohols or amines. When the functional chemical entities are part of the backbone chain of the polymers then hydrolysis will cause depolymerization followed by release of the hydrolyzed monomers from the polymer mass. In case the hydrolysis-sensitive groups are present as side groups then following hydrolysis no chain cleavage will occur but small molecules will be released in the environment [13].

< Apart from the case of polymers with ester and amide structures in the side groups rather than in the backbone, hydrolysis leads to a rapid loss in the physical properties as a result of cleavage of the chains > [4].

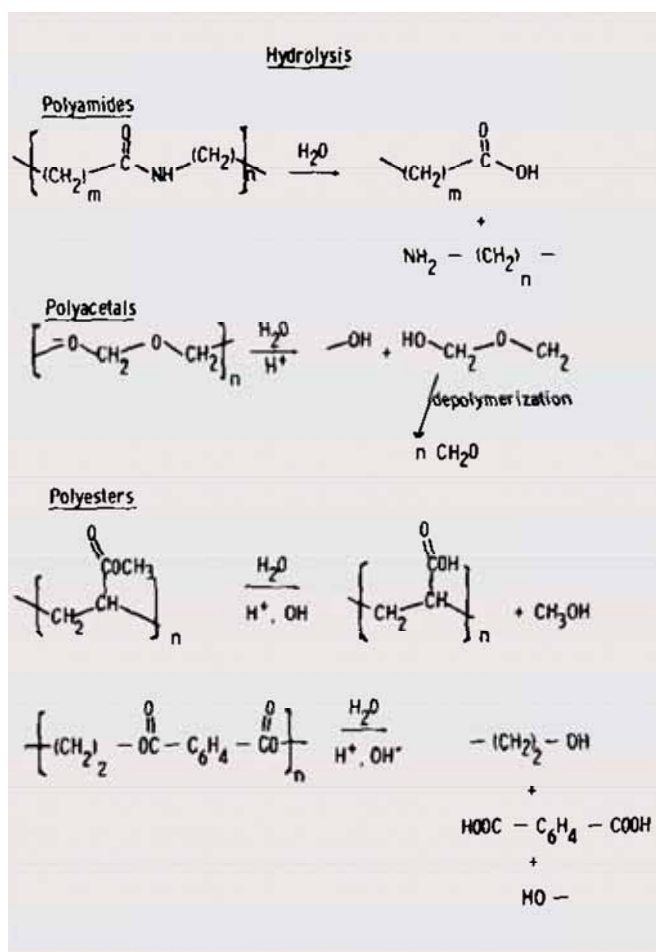


FIGURE 19: Hydrolysis reactions of some common polymers [14].

According to literature data humidity and a $\text{pH} < 7$ generally favour the reactions of hydrolysis of polymers [4].

Examples of reactions of hydrolysis are schematically described, for some common polymers, in figure 19 [14].

In the case of polyesters, especially during processing at high temperature and pressure, hydrolysis may occur also in absence of acids acting as catalysts. As matter of fact in such a case the water molecules are capable to attack the C-O ester link causing the cleavage of the chains.

< The water molecule will then dissociate, with one hydrogen atom forming a carboxylic acid group on the carbon atom with the double bonded oxygen, while the remaining atoms form an alcohol on the other chain end. These reactive products may also cause further degradation of the polymer chain. This chain scission lowers average molecular weight of the polymer, decreasing the number and strength of intermolecular bonds as well as the degree of entanglement. This will increase chain mobility, decreasing strength of the polymer and increasing deformation at low stresses > [12].

The alkaline hydrolysis of cellulose nitrate, the major component of celluloid, is a very important process as it represents one of the main mechanisms of deterioration in artefacts of artistic and historical interest such as archival cinematograph films, based on such type of plastics [14].

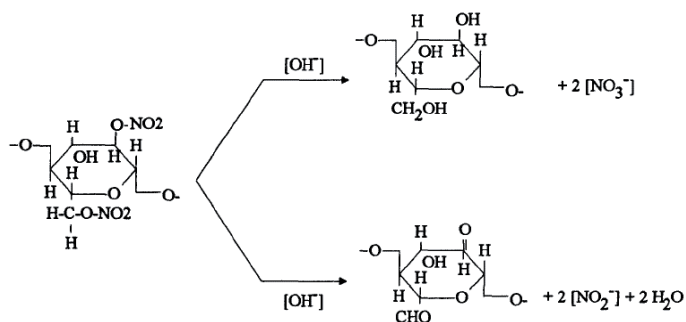


FIGURE 20: The two mechanisms of alkaline hydrolysis of nitro-cellulose the main component of celluloid plastics (see text) [14].

According to Edge and others the alkaline hydrolysis of nitrocellulose may occur through the two mechanisms described in figure 20 [14]. The top mechanism in figure 20 leads, through the hydrolysis of the side ester groups along the chains, to the formation of nitrate. The mechanism depicted at the bottom part of figure 20 produces the oxidation of the cellulose chains and nitrites. [14].

The alkaline degradation of nitrocellulose may be followed by FTIR spectroscopy. As matter of fact, as shown by the trend of spectra taken at different time of treatment with a 2% NaOH water solution in the range 1640 cm^{-1} e 800 cm^{-1} the band at 1280 cm^{-1} associated to the asymmetric stretching of the NO_2 group diminishes with the increase of the hydrolysis time (see figure 21) [15]. Such a behaviour confirms the denitration occurring by alkaline hydrolysis.

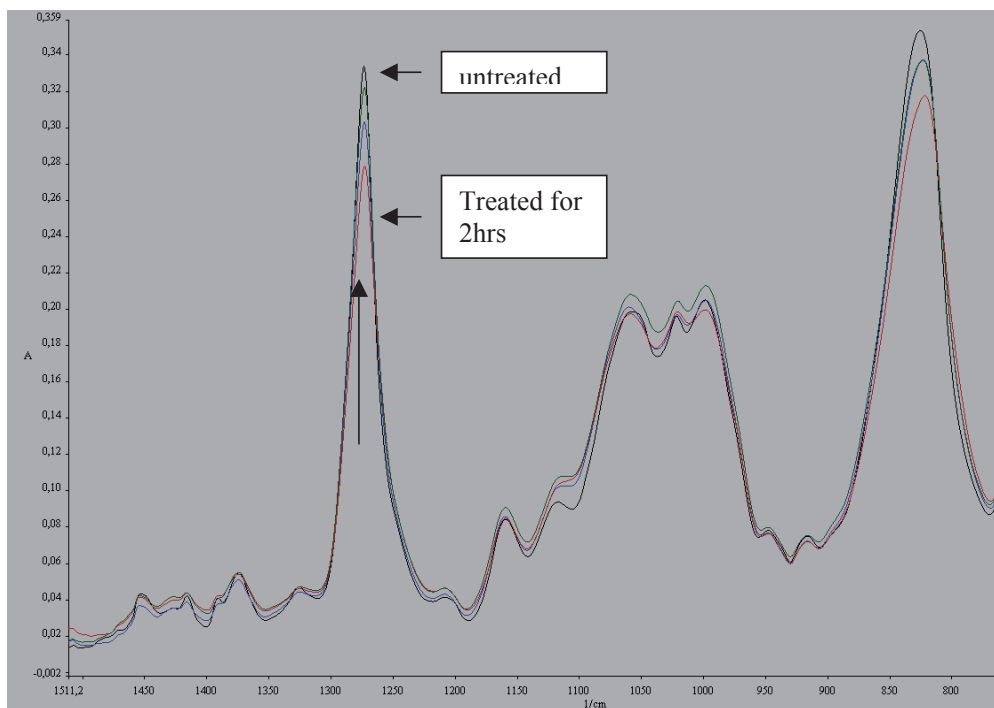


FIGURE 21: FTIR spectra, range $1640 - 800 \text{ cm}^{-1}$, of celluloid taken at different time of treatment with a 2% NaOH water solution. The band at 1280 cm^{-1} associated to the asymmetric stretching of the NO_2 group diminishes with the increase of the hydrolysis time (see arrows) [15].

Another example of base catalysed hydrolysis is that leading to the cleavage of polyesters macromolecules and whose mechanism, depicted in figure 22, is so described in reference [16]:

< The OH comes in to "attack" the carbon atom. Temporarily, five bonds form. Since carbon can only hold four bonds, the oxygen becomes negatively charged. Then, to fix this, the OR's bond breaks apart > [16].

7) Chemical modifications induced on some polymers by various chemical agents

Many organic based polymers undergo chemical modifications following the attack by various kind of reactive molecules.

Two examples are hereafter mentioned:

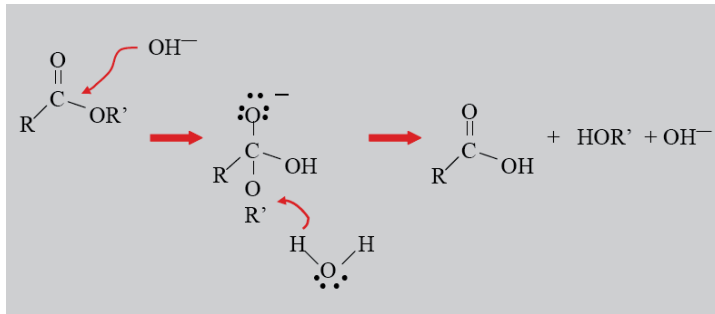


FIGURE 22: Schematic representation of the mechanism of base catalyzed polyester hydrolysis [16].

--- Sulphonation of polystyrene

Sulphuric acid, as described in figure 23, top, easily reacts with polystyrene by forming a sulfonated derivative [17].

---Chlorination of polyethylene

In such a reaction the substitution the H-atoms in adjacent backbone carbon of polyethylene are substituted by Cl atoms (see figure 23, bottom) [17].

The above reported reactions induce in the polymer deep changes in their properties (chemical and physical) that may cause serious problems concerning the conservation of the parent artefacts.

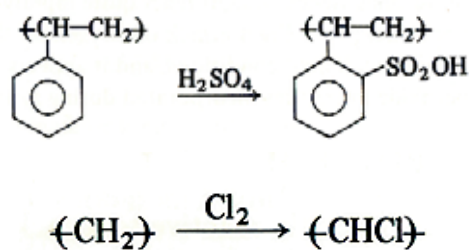


FIGURE 23: Modification of molecular structure of polymers by chemical attacks.
Top, sulphonation of polystyrene.
Bottom, chlorination of polyethylene [17].

REFERENCES

- 1) A. L. Andrady et Al., < *J. Photochem. Photobiol. Sci.* >, **2**, 68 (2003).
- 2) E. Martuscelli, < *Degradazione delle Fibre Naturali e dei Tessuti Antichi* >, PAIDEIA, Editore, Firenze (2006).
- 3) A. L. Andrady et Al., *J. Photochem. Photobiol. Sci.*, **46**, 96 (1998).
- 4) I. C. McNeil, < *Fundamental Aspects of Polymer Degradation* >, in “*Polymers in Conservation*”, Edt. by N. S. Allen, M. Edge, C. V. Horie, Royal Society of Chemistry, pp. 15-32, (1992).
- 5) www.nps.k12.nj.us/.../ChemSite/degredation.h, (2009).
- 6) A. Keller, E. Martuscelli, < *Die Makromolekulare Chemie* >, **151**, 189 (1972).
- 7) A. Keller, E. Martuscelli, < *Die Makromolekulare Chemie* >, **151**, 169 (1972).
- 8) http://en.wikipedia.org/wiki/Polymer_degradation, (2009).
- 9) E. Martuscelli, from personal archive (2009).
- 10) A. Keller, E. Martuscelli. D. J. Priest, Y. Udagawa, < *J. of Polymer Science: Part A-2* >, **9**, 1807 (1971).
- 11) L. D’ilario, A. Keller, E. Martuscelli, < *J. of Polymer Science: Part A-2* >, **10**, 239, (1972).
- 12) < *Chemically Assisted Degradation of Polymers* >, *Wikipedia*, the free encyclopedia, (2009).
- 13) D. L. Allara < *Environmental Health Perspectives* >, **11**, 29, (1975).
- 14) M. Edge, N. S. Allen, M. Hayes, P. N. K. Riley, C. V. Horie, J. Luc-Gardette, < *Eur. Polym. J.* >, **26**, 623, (1990).
- 15) Conclusions of the Project: < *Sviluppo industriale di procedure semplificate per la caratterizzazione chimica non distruttiva e per il recupero di manufatti in plastica: applicazioni nella catalogazione e restauro di beni culturali e nel controllo qualità di prodotti industriali a base di materiali termoindurenti* >, financed by MIUR (n.: Prot. 915 del 30/01/2004 ammesso al finanziamento con D.D. n°2059 del 21dicembre 2007 a valere sui contributi del Dlg. n° 297/99 (D.M 8 agosto 2000 n. 593 art. 9)) by AET- CO.BE.CAM. – CNR-ICTP – UNI SALERNO– PERKIN ELMER (2009).
- 16) www.nps.k12.nj.us/.../ChemSite/degredation.h, (2009).
- 17) C. Hall, < *Polymer Materials* >, the Macmillan Press LTD, London (1981).

SECTION-1

SIXTH-CHAPTER

BIODEGRADATION OF POLYMERS BY MICROORGANISMS

A given material is biodegradable when, through an enzyme-catalyzed degradation process induced by microorganisms (bacterial, fungi, and algae), it is chemically transformed in carbon dioxide, water, and new biomasses.

A polymer is considered to be biodegradable if it may be assimilated by naturally occurring microorganisms which are capable to induce a process of fragmentation with loss of mechanical properties or chemical modifications [1,2].

According to the schemes of reaction below reported biodegradation can occur in two different environments: ***aerobic*** (when oxygen is present) and ***anaerobic*** (in absence of oxygen) [1].

Aerobic conditions



Anaerobic conditions



< Complete (or total) biodegradation (or Mineralizations) occurs when no residue remains, i.e., when the original product is completely converted into gaseous products and salts > [1].

Synthetic high molecular weights homopolymers such as polyethylene, polypropylene, polyvinyl chloride, polystyrene, etc., with only carbon atoms along the backbone chains and with no hydrolysable functional groups are generally bio-resistant (this is the case represented in figure 1-top). Nevertheless it can be observed that if these polymers are degraded, following photo/thermo-oxidation or mechanical stresses, to molecular fragments sufficiently short with a large number of their chain ends accessible at the surface, where also functional groups capable to render the substrate less hydrophobic have been formed, then, under suitable conditions, such products may be assimilated by specific microorganisms (this could be the case shown in figure 1-bottom) [3,4,5,6]. Thus it is interesting to point out that in principle it can be observed that polymers, intrinsically bioresistents, when molecularly transformed, functionalized and deeply degraded by some other factors (for example light, heat, oxygen etc.) may become sensitive to biodegradation.

Natural (for example starch and proteins), semi synthetic (cellulose nitrate and cellulose acetate) or synthetic polymers characterized by the presence in their structural units of hydrolysable functional groups, such as esters, amides and urethanes, are, under favourable conditions, biodegradable. Such a tendency is further implemented in the case of high flexible chain backbone as this facilitates the binding of the specific catalyzing enzymes to the polymer active sites [3,4,5,6].

The molecular structures of some biodegradable aliphatic polyesters, namely polycaprolactone (PCL) and hydroxybutyrate/hydroxyvalerate copolymers P(HB-co-HV) (the later, commercialised as “*Biopol*” by ICI, being produced directly by bacterial fermentation) are shown in figure 2.



FIGURE 1: Films of linear low density polyethylene.
Top, practically undegraded.
Bottom, fragmented following severe molecular and mechanical degradation, thus suitable to be biodegraded by microorganisms.

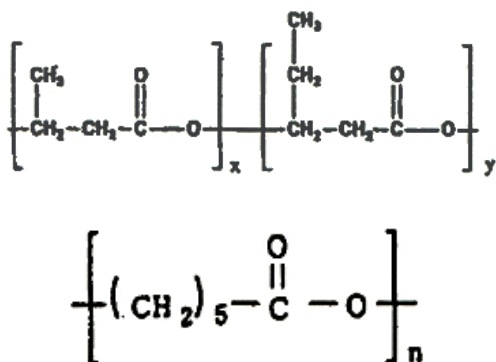


FIGURE 2: Molecular structure of some biodegradable aliphatic polyesters.
Top, hydroxybutyrate/hydroxyvalerate copolymers P(HB-co-HV).
Bottom, Polycaprolactone (PCL).

Data of literature have shown that thermoplastic items in PCL buried in soil are almost completely degraded after 12 months being converted into microbial biomass, CO₂ and H₂O, by some specific microorganisms capable to use the polymer as a growth substance [7].

The biodegradability of alifatic polyesters is also facilitated by the fact that under relatively mild conditions they hydrolyse to yield molecular fragments with acid or alcohol end groups.

Thus the bio-assimilation of the above polymers is the consequence of a synergistic interaction between hydrolysis and biodegradation [8].

The aerobic solid-state biodegradation represents the main degradation event, involving microorganisms, that conservatorists have to take care for an appropriate conservation of plastics artefacts.

The process is based essentially on the following steps:

1) Chain cleavage, depolymerization and plastic fragmentation.

< During this phase the contact area between enzyme and substrate increases. Then, decomposition of the macromolecules into shorter chains takes place. The enzymes involved in this step are either endo-enzymes (random cleavage) or exoenzymes (sequential cleavage on the terminal monomer units in the main chain) > [1].

2) Mineralization [1].

The enzymes active as catalysts are classified according to their mechanisms of action as: *hydrolases, esterases, isomerases, reductases, lyases, and ligases* [9].

Polymer biodegradation mainly occur when enzymes capable to catalyse biological hydrolysis and biological oxidation are available.

The enzymes, called *depolymerases*, involved in the biological hydrolysis are effective in determine the rupture of several kind of bonds: glycosidics, peptides and esters.

It has been widely demonstrated that biological hydrolysis and biological oxidation occur preferentially in the amorphous less ordered regions of the polymer materials.

The naturally occurring bioassimilation mechanisms of polymers, occurring on already pre-degraded polymers due to peroxidation and hydrolysis, is schematically represented in figure 3.

Such a complex mechanism in reference [3] is accounted for as follows:

< microorganisms colonizing a substrate form a biofilm, consisting of bacteria and fungi in a highly hydrated (85-98% water) matrix of extracellular polymers. Both hydrolysis and oxidation of the substrate can be mediated by the biofilm, by release of extracellular enzymes or free radicals. Fungi in particular can spread rapidly by secreting enzymes and free radicals... ..

Cell enzymes,produced by many bacteria, continue peroxidation by reducing ground-state oxygen to the free radical superoxide (O₂⁻). When protonated, this species is converted to the much more reactive peroxy radical and hydrogen peroxide, which can be reduced by transition metal ions in the polymer to give the highly reactive hydroxyl radical. OH radicals initiate further peroxidation leading to continued biodegradation and ultimate bioassimilation to biomass and CO₂ as long as environmental oxygen and cell nutrients are available. Thus, the bio-assimilation of degraded polyolefins is a synergistic oxo-biodegradation (Figure 3). In that sense it is totally analogous to the two-stage, hydro-biodegradation, by which linear polyesters are microbially assimilated > [3].

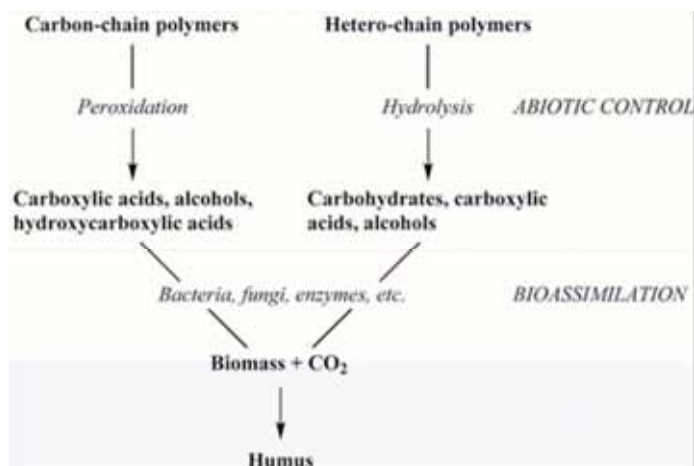


FIGURE 3: The bio-assimilation of partially degraded carbon chain or hetero chain polymers is a synergistic process of oxo-biodegradation (see text) [3].

In agreement with above statements on the surface of pre-degraded PE film incubated with cultures of a bacterium (*Rhodococcus rhodochrous*) or a fungus (*Cladosporium cladosporoides*) the growth of microorganisms together with clear symptoms of bioerosion of the peroxidised PE were observed (see electron scanning microscopy micrograph in figure 4) [3,10].

The further finding that on the surface of the polymer film < ... proteins and polysaccharides, associated with the growth of microorganisms at the expense of the polymer oxidation products, are both formed > represented a confirmation of the above assumed bioassimilation mechanism [3].

It is interesting to point out that after the < removal of the microorganisms, the surface was pitted, eroded and physically weak > [3].

J. M. Cangemi and others demonstrated with their studies that the following microorganisms:

- *Aspergillus sp* (Fungi) and,
- *Chryseobacterium meningosepticum*, (Bacteria,)

are capable to attack polyurethane foams (PU-foams) derived from castor oil, a natural tri-functional polyol polyester whose molecular structure is represented in figure 5 [11].

First evidence of biodegradation were attained by scanning electron microscopy (SEM) of the treated surfaces of PU-foams.

As matter of fact from the examination of SEM micrographs of the sample in contact with the *Aspergillus sp* it was possible to note the presence of small erosion areas on the cells' together with whitish regions and greater erosion regions, similar to webs. Such patterns were attributed to biodegradation (see figure 6) [11].

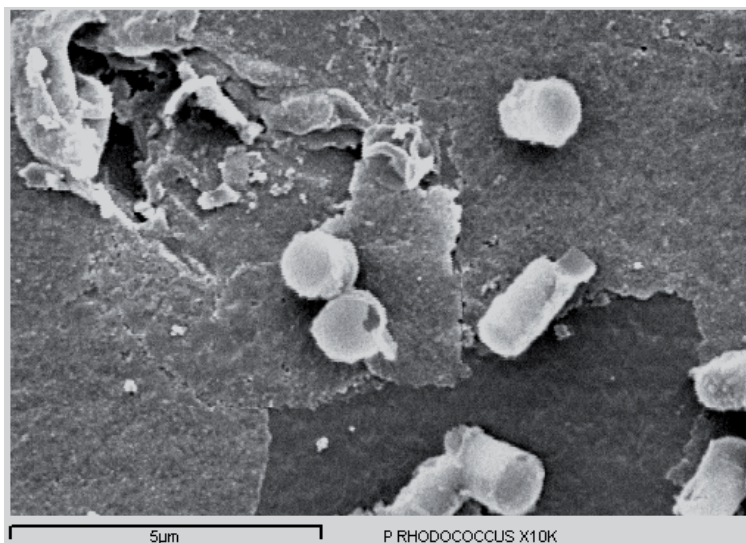


FIGURE 4: Bioerosion of peroxidised PE films and the growth of *Rhodococcus rhodochrous* bacterium observed by scanning electron microscopy after 1 month (see text) [3,10].

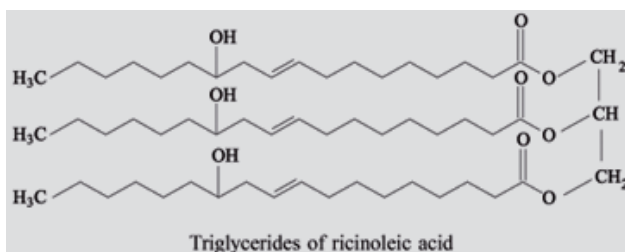


FIGURE 5: Molecular structure of castor oil, a natural tri-functional polyol polyester used in the production of polyurethane [11].

The fact that biodegradation occurred was demonstrated by comparing the FTIR-ATR (attenuated total reflectance mode) spectra of the samples of PU-foam assumed as control with those of PU-foam kept in contact with the various microorganisms (see figure 7) [11]. From such a comparison it emerged that:

< the modification of greatest interest is the band located at 1042 cm^{-1} , which diminished in intensity after the attack, indicating a process of biodegradation and a possible change in the structure of the polymeric material. In this region of the infrared spectrum, the so-called ester C-O stretching vibrations are found; whose occurrence shows the coherence of the results, considering that this mechanism is the same as utilized in the degradation of fats > [11].

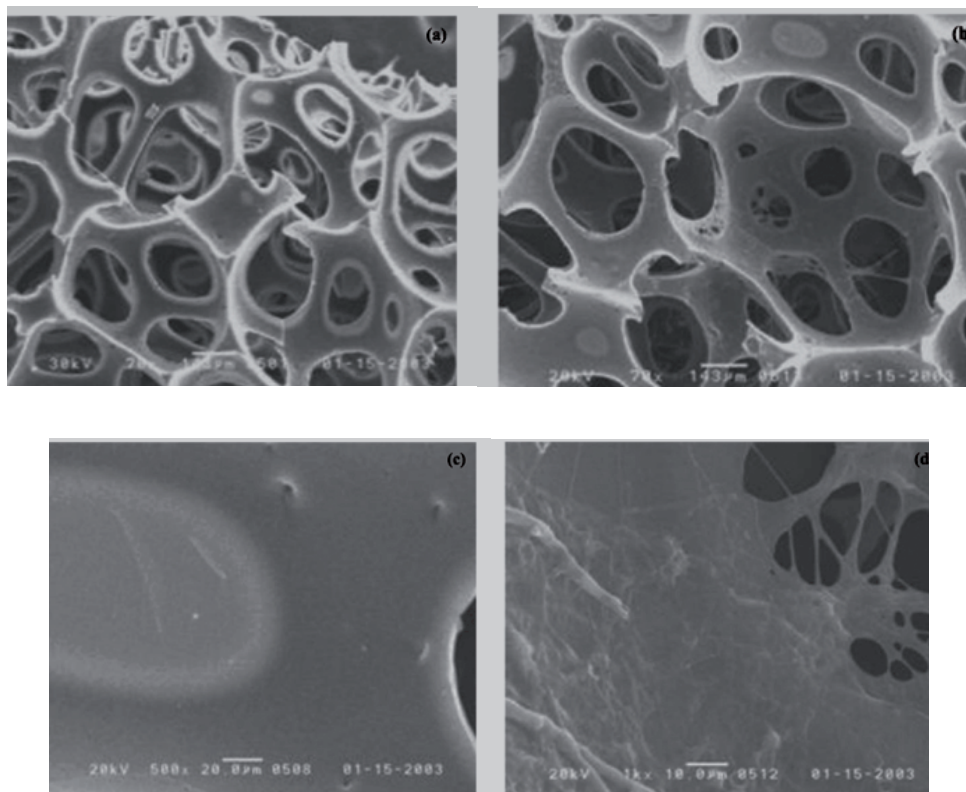


FIGURE 6: Electron scanning micrographs of castor oil-based polyurethane foams.

Top, left: Reference sample, only kept in a media without microorganisms (no biological attack).

Top, right: Sample biodegraded by the fungi: *Aspergillus sp.*

Small erosion areas on the cells' walls are clearly visible suggesting that the biodegradation occurred.

Bottom left and right: Samples in contact with microorganisms showing whitish regions (left side) and greater erosion regions, similar to webs (on the right side) both clear symptoms of biodegradation [11].

The finding that the intensity of the bands of the isocyanate (at 2230 cm^{-1}) and of the urethane groups around 1700 cm^{-1} and 1500 cm^{-1} , related to the stretches of C=O and N-H respectively are not influenced by the presence of microorganisms strongly support the idea that in such PU-foam and under the conditions used biodegradation occurs preferentially on of the ester links of PU macromolecules [11].

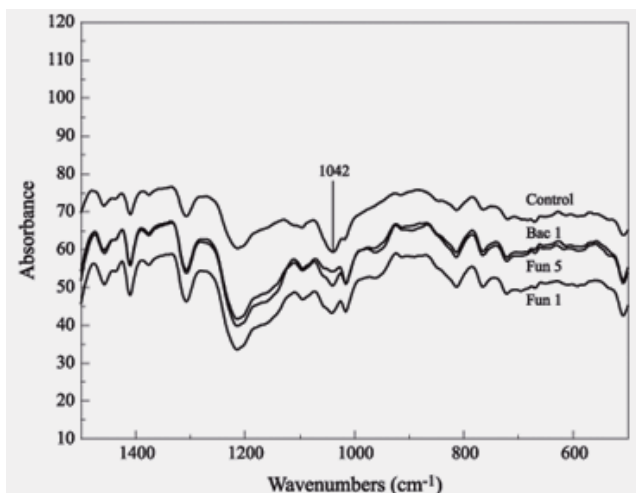


FIGURE 7: Comparison of FTIR-ATR spectra (range 500-1500 cm^{-1}) for samples of castor oil-based polyurethane foams used as control and samples subjected to microorganisms attack (see the text) [11].

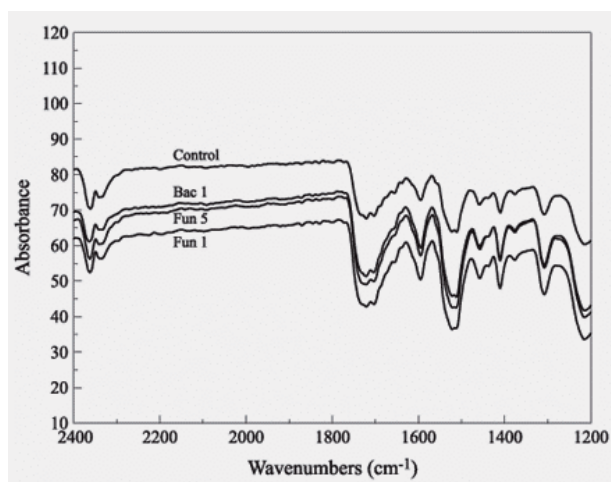


FIGURE 8: Comparison of FTIR-ATR spectra (range 1200-2400 cm^{-1}) for samples of castor oil-based polyurethane foams used as control and samples subjected to microorganisms attack.

The bands of the isocyanate group at 2230 cm^{-1} and of the urethane around 1700 cm^{-1} and 1500 cm^{-1} , related to the stretches C=O e N-H, are visible (see text) [11].

Of the two types of PU namely polyester polyurethanes and polyether polyurethanes the former appear to be less bio-resist.

The electron micrograph reported in figure 9 clearly demonstrates how natural fibrous proteins as keratin wool fibres are naturally biodegraded following the attack of fungi agents as the *Aspergillus flavus* [12].

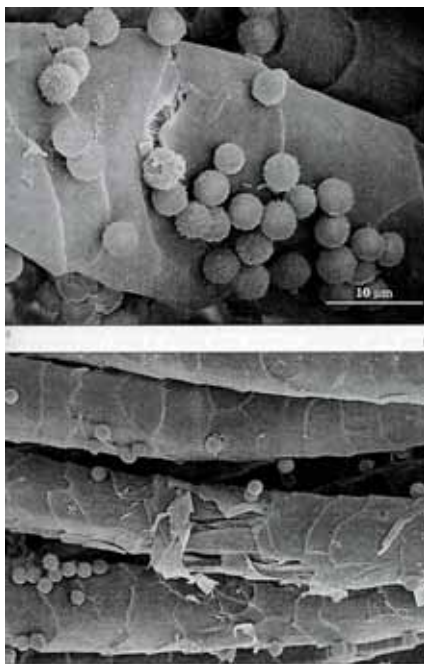


FIGURA 9: Electron scanning micrographs showing wool fibres biodegraded following the attack of the fungus *Aspergillus flavus* [12].

Generally the percentage of biodegradability, for a given polymer-microorganism system, may be obtained by properly measuring the percentage of plastic that is converted to CO₂ by using appropriate standardized tests.

An example of a generic biodegradation test-curve is reported in figure 10-bottom [7].

The amount of CO₂ produced with the increase of the time compares with the evolution of disintegration and fragmentation of the polymer sample as it appears in the sequence of photos reproduced in figure 10-centre [7].

The corresponding growth of microorganisms on the surface of a degradable polymer is documented through the electron micrograph in figure 10-top [12,13].

The molecular structure of commercial biodegradable polymers, including the already mentioned PCL and P(HB-co-HV), belonging to the family of polyesters are represented in figure 11.

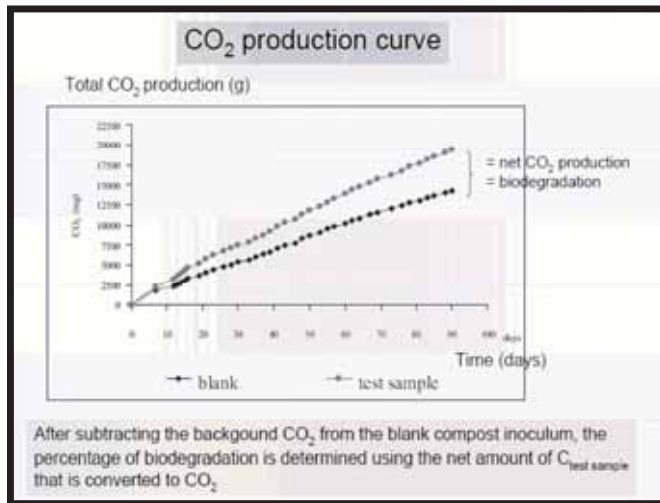
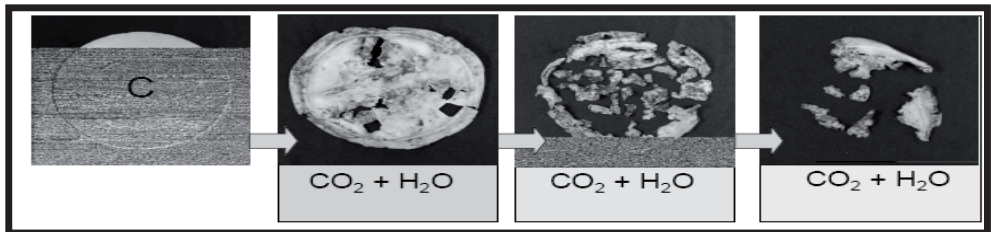
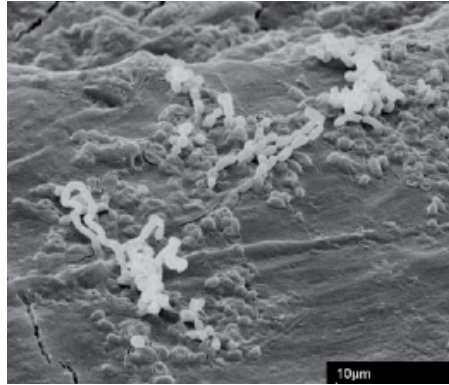


FIGURE 10: Example of test to assess the degree of biodegradability of a polymer.
Top- Growth of microorganisms on degradable polymer film surface [12].
Centre- The evolution of mechanical disintegration in polymer sample caused by bio-attack.
Bottom- CO₂ production curve, see details in the figure and in the text [7].

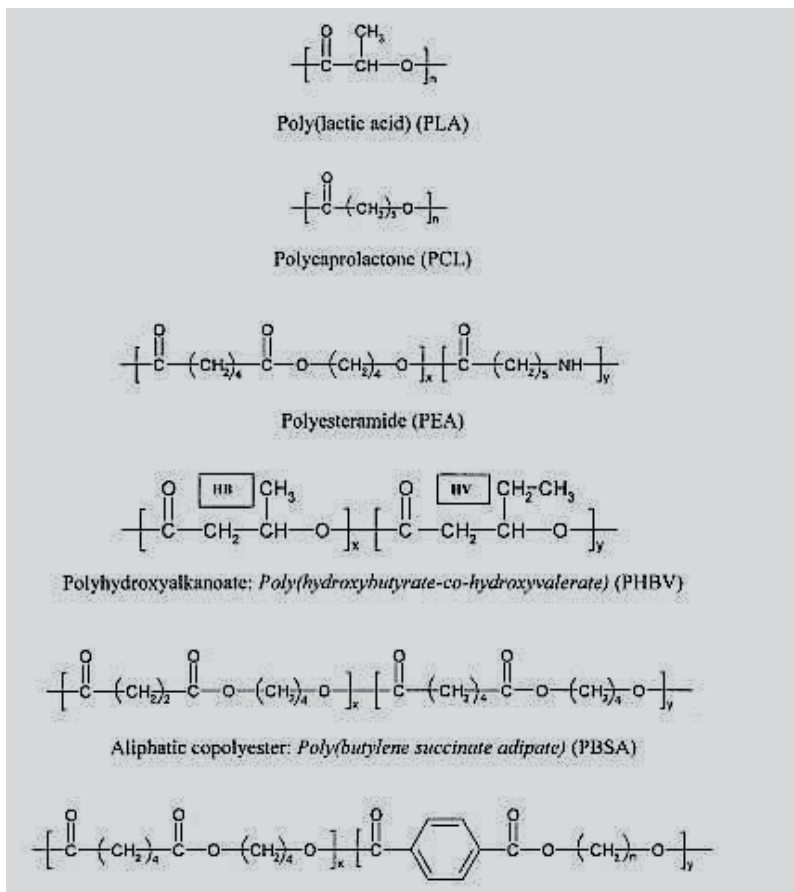


FIGURE 11: Molecular structure of biodegradable polyesters

It is well known that many modern paints are formulated using synthetic polymers as binding media (i.e., acrylics, alkyds and polyvinyl acetates, see examples in table 1) [14]. The knowledge of the attitude showed by those formulations against biodegradation is of great relevance in order to predict their environmental durability.

The resistance against fungal degradation of different types of commercial synthetic polymer resins used in the modern paint industry was studied by F. Cappitelli and others by using vibrational spectroscopic techniques (FTIR, FTIR-Photoacoustic (FTIR-PAS) and Raman) [14]. The following kind of fungi were used for the biodegradability tests: *Aspergillus niger*, *Gliocladium virens*, *Chaetomium globosum*, *Aureobasidium pullulans* and the *Penicillium pinophilum* [14].

From the quantification of the degree of fungal growth, evaluated at different times, as shown by the data in table 2, it emerges that acrylic resins are generally bio-resistant while alkyds seem to be more susceptible to fungal attacks. As far as polyvinylacetate resins are concerned it can be seen that their biodegradation behaviour depends on the origin but never reach the highest value of 4 as in the case of alkyds resins.

TABLE 1: List of commercial formulations used as painting media. In the table together with the name of the products, the chemical class and the composition are also indicated [14].

Product	Chemical class	Composition
Acrylic Emulsion D 498-M	Acrylic resin	methyl methacrylate/butyl acrylate 55/45
Synolac 28w	Alkyd resin	linoleic rich + pentaerythritol
Synolac 60w	Alkyd resin	linoleic rich + pentaerythritol
A2/1028	Alkyd resin	phthalic anhydride + glycerol + linseed oil
Crodakyd 444w	Alkyd resin	phthalic anhydride + soybean oil + glycerol
Crodakyd 826w	Alkyd resin	phthalic anhydride + pentaerythritol + linseed oil
Crodakyd 850w	Alkyd resin	phthalic anhydride + soybean oil + pentaerythritol
Plastyrol s99x	Modified alkyd resin	phthalic anhydride + drying oil + styrene + glycerol
Plastyrol t35w	Modified alkyd resin	phthalic anhydride + linseed oil + vinyl toluene + glycerol
Sobral 1241 ML 70	Alkyd resin	linoleic rich + pentaerythritol
Texicryl 13-031	Modified acrylic resin	styrene-acrylic copolymer
PVA		poly(vinyl acetate)
Vilkyd 211	Alkyd resin	linoleic rich + phthalic anhydride + pentaerythritol
Vilkyd 270	Alkyd resin	linoleic rich + phthalic anhydride + pentaerythritol
Emulsion A	Poly(vinyl acetate)	vinyl acetate + VeoVa 10 (Shell trade name for the vinyl ester of versaric acid)
Emulsion B	Poly(vinyl acetate)	vinyl acetate + VeoVa 10 + alpha olefin
Emulsion C	Modified poly(vinyl acetate)	vinyl acetate + vinyl chloride + ethylene
Emulsion D	Modified poly(vinyl acetate)	vinyl acetate + vinyl chloride + ethylene + 2-ethylhexylacrylate
Emulsion E	Modified poly(vinyl acetate)	vinyl acetate + ethylene + 2-ethyl hexylacrylate
Emulsion F	Acrylic resin	butyl acrylate + methyl methacrylate
Emulsion G	Modified acrylic resin	butyl acrylate + styrene + acrylic acid

The evidence of fungal growth on the surface of an alkyd based resin (Crodakyd 444w, Croda Resins), growth degree=4, is documented through the optical micrograph shown in figure 12 [14]. Evidence of biodegradation can be obtained by comparing the FTIR-PAS spectra of untreated and treated resins in the case of samples showing clear signs of surface fungal growth (see as example the the FTIR-PAS spectra of the stearyl methacrylate resin (high value of the degree of fungal growth, see table 2) reported in figure 13) [14]. The spectrum (b) in figure 13 reveals the presence of intense bands that are not visible in that of the starting untreated resin (spectrum (a) in figure 13).

< Namely a strong and broad absorbtion from 3700 to 2000 cm^{-1} assignable to the OH and NH stretching with hydrogen bond, the peak at 1655 and 1548 cm^{-1} characteristic of amide, a broad band centred on 630 cm^{-1} due presumably to the deformation of NH hydrogen bond. The FTIR-PAS additional peaks were due to peptidic bonds.....and these absorbancies are not caused by degradation products, but to the presence of the fungi and fungal products > [14].

TABLE 2: Degree of fungal growth evaluated at different time, 14 and 28 days (0= no growth; 4 = highest growth) [14].

Type of resin	Resin class	14 d	28 d
Sinolac 28w (Cray Valley)	alkyd	2	3
Sinolac 60w (Cray Valley)	alkyd	2	3
A2/1028 (Croda Resins)	alkyd	3	3
Crodakyd 444w (Croda Resins)	alkyd	3	3
Crodakyd 826w (Croda Resins)	alkyd	1	3
Crodakyd 850 W (Croda Resins)	alkyd	3	3
Plastirol S 99 X (Croda Resins)	alkyd	3	3
Plastirol T 35 W (Croda Resins)	alkyd	3	3
Vilkyd 270 (Spectrum Oil Colours)	alkyd	2	3
Vilkyd 211 (Spectrum Oil Colours)	alkyd	3	3
Sobral 1241 ML (Scott Bader)	alkyd	3	4
PVA (Spectrum Oil Colours)	poly(vinyl acetate)	0	2
Emulsion A (Vinamul)	poly(vinyl acetate)	0	2
Emulsion B (Vinamul)	poly(vinyl acetate)	0	0
Emulsion C (Vinamul)	poly(vinyl acetate)	2	3
Emulsion D (Vinamul)	vinyl acetate-acrylic	2	3
Emulsion E (Vinamul)	vinyl acetate-acrylic	0	2
Emulsion F (Vinamul)	acrylic	0	0
Emulsion G (Vinamul)	acrylic	0	2
methyl methacrylate/butyl acrylate 90/10	acrylic	0	0
ethyl methacrylate/methyl acrylate 70/30	acrylic	0	0
ethyl methacrylate/methyl acrylate/TFEMA	acrylic	0	0
butyl methacrylate/ethyl acrylate/TFEMA	acrylic	0	0
methyl methacrylate/ethyl acrylate 50/50	acrylic	0	0
methyl methacrylate/ethyl acrylate 25/75	acrylic	0	0
<i>tert</i> -butyl methacrylate	acrylic	0	0
Texicril 13031 (Scott Bader)	acrylic	0	0
Acrylic Emulsion D 498-M (Lascaux)	acrylic	2	2
stearyl methacrylate	acrylic	3	4

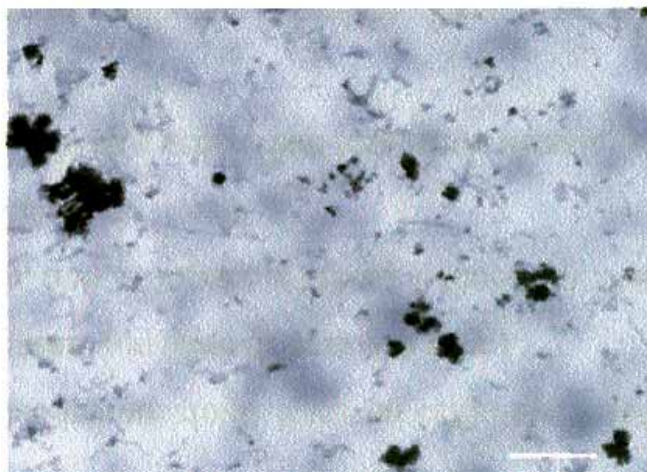


FIGURE 12: Optical micrograph showing fungal growth on the surface of a film of a commercial alkyd resin (Crodakyd 444w, Croda Resin) used as binding in paint media (growth degree =4) [14].

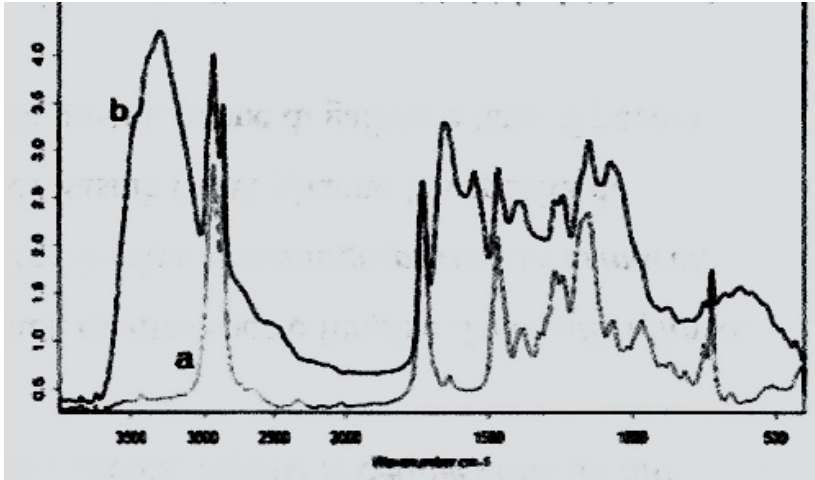


FIGURE 13: Photoacoustic-FTIR spectra of styrylmethacrylate resin: (a) untreated; (b) after 28 days from fungal inoculum [14].

The above observation led the Author to underline the effectiveness of FTIR-PAS technique in assessing the biodegradation degree of polymers following the action of specific fungi.

On the contrary, at least under the conditions investigated, FTIR and Raman spectroscopy were not sufficiently sensitive to detect modifications induced by fungal attack and this even in the case of heavily observed fungal growth on the surface of the samples [14].

In summary from the study above cited was possible to conclude that generally *< the order of binding media susceptibility to fungal attack was acrylics < polyvinylacetates < alkyds >* [14].

Some general conclusive considerations about biodegradation of polymers are hereafter summarized [14-19].

1) Biological degradation of synthetic polymers occurs when some heterotrophic microorganisms are specifically capable of utilize the material as carbon and energy source or in co-metabolism.

2) Microorganisms have the possibility to colonize intrinsically biodegradable polymers only if they are capable to release or secrete specific enzymes that by acting as catalysts make possible the bioassimilation process that leads to chain cleavage and mechanical disintegration of polymers.

< The most versatile microbial strains involved in polymer degradation are Pseudomonas sp., actinomycetes and mycetes such as Aspergillus, Penicillium and Aureobasidium sp.. Enzymes involved in degradationcan be either substrate inducible or constitutive > [14].

3) Synthetic polymers, non containing in their structural units functional reactive groups (esters, amides, urethanes, etc.), usually are bioresistent.

4) Biodegradation is strongly affected by both molecular mass and structure of polymers. It has been found that very low molecular weight carbon based homo polymers such as polyethylene may be susceptible to biodegradation while chain branching generally inhibits biodegradation.

5) The optimum conditions of the bio-attack depend, for a given polymer, by the nature of the

microorganisms. Fungi are more active in presence of oxygen, at values of pH between 4.5-5 and at a temperature of $\approx 35^{\circ}\text{C}$. Actinomycetes and bacteria seem to be more effective at less acid conditions (pH 5-7) and at higher temperature ($\approx 60^{\circ}\text{C}$).

6) Whatever the polymer substrate is, the biodegradation is a surface erosion mechanism. Thus, the area/volume ratio must be maximum.

7) Samples in powder are more easily degraded.

8) The presence as additives or impurities of natural biodegradable substances such as starch and proteins etc., may improve the biodegradability of a normally bio resistant polymer.

9) The introduction, by chemical modification, of reactive and functional groups along the chains may determine in some polymers bio-sensitivity (see the case of conversion of cellulose in nitrocellulose and cellulose acetate and the insertion of hydrolysable functional groups such as esters, amides and urethanes in the backbone chains).

10) In the case of polymers containing large amount of plasticisers, as in PVC, it may happen that microorganism attack first the additives, then some of the degradation products, capable to induce degradation on polymer macromolecules, may indirectly favour also biodegradation processes.

The bio-assimilation of additives may be cause of cracking and mechanical deterioration of the related items.

REFERENCES

- 1) S. Grima, V. Bellon-Maurel, P. Feuilloley, F. Silvestre, < *Journal of Polymers and the Environment* >, **8**, 183 (2000).
- 2) F. Cappitelli, E. Zanardini, C. Sorlini, < *Macromol. Biosci.* >, **4**, 399 (2004).
- 3) N. C Billingham¹, E. Chiellini, A. Corti, R. Baciú, D. M. Wiles, < *Environmentally Degradable Plastics Based On Oxo-Biodegradation Of Conventional Polyolefins* >, PDF (2009).
- 4) J.E. Guillet, in < *Degradable Polymers, Principles and Applications* >, G. Scott, Ed. Kluwer Academic, Dordrecht, 2nd Ed. (2002).
- 5) G. Scott, < *Polymers in the Environment* >, RSC Paperbacks Royal Society of Chemistry, London, (1999).
- 6) G. Scott, Ed., < *Degradable Polymers, Principles and Applications* >, Kluwer Academic, Dordrecht, 2nd Ed. (2002).
- 7) Puan Norhayati Abdullah, Lecture Week 5, < *Biodegradation of Plastics, Bioremediation, Biodegradation* >, PDF (2009).
- 8) T.U. Gerngross, S. Slater, < *Scientific American* >, **25**, August (2000).
- 9) G. Durand and P. Monsan, < *Les enzymes. Productions et utilisations industrielles* >, Bordas, Paris (1982).
- 10) S. Bonhomme, A. Cuer, A. M. Delort, J. Lemaire, M. Sancelme, G. Scott, < *Polymer Deg. Stab.* > (2003).
- 11) J. M. Cangemi, S. Claro Neto, G. O. Chierice, A. M. dos Santos, < *Polímeros* >, **v.16, n.2**, São Carlos abr./jun., (2006).
www.scielo.br/scielo.php?script=sci_arttext..(2009).
- 12) E. Martuscelli, < *Degradazione delle fibre naturali e dei tessuti antichi* >, PAIDEIA, Firenze (2006).
- 13) M. Stephens, july-2005,
http://degradableplasticbag.files.wordpress.com/2009/03/pyxis_biodegradation_300705_page_7.jpg, (2009).
- 14) F. Cappitelli, and others, < *Macromol. Biosci.* >, **5**, 49 (2005).
- 15) I. C. McNeil, < *Fundamental Aspects of Polymer Degradation* >, in “*Polymers in Conservation*”, Edt. by N. S. Allen, M. Edge, C. V. Horie, Royal Society of Chemistry, pp. 15-32 (1992).
- 16) www.nps.k12.nj.us/.../ChemSite/degredation.h, (2009).
- 17) Y. Shashoua, < *Conservation of Plastics* >, Elsevier, Amsterdam (2008).
- 18) < *Plastics, Collecting and Conserving* >, Edited by A. Quye, C. Williamson, NMS publishing limited (1999).
- 19) M. Funabashi, F. Ninomiya, M. Kunioka, < *Journal of Polymers and the Environment* >, **15**, Number 4 / October (2007).

SECTION-1

SEVENTH-CHAPTER

GENERAL CONSIDERATIONS CONCERNING THE DEGRADATION OF PLASTICS AND POSSIBLE REMEDIATION MEASURES

As described in the previous chapters the main interacting processes leading to the degradation of polymers and plastic artefacts may be summarized as follows:

- Photo-oxidation by natural daylight and oxygen;
- Thermo-oxidation by heat and oxygen;
- Oxidation by chemical additives;
- Degradation induced by mechanical stresses;
- Biodegradation by microorganisms [1].

Quite often the various factors of degradation are concomitants and thus the observed macroscopic effects are the resultant of their synergic action on the polymer based materials. In general, regarding the component macromolecules, the degradation, through complicated chemical reactive mechanisms, produces at molecular level the following chemical modifications (see figure 1) [2].

- Random rupture of the backbone chain ;
- Cross-links ;
- Modification of side groups;
- Elimination of side groups;
- Cyclation of side groups [2,3].

The degradation reactions leading to the cleavage of chemical bonds present along the macromolecular backbones are, in general, the most effective in determining the deterioration of the properties of the polymer plastics component.

In the case of polymers it is well known that chain rupture processes may occur through the four different mechanisms hereafter listed [2,3].

- Thermolysis;
- Oxidation;
- Hydrolysis;
- Radiolysis.

The chemistry of the above reactions is schematically described in figure 2 [2,3].

In the case of condensation hetero polymers, such as polyacetals (i.e., polyformaldehyde and polyoxymethylene resins), polyamides and polyesters, the hydrolysis represents the most relevant process of chain cleavage that in severe and appropriate conditions may leads to the formation of the starting monomers [4].

The cleavage of chain backbone is the main responsible of the fragility of degraded polymer materials. Such an effect may be documented by plotting, for a given linear polymer, the dependence of the stress at rupture (σ) upon the molecular mass of samples artificially degraded.

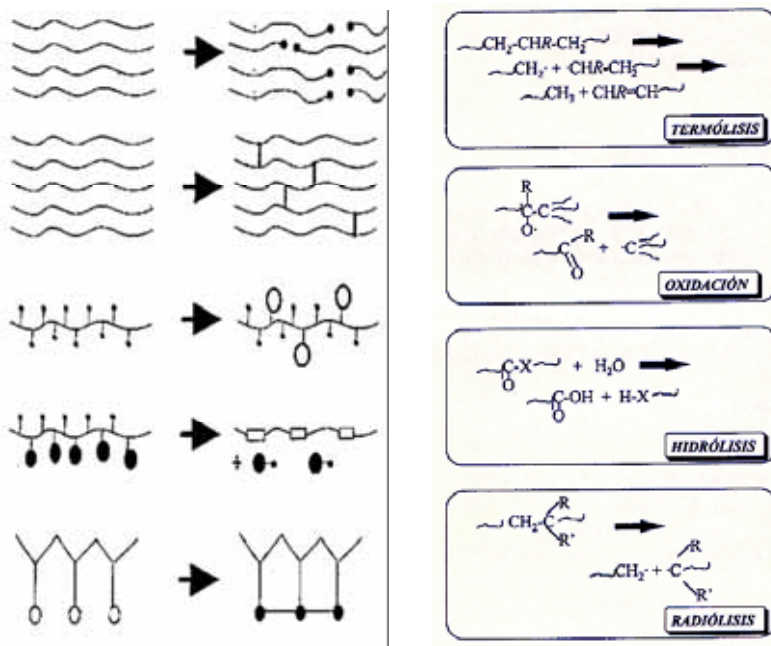


FIGURE 1, left: Chemical transformations of polymers induced at molecular level by degradation processes. From top to bottom: *random rupture of the backbone chain*; *cross-links*; *modification of side groups*; *elimination of side groups*; *cyclation of side groups* [2,3].

FIGURE 2, right: Chemistry mechanisms (schematic) of chain cleavage reactions. From top to bottom: *thermolysis*; *oxidation*; *hydrolysis*; *radiolysis* [2,3].

As can be seen by the diagrams in figure 3 the rate of the drop in the value of σ results to be higher in the case of degraded polymer samples [2].

From the comparison of the two curves it can be seen that for a given value of the molecular mass the σ at rupture of the degraded polymers is relatively lower than that of non-degraded polymer.

Polymers react differently to the action of a single factors of deterioration and this is essentially accounted for by the different molecular structure, molecular mass, degree of crystallinity and morphology, glass transition temperature, reactivity of functional groups, etc..

In reference [5] an attempt was made to establish the susceptibility of non-stabilized polymers against various types of degradation factors. The results are summarized in table 1 where susceptibility to degradation is increasing on the scale 0 (low tendency to be degraded) to 4 (higher tendency to be degraded) [5].

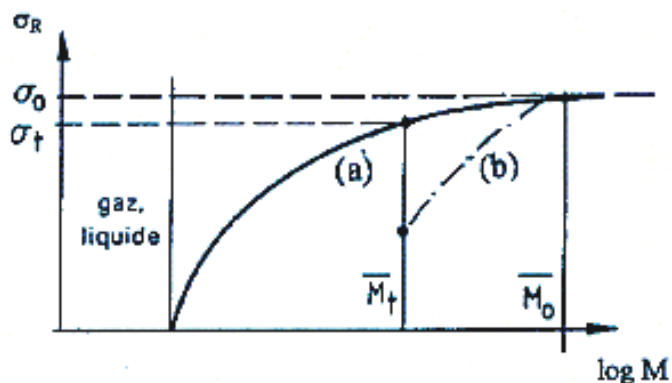


FIGURE 3: Relationships between stresses at rupture σ and the molecular mass of polymer samples.

- (a) non degraded samples;
 (b) degraded samples [2].

TABLE 1: The sensitivity of some common polymers against various types of degradation factors [5].

POLYMER	Susceptibility to				
	Thermal Degradation	Photo-oxidation	Ozone	Hydrolysis	Bio-degradation
polyethylene	2	3	1	0	1
polypropylene	2	4	1	0	0
natural rubber	2	4	4	0	1
polystyrene	2	3	1	0	1
poly(vinyl chloride)	4	3	0	1	0
poly(vinyl acetate)	3	3	0	4	2
poly(vinyl alcohol)	4	1	0	0	3
poly(methyl acrylate)	2	3	0	1	1
poly(methyl methacrylate)	3	2	0	1	0
poly(ethylene terephthalate)	2	1	1	1	1
bisphenol A polycarbonate	1	3	2	1	0
polytetrafluoroethylene	0	0	0	0	0
polyamide (Nylon-6)	2	2	2	2	2
polyurethanes	3	3	1	1	2-4
polypeptides	2	2	2	2	4
alkyd resins	2	2	2	1	
epoxy resins	2	2	1	1	
cellulose	2	2	0	2	3

Key: Susceptibility to degradation *Increasing* on the scale 0 to 4

From the whole of data cited, concerning polymer degradation the following considerations can be drawn:

1) Natural polymers, cellulose and proteins, together with polymers from synthesis containing along the backbone ester, amide and urethane bonds, are sensible to hydrolysis.

2) For a given polymer the resistance to degradation, under comparable conditions, increases with the degree of crystallinity as the amorphous regions are more permeable to the penetration of degradation entities [3,6].

3) The presence along the chains of functional groups (for example, double C-C bonds, hydroxyls, ester and amide bonds) generally makes the polymers more vulnerable to deterioration.

4) Usually it is found that higher values of glass transition temperature determine higher resistance against the action of many factors of deterioration if the service temperature is below T_g. Most of degradation processes propagate with higher difficulties in a glassy polymer rather than in rubbery one.

5) The sensitivity of an aliphatic homo polymer to degradation phenomena, especially to oxidation, is correlated to the reactivity of its hydrogen atoms against radicals.

From experimental data it has been possible to arrange the various types of hydrogen according to the following degree of reactivity (see also figure 4):

hydrogen on vinyl carbon atom > methynic hydrogen (bonded to tertiary carbon atom) > methylenic hydrogen (bonded to secondary carbon atom) > methyl hydrogen (bonded to primary carbon atom)

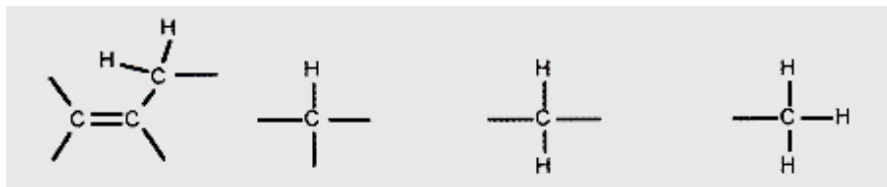


FIGURE 4: Hydrogen atoms in aliphatic homo polymers show different reactivity according to the type of carbon atom to which they are bonded. From left to right the reactivity decreases: hydrogen on vinyl carbon atom > methynic hydrogen (bonded to tertiary carbon atom) > methylenic hydrogen (bonded to secondary carbon atom) > methyl hydrogen (bonded to primary carbon atom) [7].

6) For a given polymer the degradation behaviour depends upon its molecular mass and distribution, melt and solution viscosity, glass transition temperature, degree of purity and presence and nature of residues of catalysts and additives [8].

7) In the case of stabilized polymers the diagram, changes in properties against time of aging, assumes the shape schematically represented in figure 5 [9].

The initial region (induction period), at lower aging times, characterized by practically no variations in the polymer properties, corresponds to the useful life of the material [10]. During such period of life, as indicated in figure 5, the following processes, related essentially to oxidation aging, occur:

--- Consumption and lost of stabilisers;

- Slow uptake of oxygen;
- Starting of free radicals production;
- Small increase in ROOH content;
- Limited chemical changes are initiated [9].

At a given time of aging the onset of chemical changes is observed followed by an abrupt deterioration of properties (degradation period). As already reported and as indicated in figure 5 during such a phase of oxidation phenomenon the material undergoes:

- Fast oxygen uptake;
- Rapid increase in ROOH products;
- Deterioration of physical properties;
- Carbonyl built-up;
- Changes in molecular weight and molecular weight distribution;
- Mechanical failure [9,10].

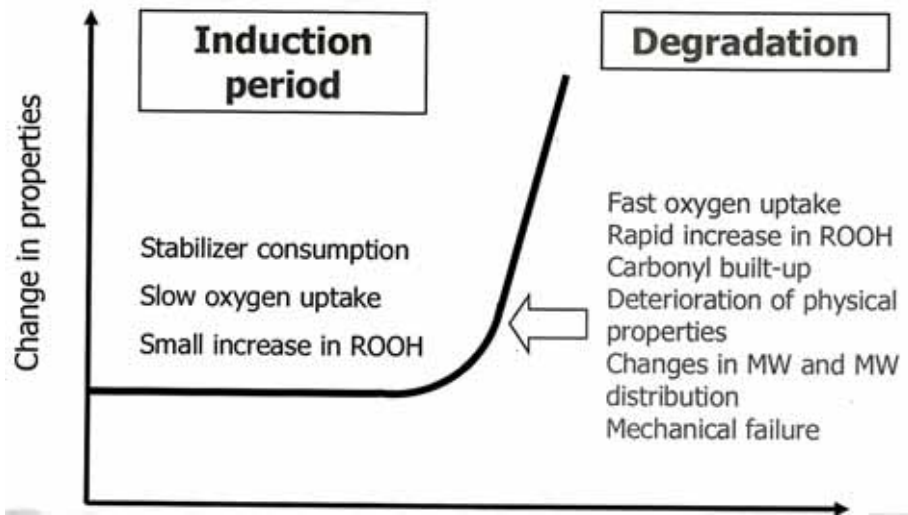


FIGURE 5: Typical diagram showing the changes in properties against time of aging (oxidation) for a general stabilized polymer [9].

Similar trend is observed when a polymer is degraded by exposure to solar UV radiations in air, see figure 6 [10]

The onset of chemical changes and polymer degradation usually manifests through the appearance of various symptoms, which, as already written elsewhere, represent a warning alert for every conservator. Some of the most common degradation symptoms observed on plastic objects are hereafter listed:

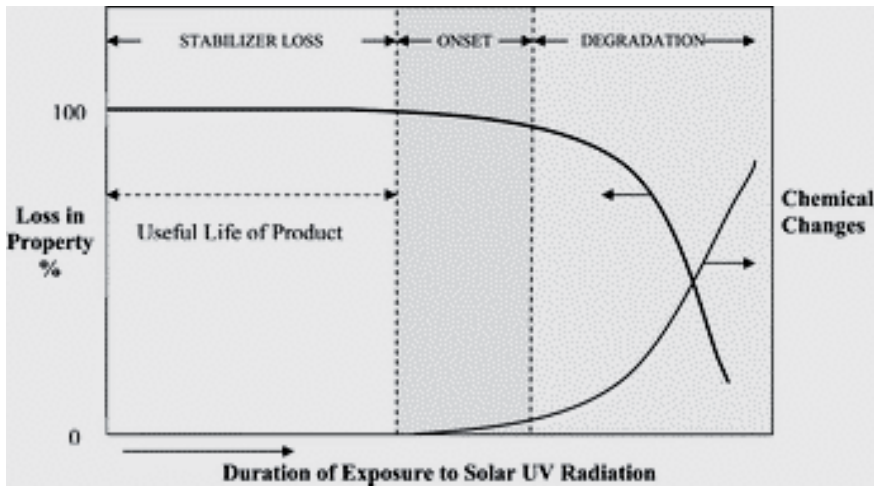


FIGURE 6: Loss of properties and chemical changes against duration of exposure to solar UV radiation in air for a generic stabilized polymer [10].

- Lowering of thermal, mechanical, optical and electrical properties;
- Yellowing and discoloration;
- Viscosity reduction/increase;
- Embrittlement;
- Tackiness;
- Loss of surface gloss;
- Surface crazing;
- Surface chalking;
- Loss of functional characteristics and delaminating;
- Release of volatile products.
- Blistering, blooming and crumbling;
- Fraying and exudation.

The photographic reproductions of objects in plastics with some of the symptoms above listed are hereafter visible.



FIGURE 7, top: Blistering observed on:
Left, a comb made in cellulose nitrate;
Right, an object manufactured in poly-carbonate.

FIGURE 8, bottom: Blooming on a comb made
In celluloid due to the migration of the camphor
used as plasticizer [11].

Blooming is quite often observed in plastic formulations with flame retardant additives (FR).

< Blooming is very slow process where the flame retardant migrates to the surface of the plastic resulting in a hazy surface (see figure 9) which often has a bronze like appearance. This effect is particularly undesirable for parts that also have an aesthetic function such as enclosures and housings. For this reason, Blooming is an important criterion to consider for some applications. Generally, Blooming depends on the compatibility of the FR with the polymer as well as the FR's molecular weight. The higher the compatibility and the molecular weight, the lower the blooming > [13].

Plastic objects showing clear effects of discoloration are shown in figure 10 [12,14], while damages due to crazing and delaminating are evidenced through the pictures in figures 11 and 12 [15,16].

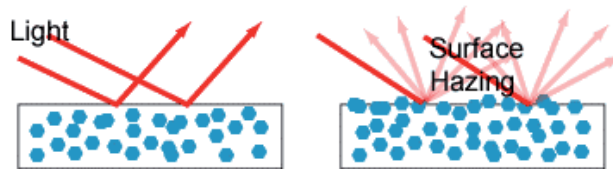


FIGURE 9: < Blooming is a very slow process where the flame retardant migrates to the surface of the plastic resulting in a hazy surface > [13].



FIGURE 10, top: Discolouration effects on a UV damaged polypropylene rope, (left). The original green colour of the undegraded rope is shown on the right [12].

FIGURE 10, bottom: Two badly discoloured green plastic chairs [14].



FIGURE 11: A white plastic jewellery box showing stains and some cracks [15].

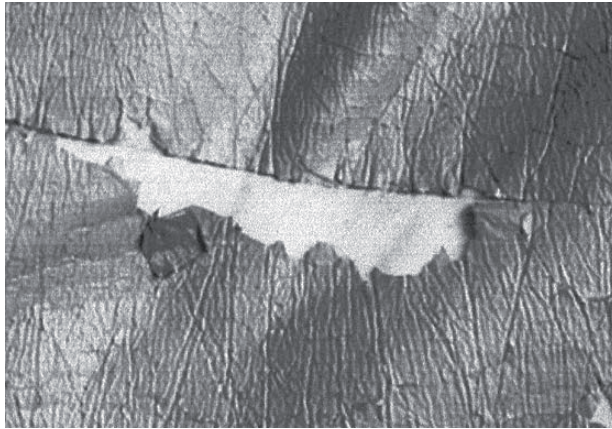


Figure 12: Delaminated polyurethane cover.
Photography by Roger Griffith [16].

Deterioration phenomena induced by migration of additives or aid processing materials and by the release of degradation products are documented by the photographs reported in figure 13 in the case of poly vinyl chloride and celluloid [17].

A prompt and thorough analysis at the first appearing of symptoms of degradation is necessary to understand the seriousness of the damages already produced and thus to provide with an accurate and appropriate treatment of conservation finalized also to the mitigation of main active factors.

J. Morgan (1994) reported the result of a questionnaire sent to a significant number of private collectors and museums in order to know the state of conservation of collected plastic artefacts as well as the most prevailing type of damages observed.

The results evidenced that the most prevalent types of degradation were cracking or crazing, discoloration, fading and bloom [18].



FIGURE 13:

Left, < wax used as a moulding release has migrated past the polyvinyl chloride skin of this 1960s doll, leaving a blotchy white coating > [17].

Right, < Early items first made of cellulose nitrate, now a common plastic, were marketed as luxurious because they resembled tortoiseshell and ivory. As the plastic naturally breaks down, it releases nitric acid. The acid corroded the lead motif on the comb > [17].

Conceptually speaking plastics are usually made by first polymerising the base polymer constituent by using controlled synthesis techniques of polyaddition, or polycondensation capable to give macromolecules with tailored:

- Molecular weight and molecular weight distribution;
- Degree of branching;
- Constitution and configuration.

A compoundization phase follows where, according to the chemical nature of the polymer and to the use functions, various types of additives are added (see previous sections). The final processing step consists in shaping the so obtained compound, usually named as plastics.

During processing the material is exposed to the action of mechanical stresses, heat, pressure, shear stresses, light, oxygen and water which inevitably induce the starting of various types of degradation reactions. The addition of specific additives in the course of those preparation steps serves the purpose to:

- 1) inhibit the initial and the propagation step of the degradation (see as example the scheme in figure 14 concerning the mitigation effects of photo-oxidation) [9];
- 2) avoid the modifications in the chemical composition and the molecular weight of the polymer component;
- 3) reduce the changes in the physical and optical properties of the polymer [19].

As already seen, in the course of their life, plastic artefacts may suffer the exposure to sunlight, oxygen, heat and aggressive chemicals present in the environment, micro organisms, wind and rain which can have deleterious adverse effects on their performances and then on their useful functions. In the reality it is observed that quite often two or more factors are simultaneously and synergistically actives [20].

From the above considerations it can be concluded that the problematic issues presented by the conservation of artefacts in plastics are essentially related to the following specific elements:

- Plastic artefacts are based upon a wide range of polymer families with different chemical structure and physical properties.
- Plastics are multicomponent systems constituted by a base polymer compounded with additives, fillers, pigments, etc.;
- The knowledge of the nature and chemical structure of the components used for the manufacturing of the artefacts, essential step for the design of any conservation project, is a necessary task not always easy to be accomplished;

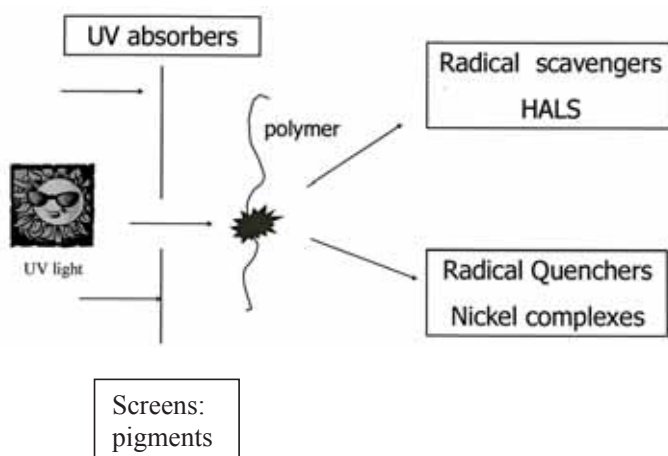


FIGURE 14: Use of specific methods of various nature and function to inhibit the initial and the propagation step of the photo-oxidation degradation of a polymer material. In figure are evidenced the effects of UV-absorbers, screen pigments, radical scavengers and of radical quenchers [9].

--- Degradation of plastics may be determined by internal factors such as additives migration towards the surface and also by the action of harmful contaminants and degradation products arising from phenomena induced by processing conditions as well as by external aggressive chemicals active in the environment during the use life of plastic artefacts.

It follows that the adoption of a proper project plan finalised to the conservation of plastic artefacts, stored in collections and museums (it must includes the phases of direct restoration, protection, prevention and maintenance) at the moment result to be still a not easy job to be pursued.

As matter of fact the conservation of polymer based items represents an area of "*Science of Conservation*" to be still developed to gain more theoretical and experimental knowledges able to take into consideration also the specificity and peculiarity of plastic nature and their behaviour against mechanisms of degradation considering furthermore that in the majority of cases *<very little can be done to reverse the degradation process, either chemically or physically. The only option is to reduce the rate at which it is happening >* [21].

Now a day most of research is concentrated in find out methods finalised to develop new polymer compounds internal stabilised against environmental effects of deterioration. While, on the contrary, *< very little is directed specifically towards the conservation of plastic objects made in the past >* [21].

Very often the artefacts in plastics, already at the moment of their acquisition, are interested by some type of deterioration process. This means that before to be stored in private or public collections and museums they may *infected* by degradation products.

Hence, the first action to be undertaken by curators should consist in analysing the type and deepness of damages suffered by the objects in relation to their chemical composition with the main goal to assess if the damage occurred at molecular level (i.e. chain scission or cross-linking) or only at macroscopic level (physical damage, discolouration, ecc.). Such information once aquired allow the activation of suitable restoration, mitigation and protective procedures.

By assessing the extent, rather than the nature of damage according to a methodology elaborated by S. Keene, et al. [22], it is possible to assign *< an object to one of four categories according to its condition. Category 1 indicates an object in perfect condition; 2, slightly damaged but stable; 3, damaged and unstable; and 4, extremely unstable and requiring urgent treatment >* [21].

The knowledge of the composition of a plastic artefact as well as the assesment of the extent and of the chemical nature of damages suffered can be accomplished by using various kind of instrumental diagnostic techniques. Some of the most common used techniques for the identification of plastics suitable also for the identification of the chemical modification induced by the various factors of degradation are listed in table 2 [21].

In such a contest of relevant interest are those non destructive instrumental diagnostic techniques capable to be applied in situ by using proper devices to perform the analysis.

In the framework of the project cited in reference [22] this approach led to the development of a mobile Raman spectrometer equipped with an optical fibre probe that can be positioned on the surface of the sample to be analysed. Thus tanks to this device it was possible to take the instrumental signal directly on the artefacts. A prototype of the system developped is represented in figure 15 [23].

Examples of Raman spectrograms taken on different points of a sample of unsaturated polyester, reported in figure 16, demonstrate the reproducibility of the above developed technique [23].



FIGURE 15: A mobile Raman spectrometer equipped with an optical fibre probe that can be positioned on the surface of the sample to be analysed, thus suitable to perform non destructive analysis on plastic artefacts [23].

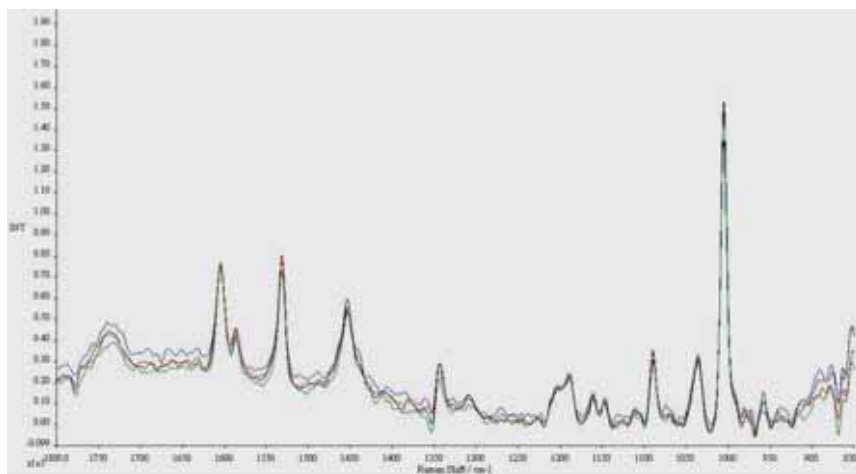


FIGURE 16: Examples of Raman spectrograms taken by using the mobile fibre optic probe on different points of a sample of unsaturated polyester to demonstrate the reproducibility of the non destructive technique developed [23].

TABLE 2: Some of the techniques used for the identification of plastics and main informations obtained [21].

Technique	Information obtained
Fourier transform infrared spectroscopy (FTIR)	Characteristic spectrum of the plastic
Differential Scanning Colorimetry (DSC)	Glass transition temperature and melting point
Nuclear magnetic resonance spectroscopy (NMR)	Chemical structure
Dynamic thermal mechanical analysis (DTMA)	Glass transition temperature

MITIGATION MEASURES TO REDUCE THE EFFECTIVENESS OF DAMAGE FACTORS: GENERALITIES ABOUT PROTECTION AND MAINTENANCE OF PLASTIC ARTEFACTS

The mitigation and the stabilisation procedures can be only selected and then adopted when the components of the artefact are known and when the mechanisms, the chemistry and the effectiveness of the deteriorative reactions still active have been defined in details.

In many circumstances the curators prefer to separate and exclude from the collection artefacts in plastics extremely unstable which require urgent direct and complicated treatments.

For the objects in perfect condition or slightly damaged but stable or damaged and unstable which do not need direct restoration treatment then proper procedures of protection and maintenance have to be studied and applied.

The main aim of protection and stabilization measures is the extension of the life time of artefacts by minimising or if possible by stopping, the effects of the active degradation processes without changing the aspect and the structure of artefacts.

In principle for the protection and maintenance of polymer based artefacts against the various factors of degradation both physical and chemical measures are used; some of them include the:

- Detection of the early symptoms of degradation by regular examination and by using proper devices and sensors;
- Rigorous and systematic control of light, temperature, humidity, ventilation and cleaning;
- Reduction of fluctuation of temperature and humidity;
- Lowering of the temperature in storage or exhibition room;
- Protection of the artefacts from UV light, to minimise the probability of thermo-photo oxidation;
- Avoiding that items made by plastics with a high plasticiser content (e.g. cellulose nitrate and acetate and polyvinylchloride) are in contact with themselves or with other objects.
- Removal of harmful contaminants and degradation products;
- Exclusion of all external harmful agents;
- Design and use of closed environment or display cases to create specific physical and chemical barrier against deterioration agents;
- Avoiding of the storage of an artefact in the proximity of other plastic items that following degradation produce and release in the environment reactive compounds capable to act as factors of degradation (for example casein items that are easily degraded by HNO_3 should never be stored close to celluloid plastics that following degradation release this compound in the environment);
- Application of proper prevention devices to control and reduce degradation [24].

In principle the best practice for the protection and maintenance of sensitive plastic objects forecasts their keeping in transparent cases hermetically sealed with inside a controlled proper “micro-environment” and by using specific indicators, sensors and scavengers to monitor early signs of degradation and to avoid further damages. In some case should be advisable to store a delicate artefact individually wrapped in acidic free tissue.

Strips of filter paper impregnated with *Cresol Purple* (*m-cresolsulfonphthalein*) are an example of an **indicator** useful to detect the offgassing of nitrogen dioxide (NO_2) from a degrading celluloid items (see next chapters for details) [25,26].

A **scavenger** is a chemical based device capable to remove or inactivate impurities or unwanted products thus improving the environmental conditions in closed or controlled museum rooms or glass show cases.

Scavengers, according to their function and nature may be classified as follows:

---Humidity scavenger

- Silicagel, with a blue colored indicator that change color in rose following hydration;
- Artsorb, constituted by amorphous silica and lithium chloride.

---Chemical scavengers

- Active carbon;
- Zeolites, silicates of Al, Ca, Na

---Oxygen scavengers

Ageless, based on fine powdered iron that in presence of O₂ form oxides and hydroxides.

--- Acid scavengers

used to neutralize traces of halogen, nitrogen and sulphur anions formed during aging

--- Free radical scavengers and quenchers

Due to the specificity of plastics materials, in principle, the above devices should be designed at least for class of homogenous plastics taking into consideration also the kind of additives present as well as their activity and function. Moreover it should be taken into account the fact that an ideal environment for a certain type of plastic may be detrimental for another type.

Thus it can be concluded that while at the moment the mechanisms of degradation and stabilization of polymers are relatively well known on the contrary the “operative” conservation of plastics based artefacts is an open problematic issue that still require large research efforts.

REFERENCES

- 1) S. Grima, V. Bellon-Maurel, P. Feuilloley, F. Silvestre, < *Journal of Polymers and the Environment* >, **8**, 183 (2000).
- 2) N. Guarrotxena, J. Millan, *Revista de Plasticos Modernos*, **78**,45 (1999).
- 3) E. Martuscelli, < *La Chimica Macromolecolare Applicata alla Conservazione dei Manufatti Lapidei* >, PAIDEIA, Firenze (2007).
- 4) < *Macromolecole, Scienza e Tecnica* >, a cura di F. Ciardelli et Al., Vol. I, pp. 849-912, Pacini Editore, Pisa (1983).
- 5) I. C. McNeil, < *Fundamental Aspects of Polymer Degradation* >, in “*Polymers in Conservation*”, Edt. by N. S. Allen, M. Edge, C. V. Horie, Royal Society of Chemistry, pp. 15-32 (1992).
- 6) E. Martuscelli, < *Plastics in Art (in Cultural Heritage) - Plastics for Art (for Cultural Heritage* >, Lecture presented at Programma Giornata AIM on ”Il restauro e la diagnostica degli oggetti d’arte e di design in plastica”, 31/10/(2008). Published through the Martuscelli web-site, <http://www.eziomartuscelli.net/> (2009).
- 7) L. Borgioli, P. Cremonesi, < *Le Resine Sintetiche Usate nel Trattamento di Opere Policrome* >, il Prato, Saonara (Pd) (2005).
- 8) R. I. Feller, < *Standards in the evaluation of thermoplastics resins* >, ICOM, (1978).
- 9) < *Stabilization of polymer matrix, polypropylene in LFT&new development* >, ADDCOMP, polymer additive solutions, SPE Automotive Composite Conference (2006). Deloitte 2005 Technology Fast 50, www.addcomp.nl
- 10) A. L. Andrady, H. S. Hamid, A. Torikai, < *Photochem. Photobiol. Sci.*>, **6**, 311, (2007).
- 11) < *Plastics, collecting and conserving* >, Edt., A. Quye, C. Williamson, NMS Publishing Limited (1999).
- 12) <http://en.wikipedia.org/wiki/File:Failedropel.jpg>, (2009).
- 13) <http://www.specialchem4polymers.com/tc/Brominated-Flame-Retardants/index.aspx?id=Non-blooming>, (2009).
- 14) www.photographersdirect.com/buyers/stockphoto, (2009).
- 15) http://www.dargate.com/224_auction/224_pics/54.jpg, (2009).
- 16) R. Griffith < *Research & Conservation, Conservation Journal Online* >, October: Number 21 (1996).
- 17) www.sciencenews.org/.../title/Long_Live_Plastics, (2009).
- 18) J. Morgan, < *A Survey of Plastics in Historical Collections* >, Plastics Historical Society and The Conservation Unit of the Museums & Galleries Commission. <http://www.plastiquarian.com/survey/survey.htm>, (1994).
- 19) UV/Light Stabilizers Center (CIBA), <http://www.specialchem4polymers.com/tc/UV-Light-Stabilizers/?id=2258>, (2009).
- 20) EDP, Environmentally Degradable Polymeric Materials and Plastics Brief Guidelines prepared by ICS-UNIDO Experts, (2003).
- 21) E. Then, A Survey of Plastic Objects at The Victoria and Albert Museum, < *Conservation Journal* >Number 6, January (1993), http://www.vam.ac.uk/res_cons/conservation/journal/conservation_journal_6/plastic_objects/index.html (2009).
- 22) S. Keene, et al.< *Report on a research project funded by the Office of Arts and Libraries* >, The Collections Condition Audit (1991)
- 23) Conclusions of the Project: < *Sviluppo industriale di procedure semplificate per la caratterizzazione chimica non distruttiva e per il recupero di manufatti in plastica: applicazioni nella catalogazione e restauro di beni culturali e nel controllo qualità di prodotti industriali a base*

di materiali termoindurenti >, financed by MIUR (n.: Prot. 915 del 30/01/2004 ammesso al finanziamento con D.D. n°2059 del 21dicembre 2007 a valere sui contributi del Dlg. n° 297/99 (D.M 8 agosto 2000 n. 593 art. 9)) by AET- CO.BE.CAM. – CNR-ICTP – UNI SALERNO– PERKIN ELMER (2009).

24) H. A. Razavi, B. G. Frushour, < *Polymer Preprints* >, **35**, Number 2, 309 (1994).

25) 4) S. C. Stinson, < *Chemical & Engineering News* >, September **9**, 34 (1996).

26) J. Fenn, < *Polymer Preprints, Division of Polymer Chemistry, Inc.* > , American Chemical Society, **37**, **N.2**, 170 (1996).

SECTION-2

PLASTICS, BELONGING TO THE PRE-SYNTHETIC PERIOD, USED AS COMPONENTS OF ARTEFACTS OF CULTURAL INTEREST:

CHEMICAL COMPOSITION, PROPERTIES, PROCESSING, DEGRADATION BEHAVIOUR AND CONSERVATION MEASURES

In reference [1-a] "*plastics*" are defined as follows:

< ...*any inherently formless material that can be molded or modeled under heat and/or pressure. It is derived from the Greek word *plastikos*, meaning a shaped or molded substance* > [1-a].

Plastics have as main component natural or synthetic polymers (polymer comes from the Greek word "*poly*", meaning "*many*" and "*mer*" meaning "*unit*"), materials constituted by macromolecules having very high molecular mass [1-b].

The use of natural polymers to make plastic compounds useful for manufacturing artefacts started as early as 1760, when Enoch Noyes established an activity for making combs by using organic proteins contained in animal horns and horse hoofs and in blood and eggs [1-b].

Plastics represented not only an industrial and technical innovation, they were also a cultural phenomenon as they changed the way according to objects could be produced, designed and used. Plastics based on the physical or chemical transformation of natural materials such as, horn and hoof, albuminoidal organic proteins, rubber, casein, shellac and cellulose derivatives all belong to the "*pre-synthetic era of plastic industry*".

According to their source polymers, main components of plastics, are usually divided in:

---Natural;

---Artificial, derivatives of natural polymers through chemical modifications;

---Synthetic or man-made, obtained by the man by polymerisation of low molecular weight compounds named monomers.

For sake of convenience, plastics may be grouped according to the following criteria:

- 1) Plastics based on the utilization of natural pre-formed polymers with protein chemical structure;
- 2) Plastics formulated by using pre-formed natural polymers having a cellulose chemical structure;
- 3) Plastics or rubbers obtained by chemical treatments of natural polymers deriving from trees lattices ;
- 3) Plastics whose polymer component is obtained from monomers by reaction of synthesis ideated by the man (synthetic polymer or man-made polymer).

The origin, the nature and structure of the polymer component, the kind of additives used, the processing method followed and main applications for some of most common plastics used in the manufacturing of artefacts with cultural interest are henceforth reported.

The resistance to degradation and main specific symptoms of deterioration will be also described assuming that the knowledge of such elements is essential to:

--- Understand the chemistry of the mechanisms of degradation.

--- Establish suitable measures to minimise the deleterious effects of internal and external degradation factors.

SECTION-2

FIRST- CHAPTER

PLASTICS BASED ON NATURAL PRE-FORMED POLYMERS WITH PROTEIN STRUCTURE: HORN AND HOOF, BOIS DURCI AND CASEIN BASED PLASTICS

Generalities About Proteins

The main structural components of horn, hoof, bois durci and casein, are macromolecules with a protein chemical structure. Thus in order to understand the properties of the corresponding based plastic materials used for manufacturing old and often artistic objects, as well as their degradation behaviour it seems necessary to recall, briefly, the main characteristics of proteins.

The protein macromolecules, found in nature, ideally may be considered as the resultant of multiple condensation reactions between a limited number (twenty) of α -amino acids, all having the same L-configuration but differing in the chemical nature of the side groups (see table 1 and figure 1).

As shown by figure 1, α -amino acid residues are linked through the so-called peptide bond ($-\text{CO}-\text{NH}-$) which arises from the condensation between the carboxyl group of one amino-acid with the amino group of another adjacent amino-acid.

Natural proteins from molecular point of view differ each other by the number, composition and sequence of α -amino acid residues that are present along the macromolecule chains.

The macromolecules in natural proteins are organized according to the following different structural levels.

Primary structure: It represents the type of sequence of the α -amino acid residues along the macromolecular chains.

Secondary structure: May be defined as the regular conformation that long segments of chain assume. Normally such structure are stabilized by strong (intra-molecular or inter-molecular) hydrogen bonds between the $-\text{NH}$ group of a peptide bond and the $-\text{CO}$ of another one.

Proteins, for energetic reasons, may assume only two possible regular secondary structures, namely the *right handed α -helix* or the *β -sheet*, schematically represented in figure 2 [4].

Tertiary and quaternary structure: Is the resultant of the manner according to which different regular structured segments of a protein (with β -sheet or right handed α -helix conformation) through connecting irregular folded chain segments are joined each other giving rise to an overall three dimensional supra-molecular complex structure. The ternary structures are stabilized by secondary bonds between side groups of α -amino acid residues and in some cases through bi-sulphur covalent bridges (see figure 3) [4].

Proteins are classified in *Simple* or *Conjugated*.

--- Simple proteins are constituted only by α -amino acids.

--- Conjugated proteins contain a non-protein group (*prosthetic group*) chemically bonded to the protein macromolecules [6].

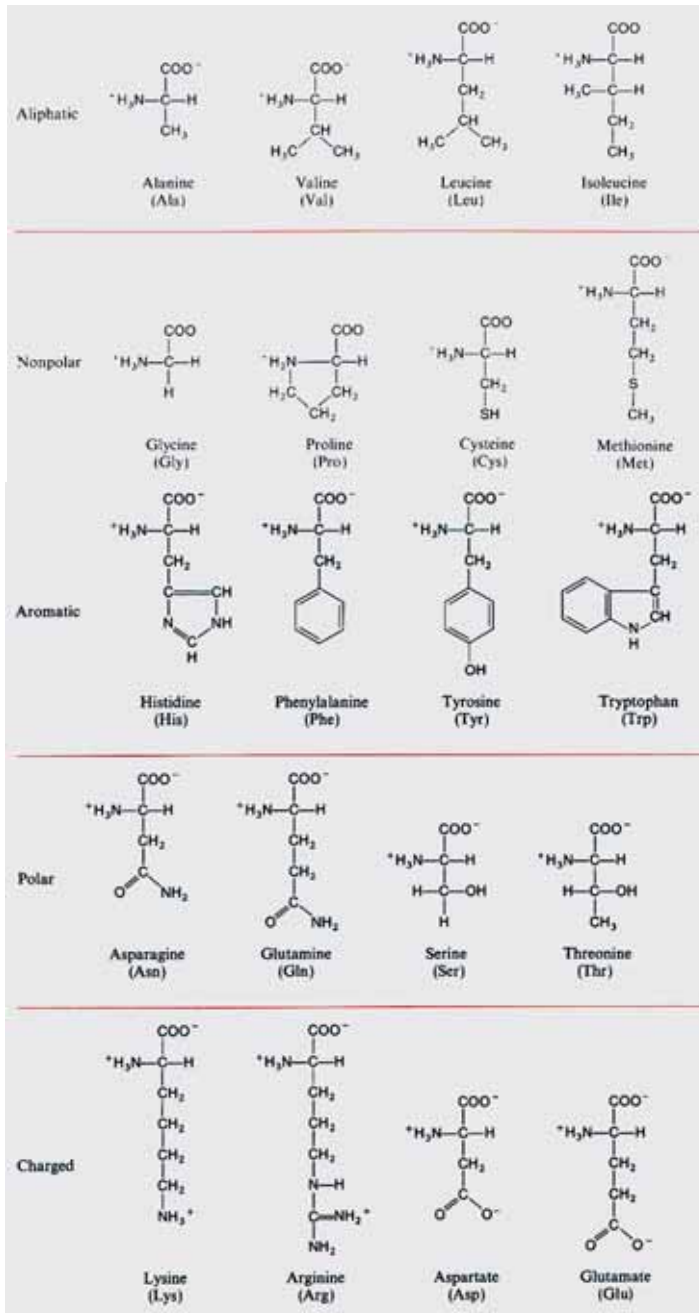


TABLE 1: Molecular structure of the 20 α -amino acids constituents of proteins at pH=7. In such conditions the α -amino group is protonated while the carboxyl is deprotonated. The structures are projected into a plane about the α -carbon atom. In the reality the amino group and the hydrogen are above the plane of the page, whereas the carboxyl and the side chain are below it (see figure 1, bottom-right) [1-b].

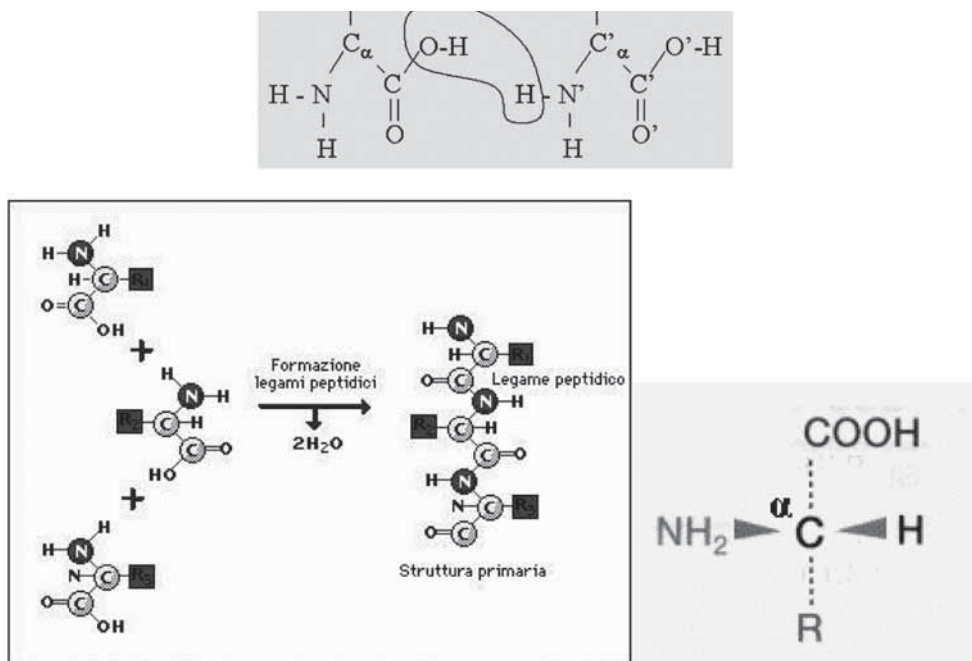


FIGURE 1, top and bottom-left: Protein macromolecules may be ideally considered as the resultant of condensation reactions between 20 different types α -amino acids [2,3]. **bottom-right:** Molecular structure of a generic α -amino acid in L-configuration [4].



FIGURE 2: Possible secondary structures (schematic) of natural proteins. Left, right-handed α -helix. Right, β -sheet [5].

According to the chemical nature of the prosthetic group proteins are divided in the following classes: a) nucleoproteins, containing nucleic acids; b) lipoproteins, with lipids; c) phosphoproteins; d) metal proteins and e) glico proteins.

Proteins whose constituent macromolecules, by repeated folding processes, may assume a spherical geometry are called *globular proteins* (see figure 3-right). Are denominated *fibrous proteins* when the chains associate each other forming a fibre-like structure whose macromolecules are aligned and elongated along an axial direction (figure 3-left) [6].

Proteins may be also labelled on the base of their specific function. Thus we may have:

--- *Enzymes proteins* (with the capability to be specific catalysts for chemical reactions);

--- *Transport proteins* (for example the albumin that transports fat acid in the blood)

--- *Etc..*[6].



FIGURE 3: Ternary and quaternary structure of proteins.

Left: In a fibrous protein the macromolecules, with a right-handed α -helix or β -sheet conformation, associate each other forming long fibres or sheets. In figure is represented the case of keratin (see later).

Right: In globular proteins the macromolecules by folding processes assume a coiled spherical geometry. On the right side it is shown the aggregation of more globular single protein chains [6].

1) HORN AND HOOF: “KERATIN” BASED PLASTICS

At earlier times animal horn and hoof (see figure 4) [7] were shaped by mechanical carving to obtain tools and items useful for the day life. Successively, between the seventeenth-eighteen centuries, it was found that powders, obtained from horn and hoof, behave like a thermoplastic material. They soft when are heated up, then by cooling they become solid. Thus horn and hoof powders were easily shaped by compression moulding by using manual screw press [8].

A. Schaverien, concerning the relevant role that horn and hoof had in anticipating the times of mass production based on thermoplastic materials wrote:

< Horn has a long history of being shaped by heat and pressure and may be regarded as the earliest forerunner of plastics. Horn with moulded impressions of fine detail are among the earliest examples of the plastic moulders art. Exactly how it was done is lost in history, but it is undoubtedly from this beginning that plastics moulding was developed > [9].

A wide variety of artefacts (ornaments, brooches, buckles, combs, buttons, backs of hair brushes and hand mirrors, snuff boxes, etc.), most of them, fine and artistic relief works, were made by

moulding horn and hoof. Such a manufacture was denominated as “*pressed horn*”.

By heating and pressing horn was possible also to produce thin transparent sheets used, in place of the more expensive glass, as windows and lantern windows (see figure 5) [8].

Some exemplars of antique artistic objects made in pressed horn are shown in figures 6,7, 8 and 9 [9,10,11].

Sheaths, essentially composed by a fibrous protein called keratin, that grow around a bony core, constitute the horn of sheeps, goats and cattles. Such kind of horn

< are never branched and, once grown, are never shed. They consist of a core of bone arising in the dermis of the skin and are fused with the skull. The horn itself forms as a hollow cone-shaped sheath around the bone > (see figure 10) [12-a].



FIGURE 4, left: Exemplars of horns of buffalo [7].

FIGURE 5, right: thin transparent sheets of horn were used in USA as lantern windows until the year 1740 when horn for such application was substituted by glass [8].



FIGURE 6, left: Artistic *< large ornate comb, made by John Evans of Roxbury, Massachusetts, was presented to President Andrew Jackson >* [8].

FIGURE 7, right: Plaques by Osborn, with very fine details, of Frederick Henry, prince of Orange, and his wife Amelia (≈ 1626), that according to Adele Schaverien are the earliest known example of pressed horn artefacts [9].

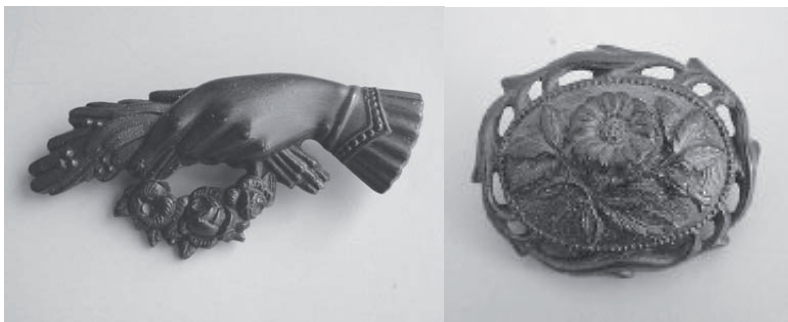


FIGURE 8, left: Victorian pressed horn hand brooch, holding roses and forget-me-nots wreath laurel sheaf symbolizing love victorious, 1870 [10].

FIGURE 9, right: Victorian pressed horn flower brooch [11].

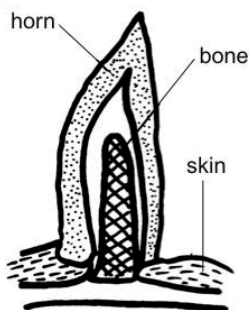


FIGURE 10: The horns, in sheep, goats and cattle; are constituted by sheaths, essentially composed by a fibrous proteins called keratin, that grow around a bony core (schematic diagram) [12-a].

Alpha-Keratins, belonging to the family of hard, fibrous proteins, constituted by the association of fibrils oriented along the chain axis, are the main structural components of horns and hooves.

As shown by figure 11, the amino acids residues of glycine, arginine and cysteine are the most abundant present in cattle horn keratin. The overall % of nitrogen and sulphur is ≈ 16 and 3 respectively [12-b].

The primary structure of alpha-keratins is characterized by a high % of sulphur-containing amino acids such as cysteine. The presence of residues of this amino acid along the macromolecular chains of keratins allows the formation of strong intermolecular disulfide bridges connecting two macromolecules. Such S—S covalent bonds are generated by oxidation reactions between the thiol functional groups, —SH, of two neighbouring cysteine residues (see figure 12 and table 1) [13,14,15,16].

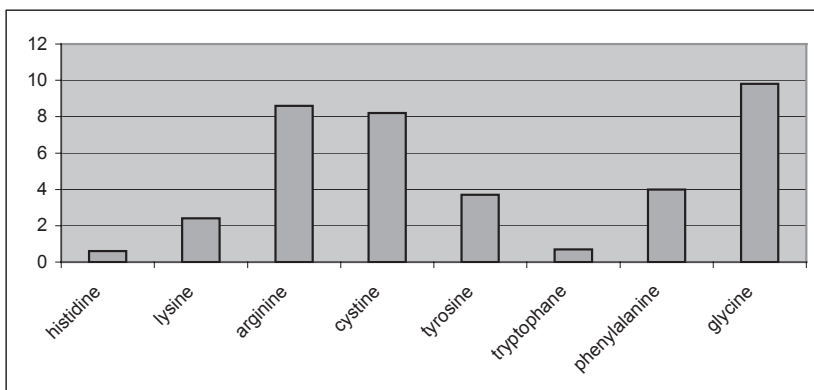


FIGURE 11: Amino acid composition of keratin in cattle horn. The cysteine values have been calculated as cystine. The quantities are in % [12-b].

The presence of intermolecular thermally-stable disulfide bonds confers, to the overall fibre of keratin, strength and rigidity contributing as well to their insolubility in most of common solvents [13].

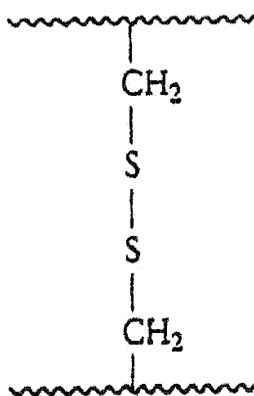


FIGURE 12: Disulphide cross-link between two adjacent macromolecules of keratin joining two cysteine residues [15].

In hard α -keratins, component of horns, the single macromolecules assume a right handed α -helix conformation that is stabilized by strong intramolecular hydrogen bonds (see figure 13) [20,17,18,19].

The macroscopic keratin fibres are constituted by a hierarchy of structures based on successive aggregations of supra molecular elements. The simplest structure, called *intermediate filaments*, is obtained through a mechanism where two macromolecules wound together form a superhelical rope-like structure (see figure 14).

Following the successive aggregation of two intermediate filaments, as shown by figure 14, a structure called proto-filament is formed.

By the association of proto-filament units, following well defined rules, proto-fibrils are obtained (see figure 14). In such elements the proto-filaments are held together by an amorphous matrix with high sulphur content. Successively a limited number of proto-fibrils, cemented by amorphous materials, aggregate to realize macro-fibrils. A single cell is constituted by the association of many macro-fibrils elements hold together by an amorphous complex compound [12-b), 16,19,20].

In horns these cells joining together form lamellae that grow around the central bone according to a concentric geometry.

< The tubular/helix structure of alpha keratin is carried over into the larger structural unit of horn tubules in the hoof wall > [12-b)].

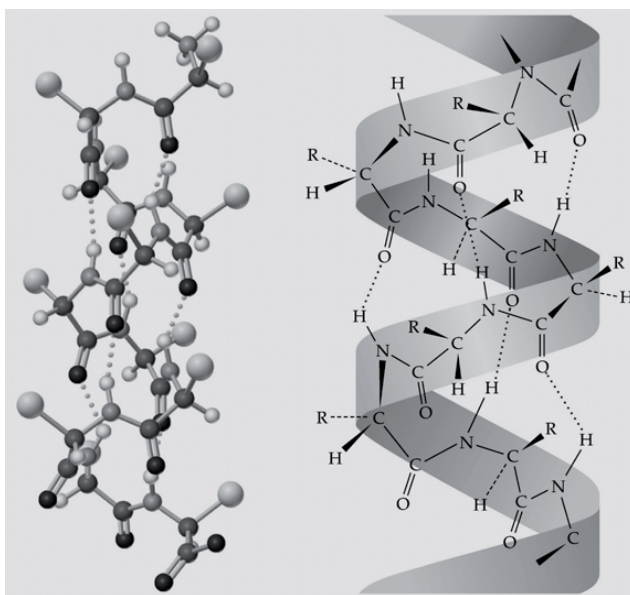


FIGURE 13: The macromolecules of alpha-keratin found in horns have a right-handed α -helix secondary structure [18].

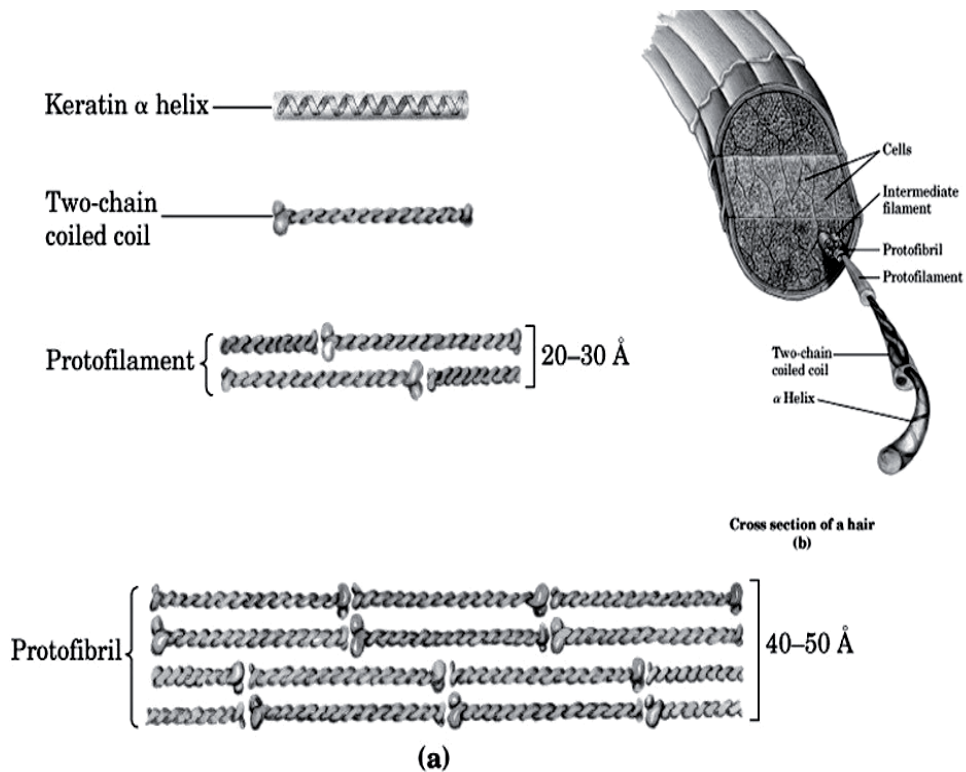


FIGURE 14: The mechanism of formation of the *alpha*-Keratin fibres. The various phases of hierarchy aggregation of supra molecular elements are depicted.

From top-left to the bottom-left: 1) Single right handed α -helix. 2) Two chain coiled coil (*intermediate filaments*). 3) Protofilament. 4) Protofibril.

Top right: Overview showing how the cells and the macro fibres are formed.

A single cell is constituted by the association of many macro-fibrils hold together by an amorphous complex compound (see text) [12-b)].

The schematic representation showing the organization of horn tubules, < each with cortex and medullary cavity, as well as melanized and non melanized intertubular matrix > [12-c)], all constituting one horn lamina in the case of white rhinoceros horn is described in figure 15-left. While in figure 15-right is reported the < transmitted light view of a thick section of white rhinoceros horn from the center of a dark patch, showing areas of melanized intertubular matrix surrounding lighter horn tubules > [12-c)].

According to literature data horns contain about the 70-80 % of keratins. Moreover from the elemental analysis it results also the presence of phosphorous (6%), calcium (6-7%) and sulphur (1%) [21].

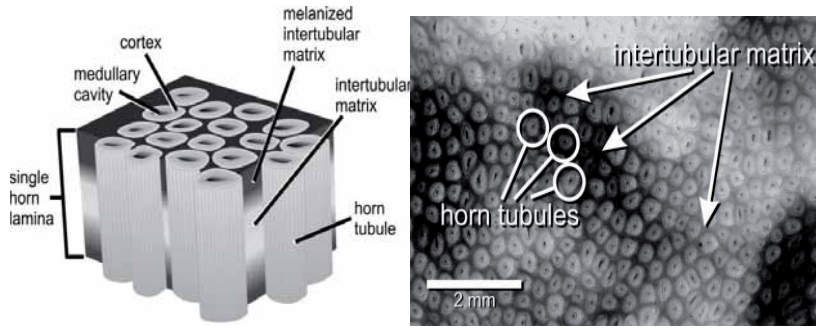


FIGURE 15: See text [12-c)].

--- The processing of horns or hooves

The processing of powders of horn/hoof is essentially based upon the following operations:

- Washing and immersion in cold water for few days;
- Dipping in boiling water or soaking in alkaline solution;
- Bleaching and dyeing;
- Heating at 110°C where the powders soften and then may be suitably manufactured in shaped objects by compression moulding.

In reference [8] is reported that *< Hans Wanders, long time secretary of the Plastics Pioneers, entered the plastics industry in 1919 at Lawson Molding Company, were they molded ground horn and dried blood into fine plastics products >* [8].



FIGURE 16, left: An exemplar of hand mould used for making buttons from horn/hoof powders.

FIGURE 17, right: A typical early screw press used for compression moulding horn and hoof materials in the USA civil war era [8].

It is possible to obtain coloured artefacts by adding lead acetate, chloride acid, red lead and potassium hydroxide. Black coloured items are realized by means of logwood dyeing [22].

Horn can be dyed to resemble *jet*, < a hard, coal-like variety of lignite. It's colour is velvety black or brownish black when passing into bituminous wood. It has a brilliant lustre and is resinous.....To test for horn, you can use the hot pin method, if it is horn it will burn with the most disagreeable odour, like burning hair or feathers. > [23].

The above mentioned *hot pin* test is recommended to identify easily horn or hoof objects.

An ancient hand mould employed in making horn buttons and a very hold manual screw press used for compression moulding horn and hoof materials (USA civil war period) are reproduced in figure 16 and 17 respectively [8].

The main factors of degradation of keratin based natural materials

--- Photo-oxidation of keratins at molecular level

Hard-keratin fibres, generally, are sensitive to the action of light in particular to UV radiations ($\lambda < 380\text{nm}$) especially in presence of oxygen and water. The main modifications induced to keratin molecules by photochemical reactions, schematically represented in figure 18, are:

- Scission of the backbone of the main protein chain (figure 18-1) ;
- Formation of new cross-links (figure 18-2) ;
- Destruction of existing cross-links (figure 18-3) [24].

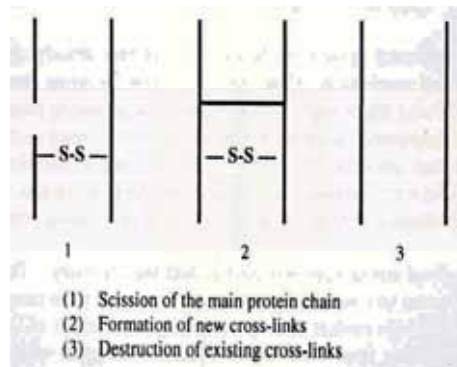


FIGURE 18: Main degradation reactions photo-chemically induced to keratin macromolecules [24].

Examples of photochemical reactions leading to the formation of a new intermolecular cross link (a disulphide bridge) and to the disruption of a pre-existing disulphide intermolecular bridge are schematically shown in figures 19 and 20 [24].

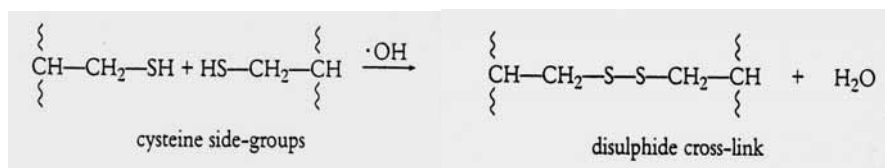


FIGURE 19: Example of a reaction of photo oxidation of keratin leading, in presence of radical $\cdot\text{OH}$, to the formation of a new disulphide cross-link [15, 24].

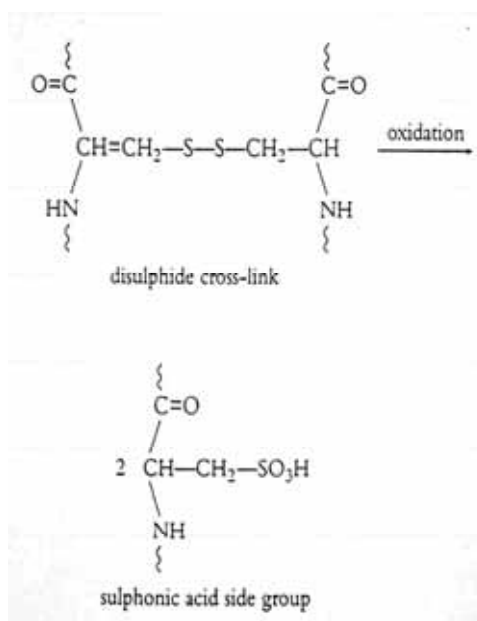


FIGURE 20: Photo-oxidation reaction causing the rupture of a pre-existing disulphide bond between two keratin macromolecules [15, 24].

--- Thermo-oxidation of keratins at molecular level

Temperatures $> 100^\circ\text{C}$, in presence of oxygen, may generate in keratin macromolecules condensation reactions between carboxyl and amino groups with the formation of peptide intermolecular cross links.

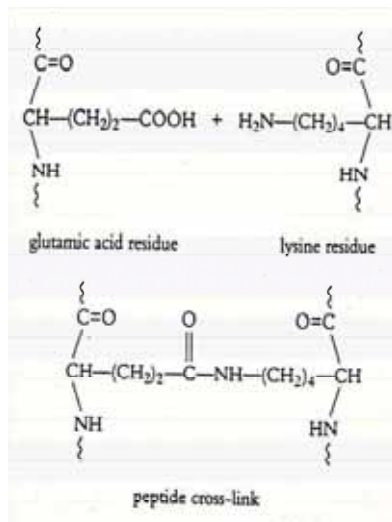


FIGURE 21: The thermo-oxidation of keratin, at temperature $> 100^\circ\text{C}$, may lead to a condensation reaction between carboxyl and amino groups with the formation of peptide intermolecular cross links [15, 24].

The chemistry of such kind of reactions is described in figure 21 [15, 21]. It is important to underline that this type of reaction determines a reduction of the capability of keratin-based materials in to absorbing water.

--- Degradation induced in keratin-based materials by acid and alkali agents

Keratin fibres, like any other natural fibres, are characterized by the co-existence of crystalline and amorphous phase that as shown by figure 22, regularly alternate along the fibre axis [25,26].

Keratin, due to this structure and to the chemical nature of the α -amino acids residues that constitute the single macromolecules, absorbs water molecules from the environment essentially through the amorphous phases.

The amount of water absorbed at a given temperature increases with the environmental relative vapour pressure (see figure 23).

As it emerges from the trend of the curve shown in figure 24 the glass transition temperature (T_g) of keratin fibres (the curve refers to wool fibres) decreases with the increase of water content (regain%). This behaviour indicates that water is a strong plasticiser agent for keratin amorphous materials [22].

Moreover it must be pointed out that the presence of water often make easier the degradation action of other chemical environmental agents by participating directly to many kind of deleterious reactions.

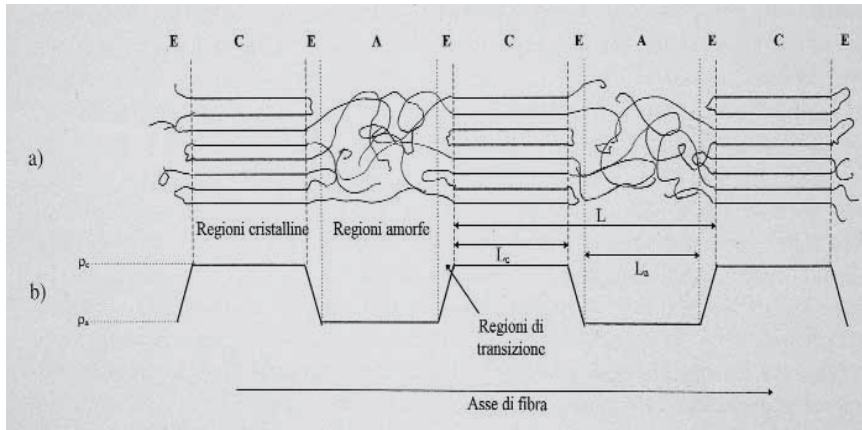


FIGURE 22: Molecular model of a generic natural fibres where crystalline and amorphous regions alternate along the fibre axis [25,26].

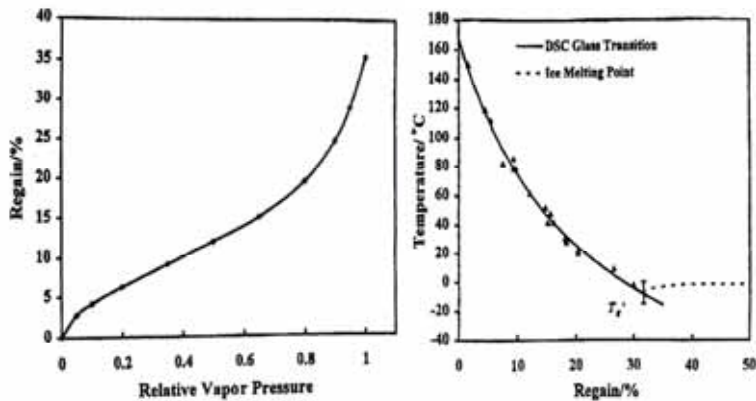


FIGURE 23, left: Isotherm curve of water absorption for keratin wool fibres (regain=the ratio between the weight of water uptake and the weight of the dry fibre) [16, 24, 25].

FIGURE 24, right: Dependence of glass transition temperature of keratin fibres (from wool) from the water content [16, 24, 25].

An example of such type of reaction is described in figure 25. The mechanism foresees the following steps:

- i) Intermolecular bi-sulphur bonds are transformed by photochemical oxidation in sulphonic acid side groups;
- ii) Water determines an acid reaction of hydrolysis with the rupture of the adjacent peptide bonds. Consequently the macromolecules is broken in two parts and a molecule of cysteic acid is formed [12]

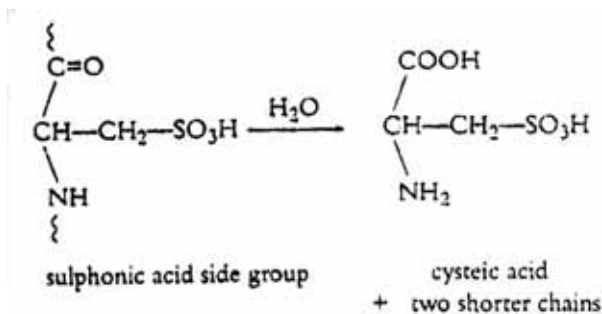


FIGURE 25: An example of acid induced reaction of hydrolysis of keratin (see text) [15].

Keratin fibres are particularly sensitive to the action of acid molecules as they can be the origin of hydrolysis degradation that lead to the rupture of chain macromolecules according to the general scheme of figure 26.

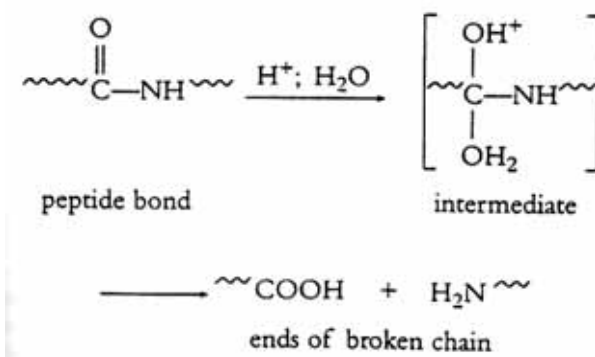


FIGURE 26: Acid hydrolysis of keratin macromolecules with rupture of intra-chain peptide bonds [15].

Alkalis result to be effective in inducing degradation processes to keratin macromolecules. Concerning such a topic, and with reference to wool keratins, P. Alexander and R. F. Hudson wrote: *< Alkali is more destructive and less selective than acid, so that smaller peptides are formed on alkaline hydrolysis on the peptide bonds. Some of the amino acids are decomposed, particularly cysteine, arginine... >* [27].

As shown schematically by figure 27, following alkali attack the cystine content in keratin fibres is reduced, contemporaneously the value of a generic property drops. Thus the content of cystine may be a measure of the entity of alkali-induced degradation [24,28].

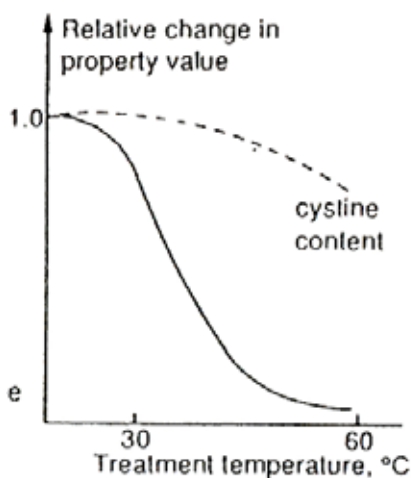


FIGURE 27: Diagrams showing the correlation between the reduction of cystine content and the decrease in the value of a generic property with the temperature at which the alkali attack is realized in the case of keratin based materials [28].

--- Biodegradation of keratin

Keratin fibres are attacked by micro-organisms (bacteria and fungi) able to produce enzymes that specifically act as catalysts of reactions causing the rupture of disulphide and peptide bonds. The presence of absorbed water makes easier the entire process of biodegradation [15].

It has been demonstrated that the optimum conditions for the growth of fungi or mould on keratin fibres are the following:

- pH = 6.5-8,5;
- Temperature 15-40C°;
- Relative humidity > 75% [15].

In the case of wool fibres, as shown by figure 28,

< mildew fungus produces filament hyphae and spores that attack cuticle cells: Once infected, they begin to lift off and curl up, sometimes freeing cortical cells > [15].

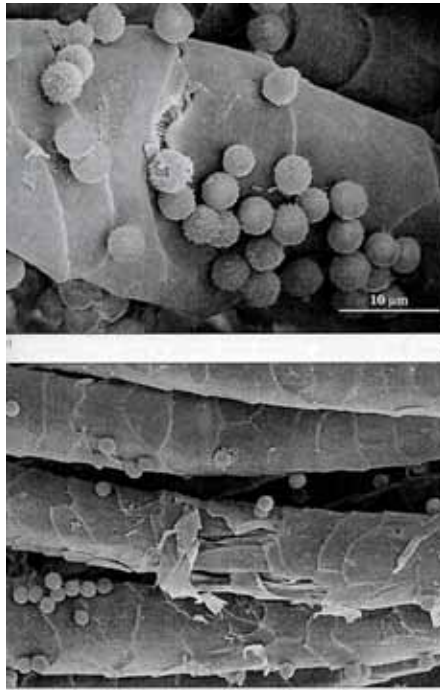


FIGURE 28: Scanning electron micrographs showing the attack of the fungus, *Aspergillus flavus*, on keratin wool fibres [15].

Suggested measures for the conservation of objects in pressed horn

For a proper conservation of items in horn the following elements should be taken under consideration:

- Horn artefacts are susceptible to bacterial and fungal growth.
- Alkaline and reducing environments will break down the disulfide linkages as well as the hydrogen bonds.
- Hot-cold and dry-wet cycles, and fluctuation in relative humidity may cause de-lamination and cracking as result of dimensional changes.
- Horn and hoof objects are also subject to insect attack due to their protein nature [29].

In reference [29] is reported an example of consolidation of badly delaminated artefacts by using commercial formulations (Rhoplex AC-33, or Acrysol WS-24) based on acrylic emulsions or colloidal dispersions [29].

Interesting artefacts in horn, manufactured in antique and modern times are reproduced in the figures 29 and 30. These items demonstrate that pressed horn and hoof are still now a days used for making objects with high added value especially as far as the design is concerned.



FIGURE 29: Artefacts in pressed horn. Left, horn brushes, 19th / early 20th century [30].
Right, a cigar pen made of both the buffalo horn & the deer antler [31].



FIGURE 30: Modern artefacts in pressed/carved horn.
Left, buffalo horn in 18k gold chain with earrings [32].
Right, eyeglass frame made in buffalo horn [33].

REFERENCES

- 1) a) <http://www.mernick.org.uk/victplas.htm>, (2008).
b) <http://www.chemistryexplained.com/Pl-Pr/Plastics.html>, (2008).
c) C. R. Cantor, P. R. Schimmel < *Biophysical Chemistry* >, Part-1, W. H. Freeman and Company, New York (1999).
- 2) <http://www.moldrek.com/Immagini/proteine.jpg>, (2008).
- 3) <http://en.wikipedia.org/wiki/File:2-amino-acids.png>
- 4) www.molecularlab.it/forum/topic.asp?whichpage, (2008).
- 5) www.minerva.unito.it/SIS/prioni/proteine.html, (2008).
- 6) A. L. Lehninger < *Biochimica* >, Zanichelli, Bologna (1984).
- 7) http://www.mtblanco.com/MtBlanco_com_Images/Catalog_Chap2/MtBlancoCtlg2BuffaloHornM.jpg, (2008).
- 8) J. Harry DuBois < *Plastics History USA* > Cahners Books, Boston (1972).
- 9) A. Schaverien, in *plastiquarian* no.22, a bridged version of a talk given to PHS members in (1999).
- 10) www.morninggloryantiques.com/collectVictJet.html, (2008).
- 11) www.morninggloryjewelry.com, (2008).
- 12) -a) [aupload.wikimedia.org/wikibooks/en/9/9a/Anatom](http://upload.wikimedia.org/wikibooks/en/9/9a/Anatom), (2008).
-b) R. J. Block, *J. of Biological Chemistry*, Downloaded from www.jbc.org by on January 1 (2009).
-c) T. L. Hieronymus, L. M. Witmer, Ryan C. Ridgely, *Journal of Morphology*, **267**, 1172 (2006). http://www.oucom.ohiou.edu/dbms-witmer/Downloads/2006_Hieronymus-Witmer-Ridgely_rhino_horn.pdf.
- 13) www.newworldencyclopedia.org/entry/Keratin, (2008).
- 14) E. Martuscelli, < *Le fibre di polimeri naturali nell'evoluzione della civiltà: le fibre di seta* >, Monografie Scientifiche, Serie Scienze Chimiche, CNR, Roma (1999).
- 15) A. Timar-Balazsy, D. Eastop, < *Chemical principle of textile conservation* >, H. Butterworth, Boston (1998).
- 16) E. Martuscelli, < *Relazioni proprietà struttura nelle fibre di lana* >, CAMPEC - Collana di diffusione e trasferimento, Vol-1, Napoli (2003).
- 17) <http://www.newworldencyclopedia.org/entry/Alanine>, (2008).
- 18) <http://www.economicexpert.com/a/Keratin.html>, (2008).
- 19) www.scibio.unifi.it/.../proteine/proteins21.h (2008).
- 20) P. R. Blakey, < *Fine structure of keratin* >, in *Applied Fiber Science*, edited by F. Happey, Vol. 3, pp. 483-515, Academic Press, London (1979).
- 21) M. Giua, C. Giua-Lollini, < *Dizionario di Chimica* >, Unione Tipografico-Editrice Torinese, Torino (1948).
- 22) A. Quye, C. Williamson, < *Plastics, collecting and conserving* >, NMS Publishing Limited, Edinburg (1999).
- 23) reviews.ebay.com/Victorian-Jet-and-Other-M, (2008).
- 24) E. Martuscelli, < *Degradazione delle Fibre Naturali e dei Tessuti Antichi* >, PAIDEIA-Firenze (2006).
- 25) E. Martuscelli, < *Nature and Structure of Natural Fibres* >, in Book of Lectures of Euro-Mediterranean Post-Graduate Advanced School on: «New Materials and Technologies for the Conservation and Restoration of Cultural Heritage Consisting of Natural Fibrous Polymers», pag. 17, edited by E. Martuscelli, L. D'Orazio, CNR – Naples, Italy (2002).
- 26) E. Martuscelli, *Chemical and Physical Behaviour of Natural Fibres*, (ibidem), p. 113 (2002).

- 27) P. Alexander and R. F. Hudson, < *Wool, its chemistry and physics* >, Reinhold Publishing Corporation, New York (1954).
- 28) K. Ziegler, J. A. Swift, in < *Chemistry of Natural Protein Fibres* >, R. S. Asquith, Ed., Wiley & Sons, London (1977).
- 29) J. A. Lauffenburger, *J. of American Institute for Conservation*, , **32**, Number 3, Article 1 (pp. 213 to 230) (1993).
- 30) flickr.com/photos/62906882@N00/1097736950, (2008).
- 31) pensbyjohn.com/db4/00319/pensbyjohn.com/_uima, (2008).
- 32) www.giselart.com/buffalojewelry.html, (2008).
- 33) www.alibaba.com/catalog/11502444/Eyeglass_Fra..., (2008).

2) BOIS DURCI, PROTEIN (ALBUMIN) BASED PLASTICS

In 1856 Francois Charles Lepage applied for a patent, in France, where he claimed:

< a new composition of materials which may be employed as a substitute for wood, leather, bone, metal and other hard or plastic substances > [1].

The composition and the manufacturing process, as described in the patent were reported as follows in reference [1]:

< His composition was made up from blood (from the Paris slaughterhouses) and powdered wood, mixed with colouring to simulate wood. He heated and stirred the mixture until it acquired the 'correct consistency' and then moulded it in a heated mould. The mixture was cured under heat and pressure yielding a hard, dense, glossy, moulding > [1].

M. Latry bought the Lepage patent and soon after at Grenelle in Paris the Societ  du Bois Durci was established. A wide range of articles were produced under the trade name of "Bois Durci" (meaning "hardened wood").

The items produced included: portrait plaques; plaques for attaching to furniture and pianos; picture and mirror frames; inkstands (encrier), pen trays; barometers and clocks; belt buckles and brooches; album and book covers; boxes; dishes; paper weights; statuettes; purses and caskets [2,3]. From molecular and structural point of view the Bois Durci composition may be suitably described as a composite materials made by a protein based continuous matrix (essentially albumin from eggs or blood) acting as binder (polymer-phase) and a discontinuous reinforcing phase made up by particles of ground wood flour (usually obtained from Brazilian Rosewood or Ebony wood).

After mixing the two ingredients the mixture (sieved sawdust mixed with 15 or 20%, by weight, of liquid blood and water) is dried and ground in order to have a fine homogenous powder.

Finally *< The powder is placed in a steel mould and compressed in a powerful hydraulic press whilst being heated by steam. The final product has a highly polished finish imparted by the surface of the steel mould > [2].*

The process for the manufacturing of items in Bois Durci was in part during the years innovated. In the Nouveau Manuel Complet du Mouleur by Lebrun and Magnier (Paris, 1917) the up dated process is described as follows:

< Wood flour, especially that made from rose-wood, is reduced to a fine powder and moistened with a quantity of blood mixed with water and dried in a stove at 50 to 60 degrees  C. The moulding is made in rings containing polished steel matrices to reproduce with the greatest fidelity various artistic creations.....

The pressure is obtained by means of a hydraulic press of high power. The plaques are gas-heated in such a manner that the heat is maintained constant during the entire operation.

The mould in their rings move in guides, so that no lateral movement is possible. During compression a stop fixes the distance travelled. The heating plaques are each furnished with separate gas supply, which moves with the movement of the plaque, following the pressure given to the different rings. Each gas tube is 'doubled' - that is, provided with a concentric tube leading in cold air - The annular space between the two carries the gas.... > [3].

The moulding powders of Bois Durci were shaped by using moulds made in malleable iron or in steel in order to reproduce exactly the fineness of details of the required design [4].

According to what reported in reference [5] in 1883 a factory was established in Sezanne, by the Hunebelle family, where items in Bois Durci compounds were produced.

The activity ended in 1926 when the factory was destroyed by fire.

In reference [6] it is reported that all the activities, including the production of items in Bois Durci in the factory established at Grenelle in Paris and the offices for commercialisation, through A. Latry & Cie. (au Marais) in Paris, around the end of the 19th century, were taken over by *La Manufacture d'Isolants et Objets Moulés*. Such Company continued to produce Bois Durci objects until ≈ 1920 .

Bois Durci compounds were substituted by newer plastics, such as celluloid and bakelite [6] even if literature data report evidences on the ground of which it is possible to conclude that objects shaped in Bois Durci were still in production after the First World War.

The continuous matrix able to bind the particles of saw dust is essentially constituted by the *Albumin*, a globular protein (molecular mass of 67 kDa) presents in human blood plasma at a concentration that varies between 30 to 50 g/L (see figure 1) [7].



FIGURE 1: Molecular model showing the globular structure of albumin protein [7].

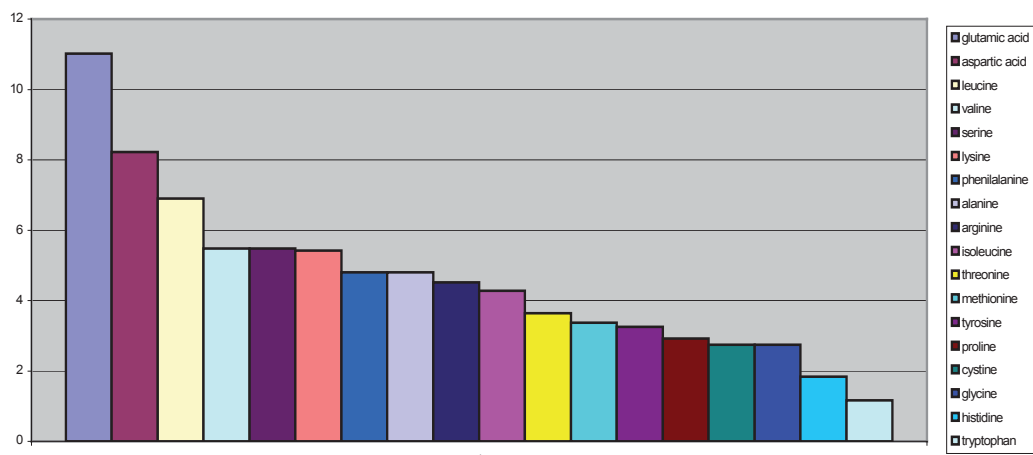
The function of such a protein is that of transporting small molecules in the blood [8,9]. Albumin is also a component of the albumen of eggs.

From the amino acid profile of albumin reported in table 1 it can be seen that along the macromolecules are present 18 different residues. Those of glutamic and aspartic acids are in major % followed by leucine, valine, lysine and serine; the others are in less %.

The binding activity of albumin is well known since many centuries. As matter of fact albumin or blood glue, composed of soluble dried blood with minor additives, is able to give strong, durable, and water resistant bonds when coagulated in plywood joints at 71-82 °C [10,11].

In order to understand the chemistry of the Bois Durci process it must be considered that cellulose, the major component of saw dust (see molecular structure in figure 2), may, through the side active functional groups, essentially hydroxyl, -OH, during the manufacturing process give rise to strong bonds with side reactive groups of albumin macromolecules. At elevated temperatures and under pressure such reactions cause the setting of the Bois Durci compound that, from a molecular point of view by forming an interconnected three dimensional network, behaves as a thermosetting material. This is the reason why, once shaped, objects in Bois Durci cannot be re-worked.

TABLE 1: Amino acid composition (%) of albumin protein (for 100g of product)*.



(*) From left to right: glutamic acid, aspartic acid, leucine, valine, serine, lysine, phenylalanine, alanine, arginine, etc.

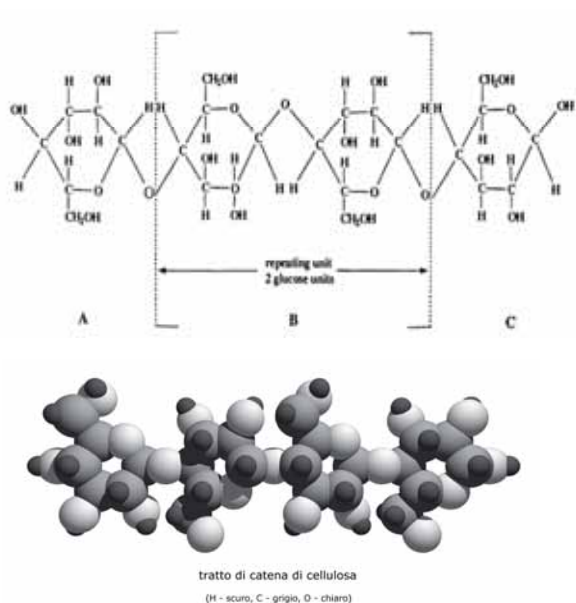


FIGURE 2: Chemical structure of cellulose chains. The anhydroglucose rings assume a *chair* conformation. The cellobiose repeating unit is indicated by arrows in the top image [12,13].

Several objects of artistic value made in Bois Durci, with different function, are shown in figures 3, 4, 5 and 6 [1,14,15,16,17,18].



FIGURE 3: Four early Bois Durci artefacts [1,14].



FIGURE 4: Boxes made in Bois Durci [15].



FIGURE 5, left: Plaque of Mozart in Bois Durci [16].
Right: Bois Durci Relief, Giuseppe Garibaldi 1855 [17].



FIGURA 6: Prayer book, Cover in Bois Durci, Bohemia 1884. The collection of the German Plastics Museum [18].

A relatively relevant number of objects in Bois Durci, showing a good state of conservation, are present in private and public collections or museums.

As above already reported this early plastic material was obtained by mixing albumen or blood with powdery fragments of hardwood (ebony or rosewood) produced when timber is sawn. According to reference [19] the sawdust was usually premixed with often-unknown vegetable, mineral or metallic powders; while other glutinous or gelatinous substances were added to blood or albumen. The compound, obtained first by allowing the sawdust powders to be soaked in the organic material diluted with water and then, after mixing, by drying, was moulded under heat and pressure. In such a conditions the material while is shaped set. After cooling a hard, dense, and glossy item was obtained. It is very probable that both composition of the compound and conditions of manufacturing act with positive synergy in inducing to Bois Durci decorative artefacts high resistance against degradation factors.

REFERENCES

- 1) <http://www.plastiquarian.com/boisdurc.htm>, (2008).
- 2) <http://www.mernick.org.uk/victplas.htm>, (2008).
- 3) http://www.mernick.org.uk/BDWeb/Documents/Manual_of_moulding_1917.htm.
Nouveau Manuel Complet du Mouleur by Lebrun and Magnier, Paris, (1917).
- 4) http://www.mernick.org.uk/BDWeb/Documents/Bois_Durci_in_1863.htm, (2008).
- 5) <http://www.mernick.org.uk/BDWeb/>, (2008).
- 6) G. Vermosen, < *Un plastique naturel - A natural plastic, 1855-1927* >, (2008).
- 7) http://upload.wikimedia.org/wikipedia/commons/6/6c/ALB_structure.png
- 8) http://en.wikipedia.org/wiki/Human_serum_albumin, (2008).
- 9) <https://www.sjhsyr.org/sjhhc/hidc07/Encyclopedia/1/003480.htm>, (2008).
- 10) < *Dizionario enciclopedico scientifico e tecnico* >, McGraw-Hill, Zanichelli, Bologna (1985).
- 11) C. A. Eckelman, < *Brief Survey of Wood Adhesives* >, <http://www.ces.purdue.edu/extmedia/FNR/FNR-154.pdf>, (2008).
- 12) E. Martuscelli, < *Degradazione delle Fibre Naturali e dei Tessuti Antichi* >, PAIDEIA-Firenze (2006).
- 13) E. Martuscelli, *Chemical and Physical Structure of Natural Fibres*, in Book of Lectures of Euro-Mediterranean post-graduate advanced School on: New Materials and Technologies for the Conservation and Restoration of Cultural Heritage consisting of Natural Fibrous Polymers, Edited by E. Martuscelli, L. D'Orazio, CNR, Naples, Italy (2002).
- 14) <http://www.mernick.org.uk/BDWeb/Brooches/Brooches.htm>, (2008).
- 15) <http://www.mernick.org.uk/BDWeb/Box/images/916X.jpg>, (2008).
- 16) <http://www.mernick.org.uk/BDWeb/Portraits/images/1016.JPG>, (2008).
- 17) <http://www.museumnetworkuk.org/materials/galleries/garibaldi.html>, (2008).
- 18) <http://www.deutsches-kunststoff-museum.de/index.php?id=77&L=2>, (2008).
- 19) <http://www.plasterarc.net/essay/essay/CassarB.html>, (2008).

3)CASEIN BASED PLASTICS

Casein is a complex protein (composed of several phosphor proteins, named: α -, β -, κ -) which is contained in the milk as colloidal dispersed micelles (50 to 600 nanometers in diameter) having a multi-molecular granular structure. Casein accounts for *ca.* 80% of the total protein in bovine milk but only 40% in human milk [1,2,3].

Every micelle is characterized by a very complex molecular structure that according to models reported in literature consists of casein aggregates wrapped up in soluble κ -casein molecules (see figure 1) [2].

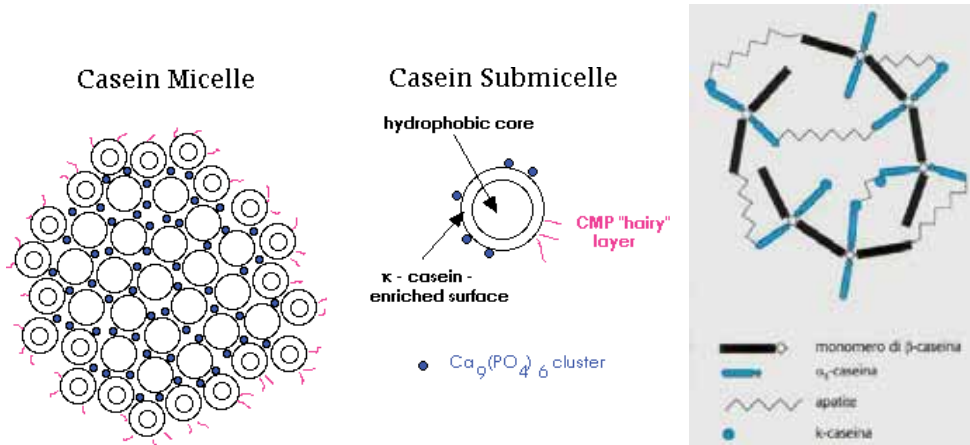


FIGURE 1, left and center: Micelle and sub-micelle models of casein in milk, see text [2].

FIGURE 2, right: molecular model of casein, a conjugated protein containing, besides C, H, O, N and S elements also P as ester of phosphoric acid. Such a ester in part is found in the inner regions of each units of α , β , κ - casein, as calcium and magnesium salts; in part as apatite, tri-calcium phosphate, acting as junction between, α , β , κ - casein units [1].

According to the micelle models calcium phosphate is uniformly distributed throughout the micelle, both within and outside the sub micelles [2].

The structure of casein micelle is described in reference [2] as follows:

< The next model shownIt shows a more or less spherical, highly hydrated, and fairly open particle. Polypeptide chains in the core are partly cross-linked by nanometer sized clusters of Ca phosphate; the internal structure gives rise to an external region of lower segment density known as the hairy layer, which confers steric and/or charge stability to native casein particles > [2].

From the data in figure 3, where the amino-acid composition of casein is reported, it emerges that casein macromolecules consists of a relatively higher number of residues of glutamic acid and of the proline amino acids. Contrary to what happen in keratins no disulfide bridges are present.

In 100g of dried protein the total content of nitrogen and phosphorus is 15.56 and 0,80g respectively [4].

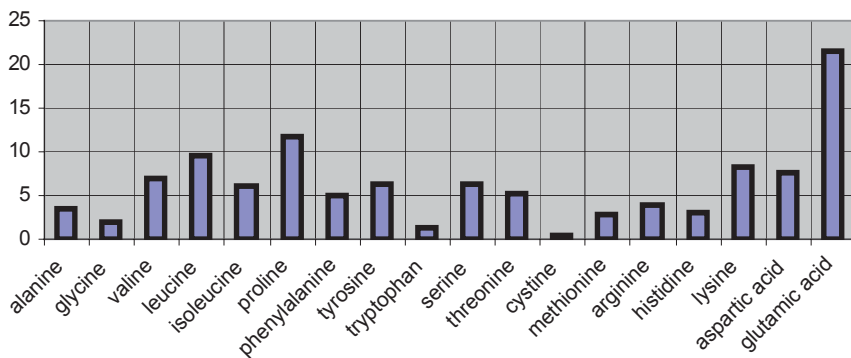


FIGURE 3: Amino acid composition of casein, values are expressed in g/100g of dried protein [4].

Casein is curdled from skimmed milk, in which is contained at a concentration of $\approx 10\%$, by using a natural specific enzyme called “rennet” [extract of calf stomach; contains the enzyme *chymosin* (rennin)] which clots milk. [5]. Casein may be also precipitated from skimmed milk by acidification.

At the beginning casein was applied as sizing or coating agent in the fabrications of industrial products such as paper, glue and paint. The discovery of the hardening effect of formaldehyde on casein was the breakthrough that allowed the development of methods suitable to obtain casein plastics.

The history of plastics based on casein begun in 1897 when two Germans W. Krische (a printer of Hannover) and Adolph Spitteler, invented the solution or wet process method. This technology was perfected in England where the so-called “*Dough-Method*” was largely developed.

The details of casein process following the dough method as described in reference [6] are hereafter textually reported.

< The process commences with milk which has been machined skimmed to remove as much cream and fat as possible. This is placed in a pan fitted with heating and cooling arrangements and a stirrer, and brought to blood temperature, or 98°F. Rennet is added and mixed and a junket of curd forms. When this has gelled to correct stiffness the stirrer is started to break it up to a suitable form for washing.....The curd is now thoroughly washed to remove milk-sugar and salts, and the washed casein is pressed and partly dried at low temperature until it contains the right % of water to make a workable plastic. Pigments are added...at this stage...together with any dyes, dissolved in...water, and... incorporated with the casein in a dough mixer. Such mixing is not sufficient to produce good plastic with a minimum amount of water and the next process is to extrude or squirt the mass several times.....in order to mix and emulsify it thoroughly. The mixture is now extruded into rods or bars and allowed to dry a little. If sheets are required, the rods are placed in a heavy frame and pressed by an hydraulic press.....The sheets, rods or bars are still plain or coloured casein, which when dried would be useless. They are therefore soaked in 5% formaldehyde for several days...until the formaldehyde reaches and reacts chemically with the casein, in the centre of the mass, and makes it insoluble in water as well as tough and strong. The pigments and dyes must be such that they are not affected by the formaldehyde.

The goods are still saturated with water containing a little formaldehyde, and are dried until they contain an amount of water such that they will never shrink nor swelldue to the gain or loss of moisture.....Moulded articles are produced from a blankThe blank is first softened and heated by immersion in....boiling water, and then ...pressed in a hot mould at a little over 212°F...> [6].

The curing with formaldehyde, due to the reactivity of such substance with functional groups present along the protein macromolecules of casein, lead to the formation of a three-dimensional network that is not easy to be penetrated by water molecules.

Following this treatment with formaldehyde casein loses most of its thermo plasticity while its resistance to water is increases.

< The molecules have been tied together securely by the formaldehyde; their movement relative to each other is restricted and water has difficulty in forcing its way between molecules > [5].

It is interesting to observe that when rods and sheets of casein are cured they become warped *< but the material retains sufficiently plasticity to allow it to be forced back into shape by pressure > [5].*

The several phases of casein process are depicted in figure 4 following the description published by J. Gordon Cook in its already cited book [5].

Some of the most relevant positive characteristics of casein are hereafter listed:

- Easy to handle and not inflammable;
- Easily sawn like wood, turned, drilled and chiselled with the normal woodworking tools;
- Simple made in the smartest colours by using different kind of pigments;
- Brilliant appearance by polishing [5].

By using suitable pigmentation techniques it is possible to produce casein-based items imitating tortoiseshell, pearl, jade or amber. By mixing casein with metal powder, artefacts with metallic lustre may be realized.

In reference [7] the positive characteristics of casein are described as follows:

< Casein has been described as "the most beautiful of plastics" and was produced in a wide variety of colours including delicate pastel shades, pearls and mottles, especially those imitating tortoiseshell and horn. The material also readily takes a surface dye and this process was extensively used to produce fashionable colours at short notice and for two colour effects by selectively cutting back the dyed surface layer. Casein plastics take an attractive polish which can be achieved mechanically with abrasives (except for surface-dyed material) or chemically by immersion in hot, hypo chlorite solution - known as dip polish > [7].

Hardened rods, sheets or blocks of casein for plastic applications were first produced in Germany and France during the early years of the twentieth century when they were commercialised under the trade name *Galalith*, successively they were fabricated and sold as *Erinoid* in Britain by the *Erinoid Company*, located in Gloucestershire, since 1914 [5,6].

< The hardened material can be moulded as thermoplastic but the stock sheet; block or extruded rod sections are usually machined to final shape > [6].

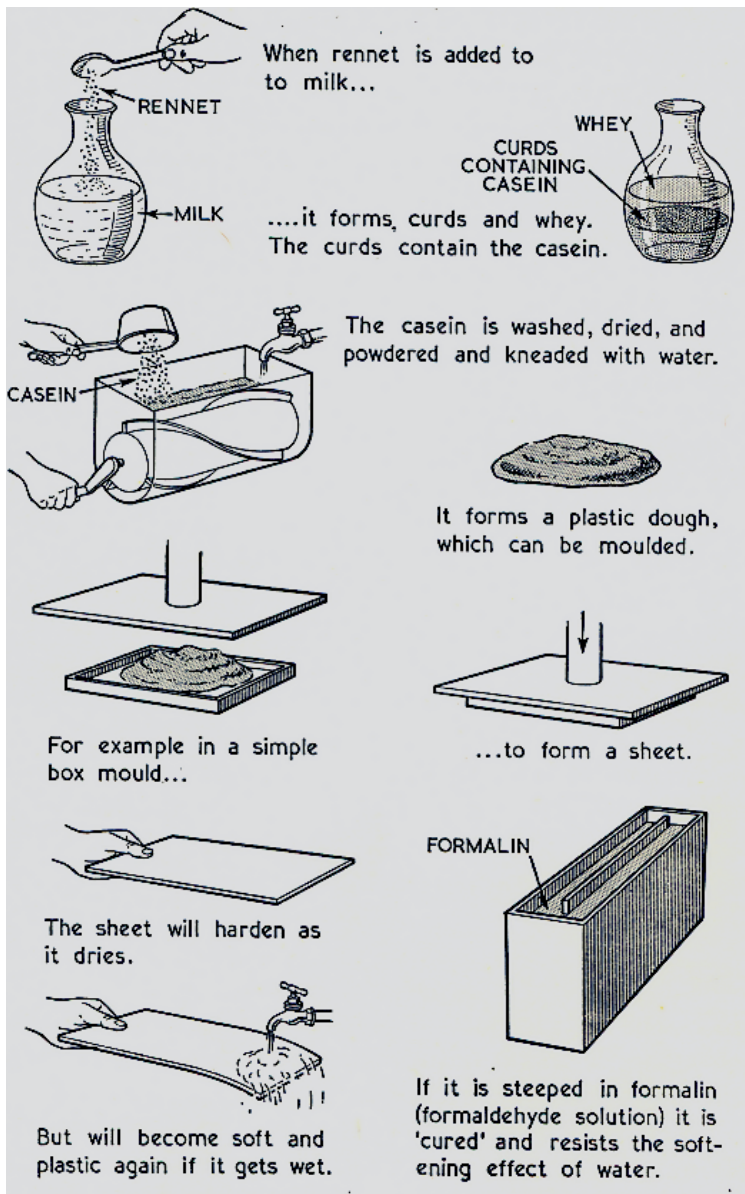


FIGURE 4: Processing phases of casein transformation [5].

< Casein plastic was first introduced to the world under the product name 'Galalithe' at the Paris Universal Exhibition in 1900. In the following years the development process of casein plastics was undertaken by two companies; Vereinigten Gummivarenfabriken in Germany and Pellerin & Orosdi in France. These companies merged under the one name, International Galalithe Gesellschaft Hoff & Company, in 1904. The company developed a manufacturing process that used dried casein granules, which became the universal standard in processing casein, and remained virtually unchanged throughout its history > [8-a].



FIGURE 5-a): Display card of samples of casein plastic, ≈ 1930s, produced by Erinoid Ltd of Birmingham. “Erinoid” was the British trade name for casein formaldehyde in the 1920s and 1930s [8-c].



FIGURE 5-b): The advertisement of modern, fine hand knitting needles in casein, with various coloration, still produced now a day by using traditional techniques of making by the Australian Swallow Needle Manufacturing Company [8-d].

Casein plastics, initially introduced in imitation of materials such as horn and semi-precious stone, were used for the manufacture of buttons and small decorative objects such as boxes and combs, artificial jewellery, knitting needles fountain pens, buckles, brooches, knife handles, etc.

< It could be produced in delicate pastel shades and, owing to its capacity to absorb acid dyes easily and uniformly, could be produced in an almost infinite range of colours and tones, including pearly effects > [8-b] (see figure 5-a and 5-b, [8-c]).

As shown by the display card in figure 5-a) and by the advertisement presentation in figure 5-b), < casein (defined as the “ most beautiful of plastics”, known as artificial horn because it closely resembled ivory and tortoiseshell, can be fabricated in a wide range of colours and can be finished and polished to a brilliant luster > [8-d].

Old artefacts in casein plastic are shown in figures 6, 7, 8 and 9 [7,9,10,11].



FIGURE 6: Table clock in casein, 1930, characterised by an innovative design [7].



FIGURE 7, left: A rare exemplar of pen in casein produced by Parker, model “*Ivorie*”, violet in colour, \approx 1922 [9].

FIGURE 8, right: Marbleised casein jewels, 1932 [10].



FIGURA 9: Casein ink well from 1920's [11].



FIGURE 10-left: “Redemption” casein and oil on canvas with wood (2008) [12].

FIGURE 11-right: Painting, “Landscape”, in casein and oil, by John Molnar, Toronto, Ontario, [13].

As already stated above casein found application also in the manufacture of binders for artistic paints, some examples are shown in figure 10 and 11 [12,13].

Degradation and conservation of artefacts in casein

Some of deterioration effects in artefacts made in plastic casein are related to the following phenomena:

- 1) After curing with formaldehyde casein is still able to absorb water, of course in a minor quantity. Migration of water molecules towards the surface may causes crazing and cracking.
- 2) Items in casein, being hygroscopic by absorbing water from the environment swell. This process may induce mechanical degradation effects.
- 3) Because of its protein nature casein is sensible to biological factors of degradation. In literature are reported cases showing that casein is sometimes liable to attack by mildew and moth larvae.
- 4) Casein is sensible to heat degradation.
- 5) Coloured artefacts easily undergo discolouration in contact with hot water [5].

Concerning the effects of water on the stability of casein items in reference [14] is textually reported:

< Casein plastics are plasticised with water and indeed will readily absorb and release moisture up to absorb ten per cent of the produced mass, expanding and contracting according to the humidity of their environment. This eventually causes a surface crazing, but is unlikely to cause complete disintegration > [14].

It has been observed that contact with water, acids, and alkalis may cause crazing to casein items. In some circumstances it has been found that when artefacts in casein get in touch with objects made in celluloid they are induced in to release part of the humidity absorbed. Such a water interacting with the nitrocellulose, main component of celluloid, favours its degradation with emission of nitric acid. The molecules of nitric acid in turn may deposit from the environment on the surfaces of the item in casein determining deep process of degradation in the protein chains [15].

A simple destructive test to recognize casein plastics is based on the fact that when casein burns a yellow flame with grey smoke and milk odour develops.

Casein plastics may be at first sight mistaken with Celluloid or Bakelite (an artificial and synthtetic plastics respectively).

A simple destructive test, to distinguish celluloid from casein, based on solubility assessment seems to be very convenient. As matter of fact acetone easily dissolve celluloid while it is unable to dissolve casein [15].

The massive production of casein plastics had a serious reduction all over the world, with the closure of most of the firms, due to strong regulations for the control of substances hazardous to health that required very expensive investment to eliminate the open formalin tanks and to adopt new treatment process for effluents [16].

Casein plastics, as shown by figure5-b), are still produced for making small objects, i.e. buttons, hand knitting needles,etc., in some countries as Austrialia and New Zealand, with large dairy interests [16].

A fine and elegant *Klingeltaster* (1900) stored at the German Plastics Museum, made in casein, is shown in figure 12 [17].



FIGURE 12: *Klingeltaster* made in casein (1900) stored at the German Plastics Museum [17].

REFERENCES

- 1) www.itisacqui.it/.../formagette/coagulazione.htm, (2008).
- 2) <http://www.foodsci.uoguelph.ca/deicon/casein.html>, (2008)
- 3) <http://en.wikipedia.org/wiki/Casein>, (2008).
- 4) T. A. Sundararajan and P. S. Sarma, *Biochem J*, **65(2)**, 261, February (1957)
- 5) J. Gordon Cook, < *Your guide to Plastics* >, Merrow Publishing CO LTD, England (1964).
- 6) H. W. Rowell, < *The Technology of Plastics* >, Plastics Press Ltd. London (1937).
- 7) www.pentrace.net/.../full_article.asp?id=276, (2008).
- 8) -a) <http://www.dhub.org/object/240409,industry>, (2008).
-b) S Lang, *Conservation Journal*, October (1996);
http://www.vam.ac.uk/files/file_upload/42730_file.pdf, (2008).
-c) www.sciencemuseum.org.uk/.../1007/10219851.aspx, (2008).
-d) <http://www.arnos.com.au/swallow/home.html>
- 9) P. Maggi, G. Negretti, F. Nencini, < *Penne da collezione, 1884-1990* >, Editoriale Wrist, Milano, (1993).
- 10) L. Scacchi Gracco, < *Pensieri di Plastica* > A. Mondatori Editore, Milano (1986).
- 11) D. Wells, < The History of Casein Use In Writing Equipment. Part 2 >, http://www.pentrace.net/penbase/Data_Returns/full_article.asp?id=276, (2008).
- 12) christinrossiart.googlepages.com/mythol, (2008).
- 13) www.artistsincanada.com/php/~painter_m.php, (2008).
- 14) < *Plastics, collecting and conserving* >, Edited by A. Quye, C. Williamson, NMS Publishing limited (1999).
- 15) J. Morgan, < *A Survey of Plastics in Historical Collections* >, Plastics Historical Society and The Conservation Unit of the Museums & Galleries Commission. <http://www.plastiquarian.com/survey/survey.htm>, (1994).
- 16) J. Morgan, < *The Centenary of Casein* >, reprinted from: Gloucestershire society for industrial archaeology journal for pages 44-50 (1999).
<http://www.gsia.org.uk/reprints/1999/gi199944.pdf>
- 17) <http://www.deutsches-kunststoff-museum.de/index.php?id=552&L=2>, (2009).

SECTION-2

SECOND- CHAPTER

PLASTICS AND RUBBERS BASED ON NATURAL PRE-FORMED POLYMERS: HARD (EBONITE) AND SOFT NATURAL RUBBERS

1) NATURAL RUBBER: SOURCE, PROCESSING, STRUCTURE AND PROPERTIES

Natural rubber is contained, as aqueous latex, in the exudates of the *Hevea brasiliensis* trees, which grow in tropical regions (South America, India, Thailand, etc.). By tapping it is possible to collect the latex from the tree trunks according to well-established modalities as hereafter reported.

< A tapper uses a sharp hook shaped knife to shave a thin layer of fresh bark from the tree. This exposes the latex vesicles. The cut is typically done at 25-30° to the horizontal, as this exposes the maximum number of vesicles. The same incision is re-opened the next time (typically the next day) by shaving off a small amount of bark. Virgin bark is exposed first working around in panels. The same area may be exploited again after about 7 years > [1] (see figure 1 [2]).



FIGURE 1: Tapping a rubber tree by using angular, semi-spiral incisions to collect rubber latex [2].

The process of obtaining raw natural rubber is based upon the following operations:

- 1) Coagulation of the suspended rubber particles by adding to the latex a dilute acid such as formic acid.
- 2) Removal by suitable washing of all protein components.
- 3) Removal of the excess water by rolling the coagulated rubber.
- 4) Rolling and shaping the resultant rubber in dried sheet [1,3].

Following the above treatments the raw rubber is ready for export and for further transformation in final products [1].

From molecular and chemical point of view the natural rubber is a *1,4-cis-polyisoprene* whose structure is described in figure 2 [3,4].

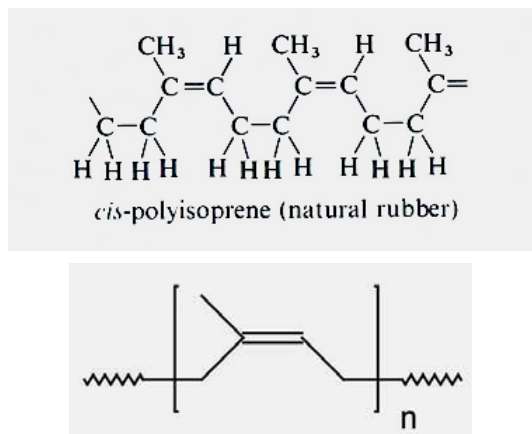


FIGURA 2: Natural rubber is a polymer whose chains have the molecular structure of: *1,4-cis-polyisoprene*. Below, in brackets, is shown the repetitive unit in the *cis* configuration [3,4].

Raw natural rubber shows the following characteristics:

- High molecular mass as well as large distribution (the molecular weights of rubber molecules range from 50,000 to 3,000,000; sixty percent of the molecules have molecular weights of greater than 1,300,000).
- Absence of intermolecular cross-links.
- Instability against temperature (it becomes soft and sticky in summer and hard and brittle in winter).
- Easily dissolved by many solvents.

The raw rubber, being not cross linked, shows elasticity at low temperatures (only in short range of temperature, from RT to about 60-70°C) while at higher temperatures and under deformation stresses the raw rubber presents a visco-plastic behaviour.

The type of response of raw rubber to mechanical axial deformation is described as follows in reference [4]:

< ...If a piece of raw rubber is stretched the molecules can extend as well as being able to slide over one another. If a stretching force is applied and then released quickly, the molecular springs will extend and return to their former position, bringing back the rubber to its original shape. This is the reason for the phenomenal elasticity displayed by rubber. If, on the other end, the raw rubber is held for some time in its extended state, the molecules may have time to disentangle themselves, in which case the rubber does not spring back to the precise shape it had originally. It has undergone some permanent deformation..... > [4].

The above properties accounted for the impossibility to transform raw natural rubber as obtained from coagulation of the latex exudates by rubber tree in suitable and commercial artefacts.

Two inventions determined the possibility to render the dry raw rubber workable and suitable to be transformed in useful products.

The first one was the invention (around 1820) by Thomas Hancock (from England, see figure 3) of the “*pickling machine*”, the prototype of the rubber mill and mixer later largely developed in rubber industry. With such apparatus (see figure 4) the raw material is masticated to a dough-like consistency while the average molecular mass is reduced following a de-polymerisation process of the *1,4-cis-polyisoprene* macromolecules (the average molecular mass may be lowered, from about 2500000 mau, to 1000000 with $T_g = -73^\circ\text{C}$ and a softening point of 28°C). As later appeared clear the masticated material having thermoplastic properties, may be easily compounded with additives and then suitable shaped and vulcanized (or cured).

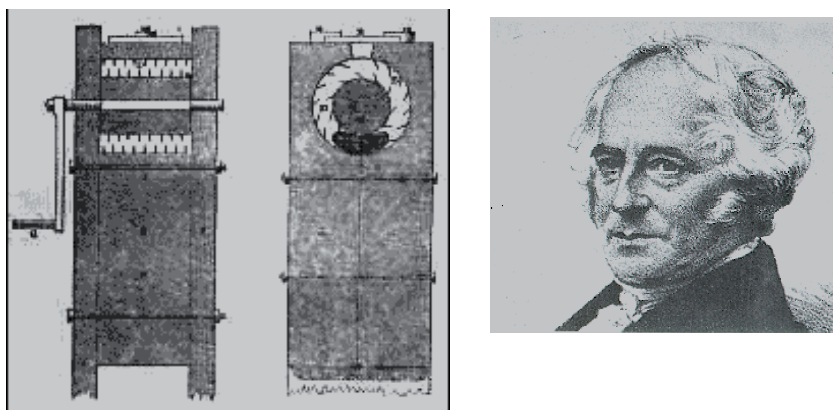


FIGURE 3, right : Thomas Hancock (from England) [5].

FIGURE 4, left: The mechanical processing of dry rubber began with Hancock’s “*pickling*” machine (1820), the prototype of the rubber mill and mixer [6].

The second important discovery, was accidentally made In 1839, by the American Charles Goodyear (1800–1860, see figure 5), who found that the properties of raw rubber could be strongly improved by mixing, at high temperature, with sulphur and litharge (lead oxide, PbO) [7].

Following such a process the raw rubber was transformed into a cross-linked polymer material characterized by:

- Insolubility and infusibility (at high degree of cross links);
- High stability to temperature variations.

The process discovered by Goodyear was named “*vulcanization*” (from *Vulcan*, the Roman God of fire and metal working) [7].

With the development of advanced mastication devices and suitable compression moulding heated presses the vulcanisation of the rubber becomes an industrial process.

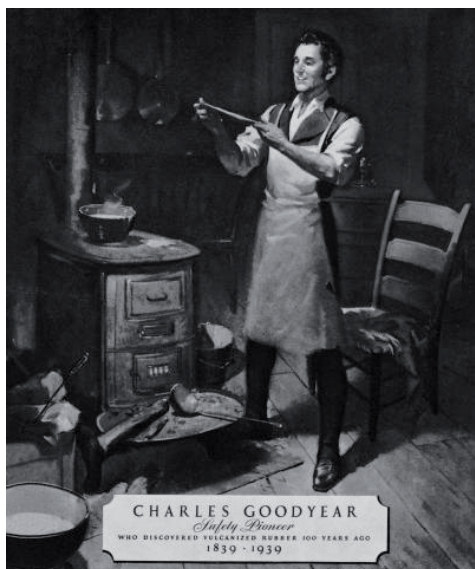


FIGURE 5: Portrait of the American Charles Goodyear (1800–1860) who in 1839 discovered the vulcanisation process of natural rubber [7].

The various phases of the process of rubber manufacturing, with reference to figure 6, are hereafter described.

a) The mixture, masticated rubber/sulphur, is placed into the open cavities of the mould kept at room temperature (the polyisoprene macromolecules are tangled together but not chemically bonded and the sulphur is homogeneously distributed in the rubber mass).

b) The press closes the mould forcing the material to take up the shape of the cavity where the temperature has been increased. *< In milled rubber the folded moleculesThey will slide over one another.....and milled rubber is sufficiently plastic to take up the shape imposed upon it by heated mould >*[4].

c) Chemical reactions occur only at high temperatures ($> 140^{\circ}\text{C}$). After the time necessary to the cure reaction being accomplished the press is open and the moulded parts are ejected from the cavities [4,8,9,10].

The development of mastication and vulcanisation processes determines the birth of the modern rubber industry, and although several innovations have modified Hancock and Goodyear original procedures, they remain basically very similar as the original ones.

From molecular and chemical point of view the vulcanisation of rubber, a very complex process, can be, partly at least, understood, by looking at the figures 7 and 8 [8,9,10].

In the course of vulcanisation sulphur reacts chemically with masticated rubber forming intra and intermolecular stable cross-links.

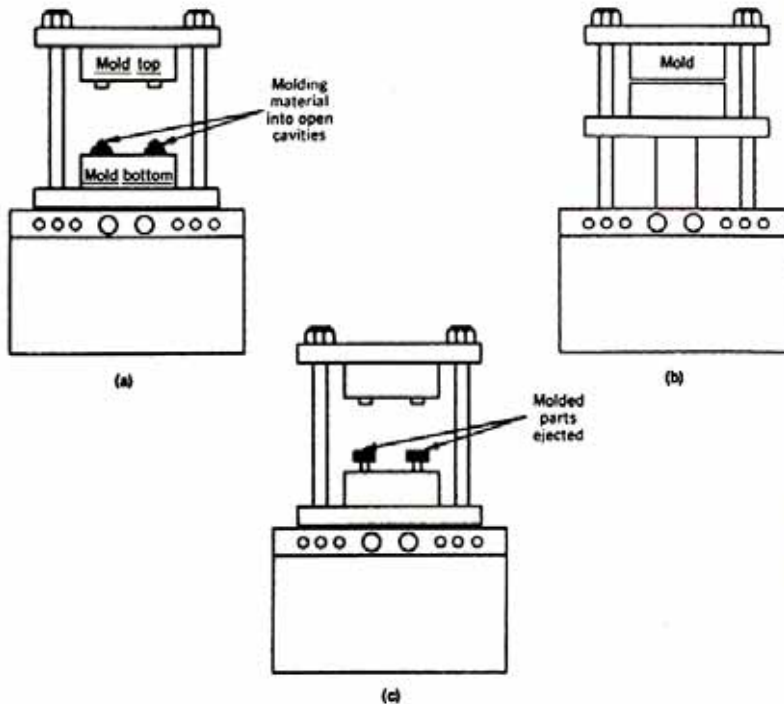


FIGURE 6: Heated press used for compression moulding process suitable to vulcanise and shape a starting masticated-rubber/sulphur compound. The operative sequences are described in the text [4].

The presence of such a cross-links prevents slippage of the chains thus rubber retains elasticity properties even at high deformation and also for a wide range of temperature. Moreover the vulcanized rubber shows a high stability against changes in temperature [11]. Thus following vulcanisation the raw rubber assumes the characteristics of an *Elastomer*, a material that according to reference [12] is defined as follows:

< a macromolecular material that returns rapidly to.....the initial dimensions and shape after substantial deformation by weak stress and release of the stress. Material that is capable of recovering from large deformation quickly and forcibly... > [12-a].

The elastomer property of natural raw rubber is mainly due to the *cis* configuration of the double bonds along the chains and to the fact that the high molecular mass macromolecules being highly coiled and contorted may be uncoiled by tensile stress. Nevertheless in order to prevent plastic flow of chains with loss of elastic recovery at relatively high deformation and to increase the stability against temperature, cross-links are necessary.

If the number of cross links is relatively low then the rubber is named “*Soft Rubber*” (see figure 7- left). In the case of a higher degree of vulcanisation the material obtained is called “*Hard Rubber*” [8]. The final properties of vulcanised rubber strongly depend upon the degree of cross-links formed (DC). It can be observed that with the increase of DC the values of both rigidity and strength also increase [12-b].

< *Temperatures of 140–180°C are used for modern vulcanization, and additives other than sulphur are often used. Accelerators permit the reaction to occur at lower temperatures and in less time, and antioxidants prolong the life of rubber products by reducing the deterioration that is caused by atmospheric oxygen (or ozone), which breaks covalent bonds and lowers the molecular weight. Reinforcing agents (e.g., carbon black) increase stiffness, tensile strength, and resistance to abrasion. Colouring agents and fillers are sometimes added* > [13].

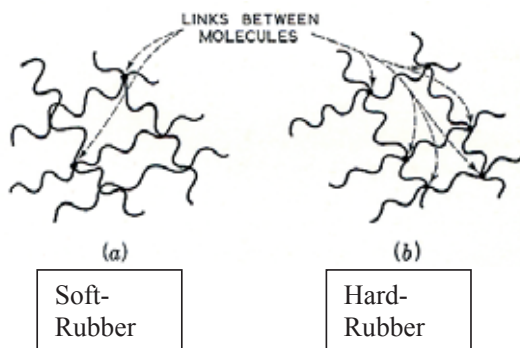


FIGURE 7: Following the vulcanisation process the sulphur reacts with rubber molecules forming intra and intermolecular stable cross-links. If the number of cross links is relatively low then the rubber is named “*Soft Rubber*” (see figure at left). In the case of a higher degree of vulcanisation the material obtained is called “*Hard Rubber*” [8].

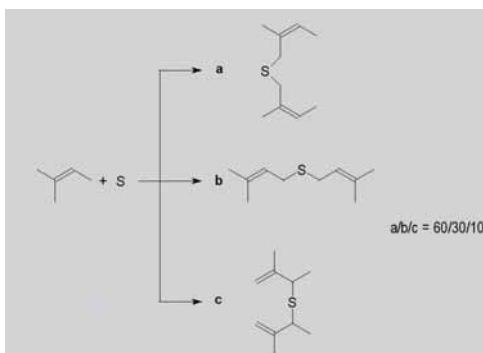
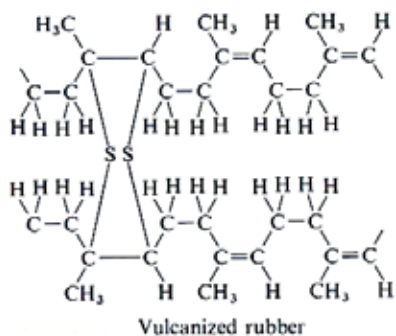


FIGURE 8: Possible chemical reactions involving, during vulcanisation, sulphur atoms and the double bonds present along the *1,4-cis-polyisoprene* chains [3,10].

2) HARD RUBBER (EBONITE): PROCESSING, STRUCTURE, PROPERTIES AND RELATED ARTEFACTS

Hard rubber, prepared for the first time in 1851 by Nelson Goodyear, brother of Charles, starting from a mixture of masticated rubber and a % of sulphur $> 30\%$ (named and commercialised as *Ebonite* or *Vulcanite*) can be considered the first thermosetting semi-synthetic plastics. As matter of facts the masticated-raw rubber containing the 30-50% of sulphur before the cure reaction may be processed as a thermoplastic polymer by using methods such as compression moulding, extrusion and injection moulding. After curing ebonite, like any hard rubber, being heavily cross linked, is a three dimensional networked material that as all thermosetting polymers cannot be thermally re-worked any more. Hard rubber is a solid body, thus it can be only worked by mechanical tools (carving, turning, cutting, etc.) [14,15].

The production of ebonite, started in the latter half of the 19th century, continued in the 20th centuries until the 1940s [16].

Ebonite (first mouldings were exhibited by both Hancock and Goodyear at the Great Exhibition of 1851), usually black in colour, found application in many different fields: combs, buttons, match cases, jewellery, ornaments, fountain pens, pipe stems, musical instruments, imitation of jet, mourning jewellery, electrical insulator, chemically resistant linings, etc..

< A reddish colour ebonite was used for denture plates until superseded by celluloid and acrylic. A reddish material rippled with black was popular about 1930 for fountain pen and pencil barrels. It was originally based on natural rubber but since the 1930s has been based wholly or partly on various synthetic rubbers > [17].

During the so called “*Victorian Era*” (the time when Queen Victoria ruled Great Britain, 1837-1901) many different styles of jewellery were developed, many of them used ebonite (see figures 9, 10, 11 and 12) [15,18,19,20,21]. As shown by figures 13 and 14, ebonite was widely employed also for making fountain pens and for the manufacturing of components for telephones [22, 23].

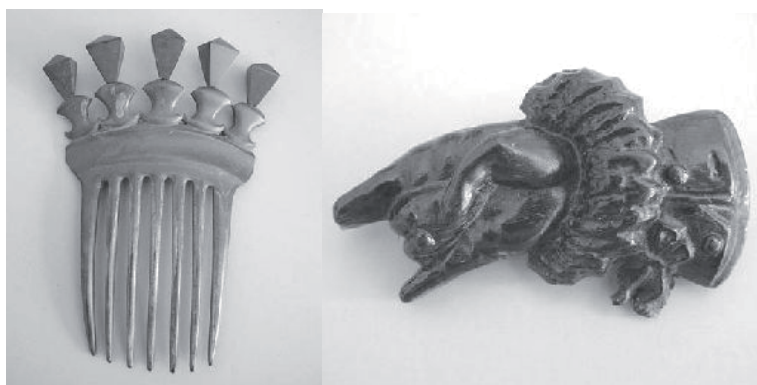


FIGURE 9: Artefacts in vulcanite manufactured during the *Victorian Era*. Left: hair comb. Right: hand brooch [18].



FIGURE 10: Objects in ebonite (Victorian Era) [19].



FIGURE 11: Victorian vulcanite hand and flower brooch. Roses and forget-me-nots wreath laurel sheaf symbolize love victorious [20].



FIGURA 12: Artefacts in ebonite/vulcanite produced between 1878 and 1900 [15,21].



FIGURA 13: Old fountain pens made in ebonite.
Left. Waterman pen with “coin filler” system in black ebonite (1913-1914).
Right. Waterman (1930s) advertises the new technology for making pens in coloured ebonite [22].



FIGURE 14: Ebonite was also used in the manufacturing of components for telephones (year: 1900), Plastics Museum Cannon for the Culture of Plastics [23].

From the above figures it can be understood why many artefacts in ebonite, at the present time, find collocation in museums and private collections. As matter of fact they represent evidences of the advent of a new industrial *Era* that made profit of new materials as well as of innovative technologies able to produce moulded products more rapidly and therefore more cheap than carved counterparts. Moreover by developing engraved die able to leave an embossed design was possible to mould items having an artistic and fine shape [24,25].

For this reasons the conservation of those objects, part of cultural heritage, is becoming an important issue.

3) DEGRADATION PHENOMENA IN ARTEFACTS MADE IN SOFT AND HARD RUBBER (EBONITE) AND MAIN SYMPTOMS OF DETERIORATION

Both soft and hard natural rubber, even if with their own specificity, following natural aging undergo chemical and physical changes.

Chemical changes derive from reactions that may determine at molecular level, chain scission, oxidation and cross-links. Such reactions are essentially *< initiated or accelerated by ultraviolet light, heat, oxygen, peroxide, acids, metal particles, and mechanical stress >* [26-a].

Physical modifications are mostly related to the capability of *1,4-cis-polyisoprene* to crystallize. Such a process, very slow at R T, can be accelerated by lowering the temperature (the rate of crystallization reach a maximum value at $\approx -25^{\circ}\text{C}$) [26-a].

The rate and the entity of both chemical induced degradation and of physical modifications will be dependent upon the composition of rubber, the degree of vulcanisation and the environmental conditions under which the samples have been exposed in the course of their service life.

According to reference [26-b)] in the case of sulphur vulcanised natural rubber the aging is the resultant of *< three distinct and potentially co-synchronous processes....*

1. *continuing sulphur chemistry*
2. *shelf ageing*
3. *atmospheric ageing >* [26-b)].

The first one (*continuing sulphur chemistry*) is related to the fact that even at RT chemical rearrangements occur in the mass of vulcanised natural rubber *< ...caused by the polysulphidic bonds which form the chemical cross links between polymer chains breaking and the loose ends re-attaching to either their original partner or another loose end (cross link reversion...).... The result is a slow "slippage" of the vulcanised which cannot be reversed although it can be minimized by the appropriate choice of cross linking agents, an option not available to the conservator >* [26-b)].

The process of *shelf ageing* is an oxidative degradation based phenomenon strongly influenced, besides by the oxygen, by the catalytic effects of heat, light, internal and external stresses or strains and pro-oxidant metals. The oxidation of a sulphur vulcanized natural rubber *< ...proceeds via at least one chain reaction sequence which introduces C-C and C-O-O-C cross links between polymer chains as well as C-O-O-C rings within the same polymer chain, and another set of chain reactions*

between oxygen and the sulphur atoms of the cross links or pendent groups. These two sequences of chain reactions can result in both chain scission and the formation of additional cross-links. The reactions between sulphur and oxygen can also, eventually, lead to sulphuric acid formation, a particular problem with ebonite > [26-b)].

In some samples it has been observed that the oxidation gives rise to the formation of a hard surface skin. *< As oxidation continues the chain breakdown may become more significant and the hard surface then softens and turns sticky > [26-b)].*

The catalytic action of UV-light is due essentially to the fact that the energy of such radiations is high enough to break C-H bonds present along the *1,4-cis-polyisoprene* chains. Radical species able to react with O₂ molecules are formed causing the occurrence of the same sequences of reactions observed in the case of direct oxidation [26-b)].

< Light-catalysed oxidation can result in an inelastic skin which, as it thickens, cracks in random directions and produces a pattern known as "crazing". In the early stages, in thin sheets, the effect has been called "light stiffening"..... In many real life vulcanises of reasonable bulk under ambient conditions, it seems that the ingress of oxygen is limited and, apart from the surface few millimetres or so, the bulk rubber remains in excellent condition > [26-b)].

Atmospheric ageing refers essentially to the degradation induced to rubbers by ozone attack. The mechanism of such a process, *< a simple bimolecular ozonolysis of the rubber olefin double bond being followed by immediate cleavage to give two carbonyl end groups >*, is different from that of oxygen-induced degradation.

The ozone degradation will produce, in stressed rubber, cracks oriented perpendicular to the direction of elongation [26-b,c)].

Atmospheric ozone reacts with the double bonds of rubber. First, according to the scheme of figure 15-top, an unstable ozonide compound is formed. Then the macromolecule is broken in two parts (the details of such a process has been described in a previous chapter) [27].

Generally the double bonds present along the macromolecular chains of cross linked rubber (CLR) are potential sites of degradation reactions caused by external environmental agents (light, especially UV-radiations , moisture, oxygen, temperature and chemical pollutants) [26-c)].

It has been demonstrated that the combined action of light and oxygen on CLR gives rise to the increase of the degree of cross-linking during the life of the artefacts. That is the reason why *< filter such as carbon black is introduced to exclude light from all but the surface, and other chemicals which readily combine with free oxygen atoms may be added > [26-a)].*

The joint attack by light, oxygen and moisture determines in the case of ebonite objects brittleness, discolouration and increase of matting [29]. The objects, usually black in colour, fade to a brown or greenish brown colour, *< vulcanite imitation jet jewellery in collections was often faded through exposure to light > [29].*

It has been observed that for red brown coloured items in ebonite the symptoms of discolouration may be masked.

Traces of metal contaminants (copper, chromium and iron), present as impurities in some of the additives or fillers used for formulating the compound, may determine the acceleration of the rate of degradation of the rubber.

Some of the degradation factors and related damages observed in samples of hard and soft natural rubber, occurring during service life or during storage, are hereafter listed:

- Cross links reversion; ■ Chemical attack; ■ Heat and oxidation; ■ Mechanical-oxidative fatigue;
- Ozone cracking; ■ Sunlight crazing; ■ Abrasion [26-b)].

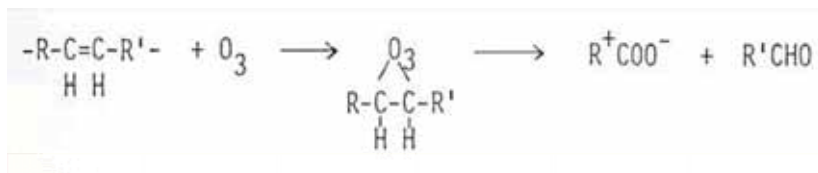


FIGURE 15: Degradation of rubber by ozone: possible reactions bringing to chain scission [27,28].

On exposure to light and moisture, due to the presence in the ebonite of a large quantity of bonded sulphur atoms but also of a certain amount of non-reacted sulphur atoms, sulphur compounds are produced which can be oxidized by atmospheric oxygen to sulphur oxides gases. These oxides in presence of environmental water vapour transform in sulphuric acid. This explains the occurrence on the surface of degraded objects in ebonite of droplets or film of sulphuric acid [30, 31].

Concerning the above phenomena J. Morgan, wrote:

< Care should be exercised when handling because of the possibility of surface acidity. Copper accelerates degradation and this effect was often observed with vulcanite objects having brass inserts or screws, eg brass inserts on a Wimshurst machine had promoted severe degradation near the inserts, as well as themselves being corroded through the acid produced. Similar effects were observed with various military apparatus where metals and vulcanite were in combination > [30].

The conservationists of cultural heritage use to define materials that behaves like CLR as “*malignant materials*” because they have the capacity to induce, following the emission of degradation products, chemical deterioration in objects located in the proximate environment [29].

As above mentioned the oxidation of both soft and hard rubber is catalysed by the presence of metals especially copper [31].

< A common use of hard rubber was as an electrical insulator in early telegraphy equipment and much corrosion occurs where the hard rubber is in contact with copper alloys used as conductors > [29].

In order to reduce the susceptibility of hard and soft rubber to environmental oxidation, antioxidants or stabilizers additives have been used (phenol, hydroquinone, alkyl naphthylamines, etc.).

At the early stages in the manufacturing of rubber compounds volatile and coloured stabilizers were often used.

The damages that the migration/emission of such stabilizers may determine are described as follows in reference [29]:

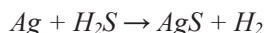
< ...It is very common to find bright yellow stains on tissues and plastics used for wrapping and storing early rubber objects, especially dark coloured ones where the yellowness of the stabilizer was not so apparent. Rubber objects that have these volatile yellow antioxidants must not be stored too close to, or sealed up with, other objects that could absorb these additives and be stained > [29].

Other additives used for making rubber items include materials as:

- Metal oxide as zinc oxide (used as accelerating agents of the vulcanisation);
- Waxes;
- Zinc stearate;
- Fillers.

Waxes and zinc stearate being soluble in rubber may migrate to the surface giving rise to the formation of blooming effects as well as to crazes [3].

Hard rubber, with its high sulphur content, produces, following degradation effects, also reactive sulphur compounds (i.e. H_2S) capable to transform, for example, silver in silver sulphide (tarnish effect) according to the following reaction:



Such emitting capacity may be used in an unambiguous spot test for the identification of ebonite. The test, (discovered by Daniels and Ward in 1982) make profit of the reactivity of H_2S against a reagent composed of Iodine/Sodium azide that gives rise to bubbles development in the reagent [29]. According to reference [4], natural rubber suffers the contact with oils with petroleum, vegetable or animal origin. On the contrary, it shows good resistance against acids and bases.

It is interesting to point out that oxygen, by causing the formation of additional cross-links, determines the decrease in the solubility of the CLR.

From what above reported it emerges that objects in rubber must be stored in place where light and oxygen must be excluded.

Fourier Transform Infrared spectroscopy (FTIR) and nuclear magnetic resonance (^{13}C NMR) are useful techniques for the molecular and structural characterization of samples of natural rubber (see examples of spectra in figures 16 and 17) [32,33].

S. A. Connors et Al. demonstrated the usefulness of Microscopy-Fourier Transform Infrared Spectroscopy (Microscopy-FTIR) and Photoacoustic-Fourier Transform Infrared Spectroscopy (PAS-FTIR) techniques for the evaluation of degradation of samples of vulcanised rubber which have been artificially and naturally aged [32].

Microscopy-FTIR spectra (attenuated total reflectance, ATR mode) of samples of vulcanised rubber, unexposed, artificially aged and naturally aged (the latest sample, recovered from a washing machine of 1910, showed clear symptoms of cracking and stiffness) are shown in figure 18, top, centre and bottom respectively.

The spectra of unexposed and artificially aged vulcanised rubber result to be very similar; they are characterized by the typical peaks of cis-1,4-polyisoprene.

< These include strong peaks in the region from $3000-2800cm^{-1}$ (aliphatic CH_2 and CH_3 stretch), a weak, broad peak between $1700-1500cm^{-1}$ ($C=C$ str.), two strong peaks between 1450 (CH and CH_2 def.) and $1370cm^{-1}$ (CH_3 def.), and a strong peak around $830cm^{-1}$ ($R_2C=CHR$) > [32].

The spectra of the vulcanised rubber naturally aged, see figure 18-bottom, does not show the peaks of cis-1,4-polyisoprene. According to the Authors this could be originated from the difficulty to realize a good contact between the sample and the ATR crystal [32].

From the PAS-FTIR spectra, as shown by figure 19, it was observed a clear peak at $1750cm^{-1}$ in the diagram of artificially degraded sample indicating the formation of carbonyl groups following oxidative reactions [32].

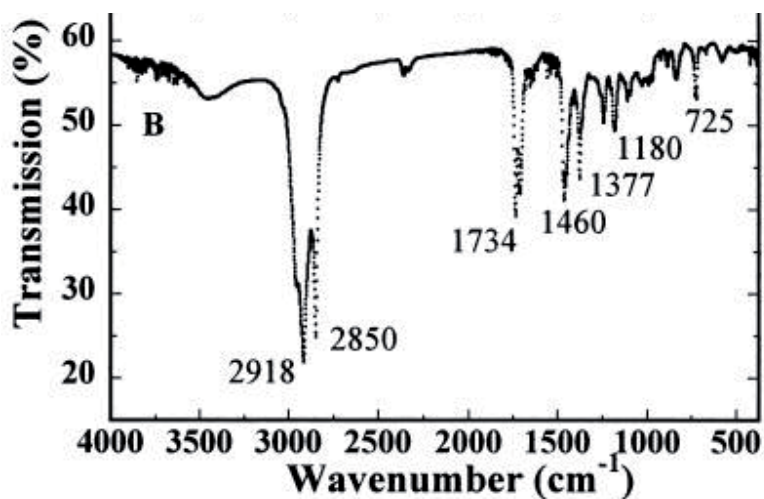


FIGURE 16: Typical FTIR spectra of natural rubber in potassium bromide disc, in the spectral range of 4,000 to 370 cm^{-1} at a resolution of 2 cm^{-1} . Characteristic bands for cis-1,4-polyisoprene are indicated together with their wave numbers [33].

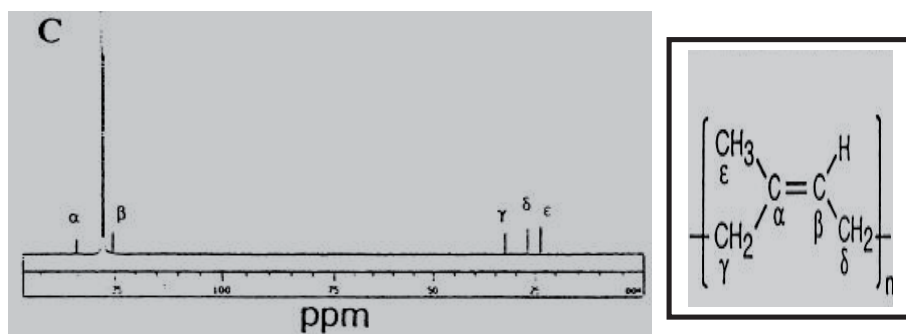


FIGURE 17: ^{13}C NMR spectra of natural rubber in C_6D_6 . Representative peaks for cis-1,4-polyisoprene are indicated as α through ϵ . The corresponding chemical groups involved are shown in the right side of the figure [33].

In the PAS-FTIR spectra of naturally aged sample the typical peaks of cis-1,4-polyisoprene are observed together with peaks due to the presence of water. The broad peak between $1250\text{-}1000\text{cm}^{-1}$ is accounted for by C-S and S- CH_2 bonds wag ($1270\text{-}1220\text{cm}^{-1}$) and S- CH_3 rock ($1030\text{-}960\text{cm}^{-1}$) [32].

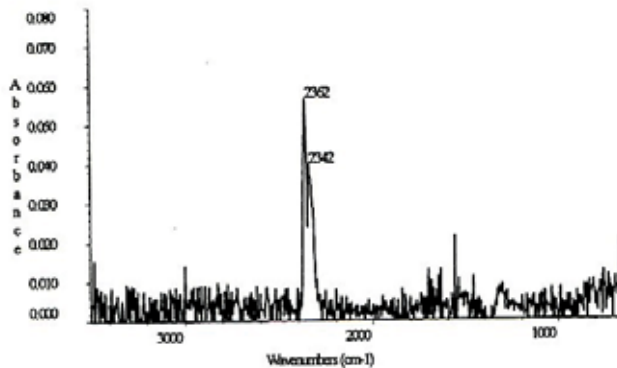
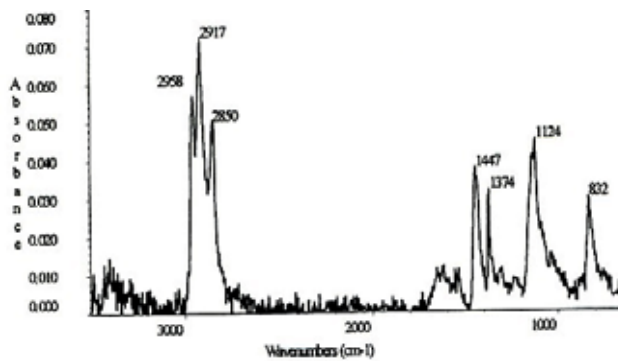
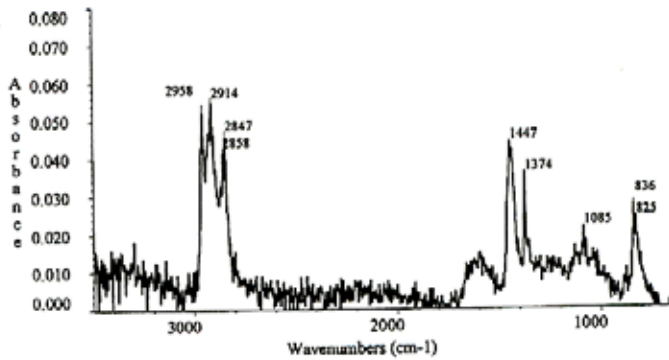


FIGURE 18: Microscopy-FTIR (ATR) spectrum of: Top, unexposed vulcanised natural rubber specimen; Centre, vulcanised natural rubber sample artificially degraded; Bottom, naturally aged sample of vulcanised rubber [32].

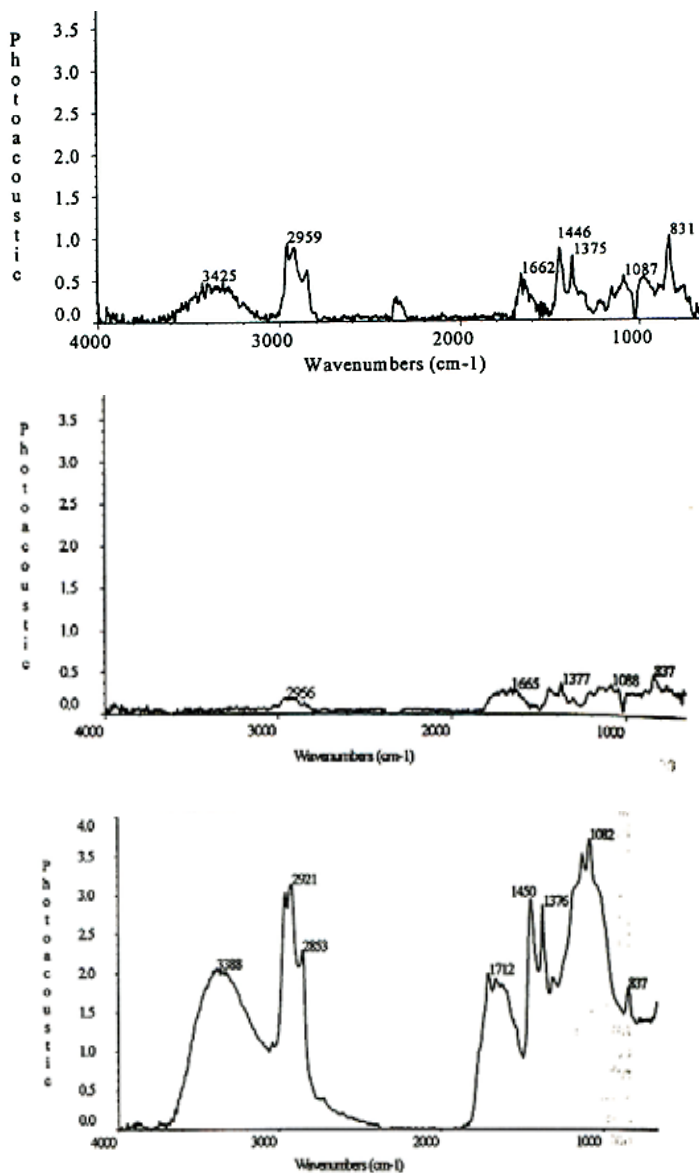


FIGURE 19: Photoacoustic-Fourier Transform Infrared Spectroscopy (PAS-FTIR) spectrum of:
Top, unexposed vulcanised natural rubber specimen;
Centre, vulcanised natural rubber sample artificially degraded;
Bottom, naturally aged sample of vulcanised rubber (recovered from a washing machine of 1910) [32].

The reported data showed that the techniques used, despite the presence of carbon black as filler, are useful for the evaluation of degradation of aged vulcanised rubber artefacts as well as of items manufactured by using elastic slightly cross linked natural rubber [32].

As mentioned above not heavily vulcanized rubbers, at relatively low temperatures, may crystallise becoming more brittle. It has been found that this process is much more common in the case of old samples where often, erroneously, the brittleness has been attributed to oxidation effects.

The phenomenon of crystallization is reversible. As matter of fact by heating the crystallized rubber at a temperature higher than that of crystallization it melt returning in the previous physical conditions.

<natural rubber..., will crystallize slowly at cool room temperatures (10 - 15°C) but then..... it can only be melted by heating to about 30°C above the temperature at which crystallization took place. An article which has undergone long-term storage in a freezer will therefore thaw quite quickly when brought to normal ambient temperature but if a similar article has been stored in a refrigerator at, say, +5°C it will remain brittle until it has been warmed to 35 - 40°C.....so any rubber article which has become brittle after prolonged storage should be warmed briefly to see if it will regain its elasticity. If the article has become brittle through oxidation, this will do no further significant damage > [34].

M. T. Baker was able, by using Differential Scanning Calorimetry (DSC) to quantify, in samples of natural aged artefacts in ancient Mexican rubber belonging to a collection at the America Museum of Natural History in New York and in rubber specimen unaged and artificially aged, the heat of melting, due to crystallization process, as function of the crystallization time.

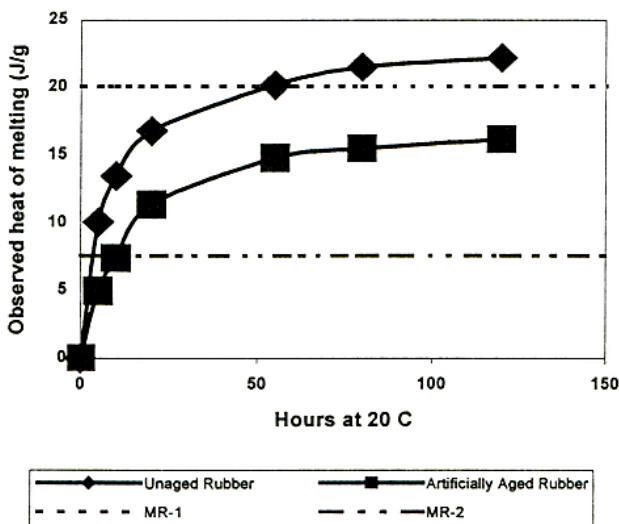


FIGURE 20: Observed heat of melting for artificially aged and unaged samples of rubber as function of crystallization time [26-a)].

From the results, reported in figure 20, the Authors reached the following interesting conclusions [26-a]):

< *The heats of melting of the "new rubber", when compared with the heat of crystallization of rubber (67.3J/g) suggest that the rubber achieves, at most, 25-35% crystallization. By applying this range to Mexican rubber the amount of non-rubber filler could be estimated at between 50-90% filled (by weight) for MR-1, and 20-60% filled for MR-2 (where MR-1 and MR-2 are two different samples of Mexican old rubber)* > [26-a)].

The experiments performed showed that DSC technique allows the determination of the filler amount present in a rubber samples and moreover to have an idea of how much crystallisable rubber is available in deteriorated specimen [26-a)].

This last information is interesting in forecasting the degree of brittleness potentially induced by crystallization in rubber samples following low temperature storage.

4) BIODEGRADATION OF SOFT AND HARD RUBBER

In reference [35] the concept of biodegradation, from a general point of view is expressed as follows:

< *Biodegradation is a natural process by which organic compounds in the environment are converted to simpler compounds mineralised and redistributed through the elemental cycles. Interestingly, micro-organisms play a central role in the process of biodegradation ...*> [35].

Some bacteria and fungi have the capability to specifically biodegrade natural rubber. Additives influence the biodegradation processes of rubber: some of them may promote biodegradation, others may inhibit biodegradation.

Bacteria able to degrade rubber may be divided into two groups:

I) The first group < *belongs to the Actinomycetes that form clear zones on latex plates and metabolize polyisoprene by secretion of one or more enzymes. Most of the representatives of this group show weak growth on natural rubber and synthetic rubber*> [36].

ii) The bacteria of the second group belong to the *Corynebacterium-Nocardia-Mycobacterium* families. < *...does not grow on latex plates and requires direct contact with a polymer. However, they have shown relatively strong growth on polyisoprene* > [36].

According to literature data the bio-degradation of natural rubber is based on a mechanism based on the oxidative rupture of the double bonds present along the polyisoprene chains. The cleavage of macromolecules leads to the formation of degradation products with aldehyde and keto groups [36]. It has been demonstrated that the bio-degradation is also possible, in the case of vulcanized rubber although due to the cross links between the poly(*cis*-1,4-isoprene) chains, that reduce water absorption and gas permeability of the material, the process proceeds with much more difficulties [36].

In reference[37] is reported that < *...two Streptomyces strains were isolated from vulcanized gaskets of cement water tubes, which were the cause of 1.5-mm-diameter holes in the material after 12 months of incubation* >[37].

In a sample of an old tire found in Alexandria (Egypt) was isolated a bacterium, belonging to *Actinomycetes Nocardia sp.* Strain-MBR , capable to utilize rubber substrate as only source for carbon and energy [35].

The degradation effects of colonization by *Nocardia sp.* Strain-MBR on natural rubber substrates (NR-granules and NR-latex gloves), clearly visible by the optical micrographs in figure 21, were studied by means of Scanning Electron Microscopy (SEM).

The results obtained, after 3 weeks of incubation, extensively reported in reference [35], are hereafter summarized, also referring to figure 22 [35].

- 1) Following bacteria growth the NR-granules substrate turned orange in colour;
- 2) The SEM micrographs, shown in figure 22-lower-A,B), demonstrated that 3 weeks of incubation were enough to obtain dense microbial mass in the forms of punches on the surface of NR granules in comparison with the control (figure 22-lower –C)
- 3) The SEM micrographs of figure 22-upper-A,B, show the formation of a compact bio-film due to the growth of *actinomycete* cells at the surface of NR- latex gloves [35].

It has been found that also bacteria, belonging to *nocardioform actinomycete*, genus: *Gordonia* , are characterized by a strong biodegradation effectiveness against solid rubber samples [35].



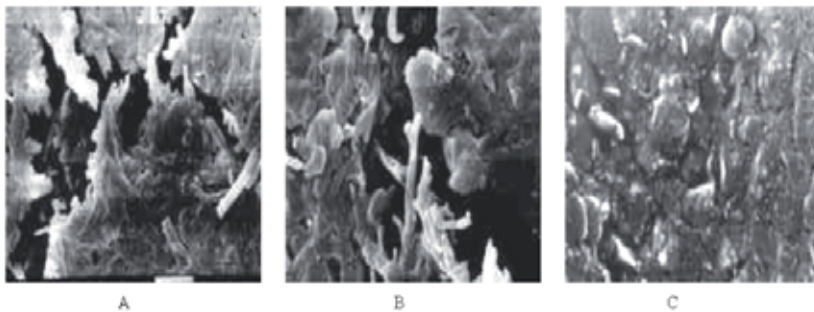
FIGURE 21: Degradation effects of bacterium colonization, *Nocardia sp.* Strain-MBR, on samples of natural rubber-latex gloves [35].

T.S. Rao et Others demonstrated the presence of fungi and bacteria on samples of ebonite used as rubber lining in carbon steel pipeline to improve their resistance against corrosive media (acids, alkalis and salt water) [38].

Generally the ebonite lining < *is applied as un-vulcanised rubber to metal surfaces and then vulcanised, to strongly bind the rubber to the metal surface as a protective materials* > [38].

By using microscopic techniques the above mentioned Authors observed the presence of filamentous biomass of fungal origin as confirmed by staining treatment with cotton phenol blue (see figure 23-left) [38].

Upper



Lower

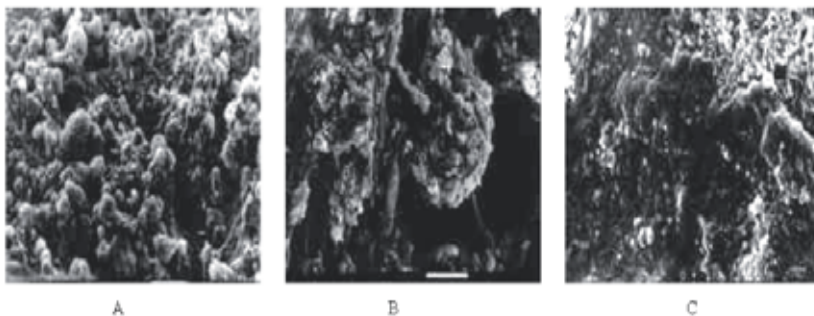


FIGURE 22: SEM micrographs taken during the growth of the actinomycete *Nocardia sp.* Strain-MBR on samples of natural rubber. Upper: Latex gloves (A and B test, C is the control). Lower: Natural rubber granules (A and B test, C is the control) [35].

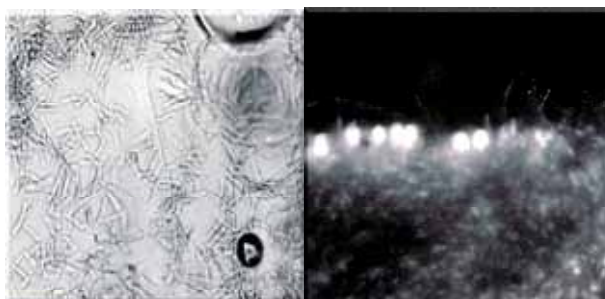


FIGURE 23: Left, Fungal mycelium stained with cotton phenol blue (1000X) found on samples of ebonite used as rubber lining in carbon steel pipeline. Right, Fluorescence image of fungal biomass on the ebonite scrapings (400X) [38].

The growth of fungal biomass on samples of ebonite scraping was confirmed in laboratory. < After 10 days of incubation, the culture flask with rubber scrapings showed significant growth of the fungus. In the control set, no growth was observed. The fungus was checked for culture purity and was confirmed by fluorescence microscopic observation (see figure 23-right) >[38].

The above results show that ebonite rubber in suitable circumstances may provide the carbon source for the growth of fungi.

The mechanism for which damages are induced by fungal growth in infested ebonite samples was clarified by means of Electron Microscopy.

It was possible to demonstrate that fungal hyphae by penetrating the polymer matrix, cause cracks and pores in the ebonite material. < The mechanism of penetration of the mycelium is still unclear, but it is theorized that the hyphae are able to create high turgor pressures, that force the cells through the material. This leads to a decrease in mechanical stability... > [38].

5) AGEING AND SYMPTOMS OF DEGRADATION OBSERVED IN ITEMS MADE IN SOFT OR HARD RUBBER (EBONITE) AND CONSERVATION STRATEGIES: SOME CASE HISTORY

In the case of rubber artefacts the ageing is essentially related to the following product variables:

- Nature of the rubber and degree of cross-links;
- Characteristics of the vulcanizing system;
- Chemical structure and functions of fillers, additives and pigments;
- The stabilization/protective system adopted;
- The presence of stresses induced by manufacturing [39-a].

Moreover other factors of deterioration may become active during service life (abrasion, external chemical attack, exposure to heat and sunlight, etc.).

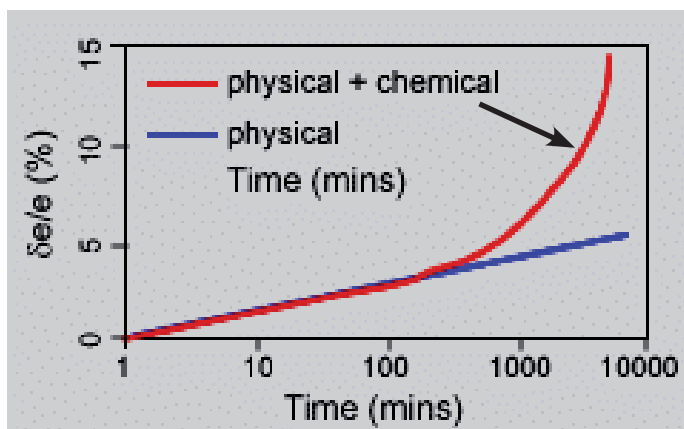


FIGURE 24: Creep tests performed during fluid exposure can differentiate between physical and chemical effects in the case of vulcanised rubbers [39-b)].

Quite often from the examination of the typologies of symptoms shown by an artefact it is possible to give an idea about the most active factors of degradation.

In some special case accurate creep tests during fluid exposure can differentiate between physical and chemical effects, as shown by the diagrams in figure 24 [39-b].

One of the difficulty encountered in the conservation of plastic items arise from the fact that the type of additives used have been modified in the course of the years. Thus the search for their chemical structure and function represents a necessary task to be accomplished as those substances may be also the origin of some deleterious effects. For example in reference [39-a)] it was reported that amines and amine-based additives, used for the protection against oxidative degradation of natural rubber, < *oxidized to various shades of blue, purple and black. Whilst this might not be too important in a black vulcanizate such as a car tyre, it was certainly of little use in the many light-coloured products, such as rubber thread or strip coming to the market at that time and used in the clothing industry* > [39-a)].

--- Case Histories concerning the symptoms of degradation observed in items made in soft or hard rubber

1) Objects in natural rubber.

In figure 25-a) is reproduced a flexible toy (stored at the Victoria & Albert Museum of London) manufactured in natural rubber by Bendy Toys in 1951 and commercialised under the name “Bendy Bunny Benny”.



FIGURE 25-a), left: A flexible toy made from natural rubber by Bendy Toys in 1951 with heavy signs of degradation (the Victoria & Albert Museum, London) [39-c)].

FIGURE 25-b), right: Rubber shooting gloves, Danish Defence Museum. Right glove highly oxidized. Left glove in good condition [39-d)].

According to reference [38] the following symptoms of degradation were observed:
< *the rubber has become dry and brittle and crumbles on touch due to oxidation* > [39-c)].

The effects of oxidative degradation on rubber shooting gloves are clearly visible by comparing the two pictures shown in figure 25-b). The used right glove is highly oxidized while the left-unused glove appears to be in a good state of conservation [39-d)

2) Objects made in ebonite

At the Canadian Conservation Institute a study was performed finalised to analyse the nature of crystalline solids and corrosion products found in ebonite artefacts in the proximity of region where brass or bronze components were in contact with the hard rubber [40].

Some of the results, published by Scott Williams [40], are hereafter summarized for some of the samples examined.

--- Marconi Wireless Magnetic Detector

< *Droplets on pulley: 2-4 mm diameter, acidic, water soluble sulfates. Crystals of the corrosion product on the brass bushings in the centre of the pulley: Pale green transparent crystals were identified as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (chalcantite) and $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$ (gunningite). Colorless transparent crystals were substituted zinc and copper sulphate hexahydrates* > [40].

--- Van de Graaf type electrostatic voltage generator

Crystalline encrustation on black accumulator wheels: ammonium sulphate with iron [40].

--- Short-wave transmitter from Marconi Wireless Telegraph Co.

Substances formed at the interface between copper conductor and ebonite: ammonium zinc sulphate hydrate, $(\text{NH}_4)_2\text{Zn}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$, with S, Zn, Cu, Sn, and traces of Fe, Si, and K [40].

The hereafter-described sequence of chemical reactions is responsible of the production of the substances observed on the surface of the above-cited objects.

First- Following to the exposition to air of ebonite objects sulphur oxides are obtained. Such a compounds reacting with atmospheric moisture give rise to the formation on the surface of droplets of sulphuric acid.

Second- If in the surrounding environment ammonia is present, molecules of ammonium hydrogen sulphate and ammonium sulphate are formed.

Third- Ammonium hydrogen sulphate and ammonium sulphate in contact with metals form as corrosion products metal sulphate and metal ammonium sulphate. These salts are deliquescent, thus at high value of the relative humidity (RH) they dissolve in their own water of hydration forming liquid droplets, while at lower values of RH the droplets dry forming a circular solid crystalline deposit. <.. *often showing a series of tide lines created by successive wetting/drying cycles as RH fluctuates* > [40].

Scott Williams [40] in order to keep away from the above observed degradation pattern suggests the following conservation strategy based upon the following steps:

- 1) Separation of the ebonite and metal components;
- 2) Cleaning of the two set of components;

3) Reassembly of the artefacts after having interposed an isolating barrier of plastic such as polyester, polyethylene/polypropylene or Teflon sheet between metal and ebonite component to prevent further corrosion.

4) Storage of the object in an environment where the RH is kept at relatively low values in order to avoid the spreading, following liquefaction, of, eventually present, deliquescent salts [40].

--- Giorgi flutes

The presence of acidic materials and white sulphate salts (probably water soluble ammonium sulphate or ammonium hydrogen sulphate) was observed on the surface of ebonite in four Giorgi flutes artefacts (see figures 26 and 27) .

To avoid further damages to the artefacts a suitable treatment method, suggested by L. Bacon, is hereafter summarised [41]:

< The surface of ebonite (vulcanite or hard rubber) undergoes severe decomposition through the action of light, air, and moisture. The surface acid formed by this process can be wiped away, but in extreme cases neutralization may be necessary. This can be done by rinsing with a dilute solution of sodium bicarbonate, and quick drying in industrial methylated spirit. For storage and display, light levels should be reduced to a minimum and ultraviolet eliminated. Relative humidity must be kept low. If possible, oxygen should be eliminated; this can be achieved by keeping the objects in special containers > [41].

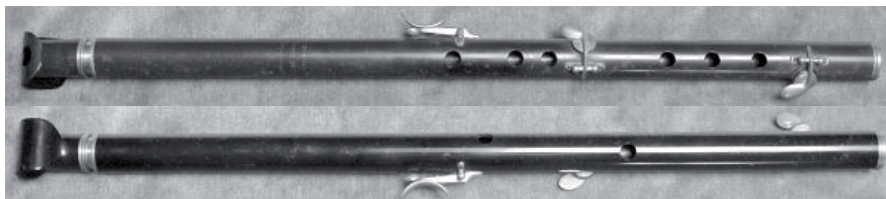


FIGURE 26: An exemplary of Giorgi flute by Wallis, London, c.1890. Top: front view. Bottom: back view [42].



FIGURE 27: Two views of the typical embouchure of the Giorgi flute shown in figure 26 [42].

6) GENERAL RECOMMENDATIONS FOR THE CONSERVATION OF ARTEFACTS IN SOFT AND HARD RUBBER

According to reference [39-b)] any project aimed at stabilize, protect and maintain artefacts made in rubber, valuable from the cultural point of view, should be based on the preliminary knowledge of :

- I) Most active factors in causing the deterioration;
- ii) Methods capable of reversing damage already suffered;
- iii) Best conditions for storage and display for both restored old items and new modern acquisitions.
- Iv) Suitable treatments to prolong the display and storage lives of collected objects.

Regarding point I) it is ascertained that oxygen and/or ozone, especially when catalysed by light, heat or pro-oxidant metals, represent for sure the most dangerous factors of degradation for rubber manufactured objects.

As far as point ii) is concerned it must be underlined that, in general, according to the state of conservation the following types of treatment are possible:

--- < *Stabilization - holding the status quo by limiting existing degradation chemistry* >;
--- < *Conservation - treating the stabilized article so that long-term degradation is minimised. The latter can entail anything from Consolidation - very limited (often invisible) reinforcement of the article through Restoration - treatment which could extend from consolidation to virtual Replication* > [39-b)].

As already underlined in the field of the conservation of artefacts made in rubber one has to face additional problems related to the following issues:

< *Rubber, through common usage, has become a generic term. It covers a multitude of different elastomers, natural and the synthetics, with different additives included for specific purposes, and with no obvious way, short of analysis, of distinguishing between either the additives or elastomers used..... Existing historical artefacts could be unvulcanized whilst modern materials could consist of a range of polymers, cure and protective systems, and fillers* > [39-b)].

In principle the conservation of rubber made objects can be accomplished through:

- The use of protective agents;
- The coating with an impermeable membrane;
- The removing of the factors of degradation (this means that in the case of indoor collections oxygen, ozone, light and temperature should be under control) [39-b)].

< *None of this will stop the 'sulphur chemistry' continuing but this will not, by itself, harm the exhibit for several centuries. It should also be realised that for modern black vulcanizates of reasonable bulk which are being stored or displayed under ambient conditions, the ingress of oxygen is limited and, apart from the surface few millimetres or so, the bulk rubber will remain in excellent condition for display purposes almost indefinitely*> [39-b)].

Protective actions should be take into account the presence of specific additives used in making the rubber compounds and their reactions to degradation factors. Some examples are hereafter briefly mentioned.

--- Para-phenylenediamines (PPD's), added as antiozonants and antioxidants, during rubber manufacturing by reacting more readily than the rubber double bonds with any ozone present at the

surface of the object give rise to the formation of a protective film < *which, as it thickens by continuing migration and further reaction of the migrated antiozonant, eventually provides an impermeable barrier to the gas. Any damage to the skin, such as by cracking, is repaired by further migration. There are many different PPD's and one of the main reasons for selecting a particular one is its solubility and rate of migration in the polymer system being protected, crucial parameters for long-term protection. PPD's oxidize to blue/purple/black materials and readily stain so their use must be selective* > [39-b)].

--- Antioxidants, based on phenol derivatives, added to rubber with the aim at stopping the progressing of chain reaction sequence induced by oxygen leading to chain breakage and to the formation of crosslinks, <*they do not stop the initiation step so their effect is... to slow down the oxidative breakdown.... They do not form a protective 'skin' if oxidized on the rubber surface and need to be intimately dispersed/dissolved in the rubber to function* > [39-b)].

In storing and displaying objects made in elastic soft rubber essentially two main degradation processes must be avoided, namely oxidation (mainly initiated by light) and crystallization. At least in principle, the deleterious effects of crystallization, especially fragility, can be removed and the properties of the degraded rubber restored by heating the object at a temperature higher than that at which the crystallization happened [26-a)].

According to M. T. Baker examples are reported in literature where it was described how by gentle warming it has been possible < *to restore a hardened, distorted rubber objects to its original shape* > [26-a)].

In order to reduce the degradation induced by photo-oxidation reactions as well as crystallization phenomena it is recommended, assuming that at room temperature the rate of crystallization is relatively low, to store soft rubber artefacts in an oxygen-free environment at a temperature of few degrees below RT [26-a)].

As above reported in objects made in ebonite, exposed to the action of oxygen, light and moisture, < *a sulphuric acid rich dull grey-brown surface layer* > is quite often observed [31].

An ancient bracelet in ebonite showing fading process deriving by exposure to light is shown in figure 28 [43]. Oxidation is not reversible thus the damages caused cannot be reversed.

Interesting attempts aimed at create a surface physical barrier capable to reduce oxygen and ozone diffusion into the rubber have been developed. Some of this kind of protective treatments are based on the topical application of protective agents dissolved in a solvent. In some treatments a solvent able to swell the rubber, thus facilitating the penetration and diffusion in deeply, was used.

In principle a protective transparent surface coating, acting as a physical barrier against the diffusion into the rubber of oxygen, ozone and water, and being also able to screen out a large percentage of damaging UV radiations, could be an efficient method for the conservation of objects made in soft or hard rubber. Of course such a coating should not cause any detriment to the substrate.

Attempts in such direction have been already tried. In reference [39-b)] is cited the use as topical coating of an oil lacquer that after application is allowed to cross link, *in situ*, on the rubber surface. Following such type of procedure the use of a pre-vulcanised butyl latex spray-coat, since butyl rubber is relatively impermeable to air, is suggested [44].

At the moment the best system to protect a rubber made object consists in keeping it in an enclosed transparent vessel filled with an inert gas. In the case of long-term storage plastic impermeable multi-laminates, not suitable for display purposes, can be used.

< Perhaps glass is the best material for both storage and display but nothing will reverse degradation which has already occurred > [39-b)].



FIGURE 28: Bracelet in ebonite showing fading from exposure to light [43].

H. A. Razavi and B. G. Frushour developed an innovative high molecular weight acrylic based polymer latex, containing a copolymerised UV absorbing co-unit, denominated *Sorbalite*, suitable to be used as protective surface agent against UV deleterious effects. The formulation could be also modified, according to the nature of the substrate to be protected, by adding substances improving the adhesion as well as coating performance [45].

The method, based on the use of *Sorbalite* coating, was checked on films of polyethylene-terephthalate (a polyester) and of polypropylene (a polyolefin).

By comparing the diagrams reported in figure 29, it comes out that in the uncoated polyester film the exposure to UV light determines a phenomenon of fragility whose entity increases with the time of exposure (both elongation and stress to break decrease with the exposure time (figure 29-top)). An almost full retention of tensile characteristics are observed in the case of films of polyester after surface treatment with *Sorbalite* for up to 1600 hours of UV exposure (figure, 29-bottom) [45].

Sorbalite coating seems to be effective also in protecting films of white-pigmented polypropylene against UV damage [45].

The above-cited Authors, concerning the extension of *Sorbalite* methodology to other types of polymer surfaces wrote:

< One can imagine many opportunities to protect and preserve a wide variety of surfaces encountered in museum. The key to success will be proper formulation for the specific applications > [45].

It could be interesting to experiment a *Sorbalite*-like approach also for the protection of surfaces of soft and hard rubber made artefacts.

Assuming that most of rubbers essentially degrade by oxidation it can be recommended the storage of artefacts in cases containing suitable scavengers (a chemical based device suitable to remove or inactivate impurities or unwanted products suitable to improve the environmental conditions in museum glass show cases).

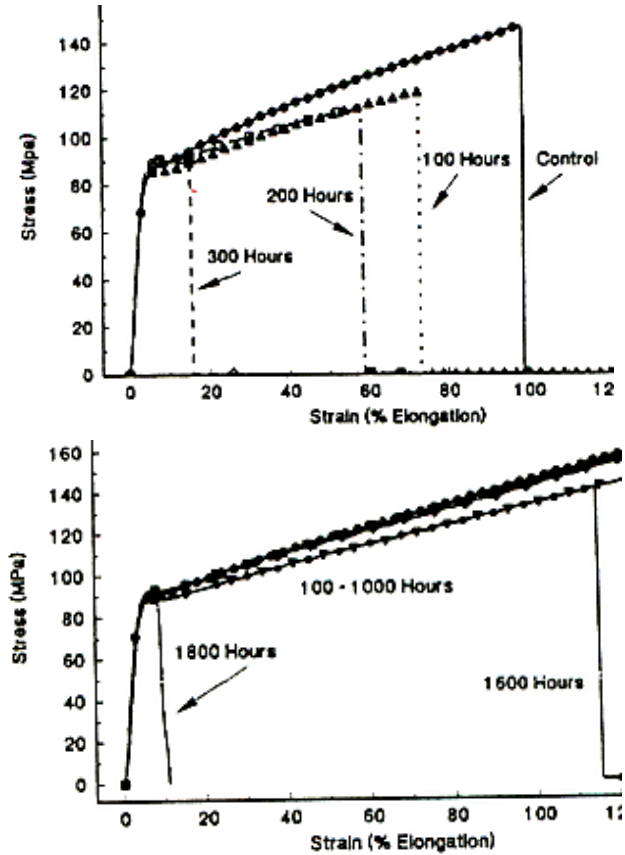


FIGURE 29: Dependence of tensile properties of un-coated and coated polymer films from the time of exposure to UV radiations.
Top: Clear polyester film (no Sorbalite coating).
Bottom: Clear polyester film coated with a 2 micron Sorbalite layer [45].

In the case of rubber items oxygen scavengers, (eg Ageless ®) developed for food storage, based on fine powdered iron that in presence of O₂ form oxides and hydroxides may be used (see figure 30) [39-b), 46]. Alternatively the objects may be stored in an oxygen-free environment (see figure 31) [39-b)].

On concluding it is worthwhile, once again, to point out that, as shown by figure 32, many different rubber products have been developed since the synthetic period of the plastics started.



FIGURE 30, left: Oxygen scavengers are based on iron powders that reacting with oxygen forms rust, iron oxides and hydroxides [39-b), 44].

FIGURE 31, right: To avoid oxidation rubber objects may be stored in an oxygen-free environment [39-b), 44].

Such synthetic rubbers, competing with the natural one, with different additives, and whose properties depend strongly upon molecular structure and source, cover a multitude of different applications.

Some of the most common types of additives used for the manufacturing of rubbers, together with their main functions and characteristics are hereafter listed [47].

Fillers: Carbon black to reinforce the compound and whiting or clay to extend the compound.

Vulcanising agents: It include, sulphur, accelerators (to achieve a higher curing rate) and activators (to contribute to the initiation of the curing process).

Ageing protectors: Antioxidants to protect the rubber from oxidation and ozone degradation.

Softeners: Mineral oils, ester and plasticizers are used to control the hardness and improve the processing of a rubber compounds.

Special ingredients: Pigments, antistatic lubricants, blowing agents, flame retardants, etc.

Reinforcing agents: Textile fabrics, textiles, steel cord and glass-fibres are used in tires, hoses and in cords to increase their mechanical strength [47].

FIGURE 32: Properties of different rubber types [47].

PROPERTY	Natural- rubber/ Isoprene NR/IR	Styren- butadien rubber SBR	Butadiene rubber BR	Ethylene- propylene rubber EPM/EPDM	Butyl rubber IIR	Chloro- prene rubber CR	Nitrile rubber NBR	Silicone rubber PMQ *
Max temp ...F	176	194	176	248	194	185	194	392
Min temp ...F	-58	-40	-103	-31	-49	-31	-22	-112
Tear strength	4	3	3	3	3	3	3	1
Abrasion resistance	4-5	4-5	5	3	3	3-4	3	1-2
Oil/fuel resistance	1	1	1	1	1	2-3	3-4	2-3
Weather/ozone resistance	1-2	1-2	1-2	5	4	3	1-2	5
Water swelling	4	4	4	5	4	2-3	3-4	2
Fire resistance	1	1	1	1	1	3	1	2
Rebound at low temp.	5	3	5	3	1	3	3	5
Rebound at high temp.	5	3	5	3	3	4	3	5
Fatigue	4	4	4	4	3	4	2	1-2
Bonding to metal	4-5	4-5	4-5	3	2	4	4	2
Bonding to textile	4-5	4-5	4-5	3	2	4-5	3-4	2

Grading of Properties: 5 excellent, 4 very good, 3 good, 2 satisfactory and 1 poor. [47].

REFERENCES

- 1) http://www.azom.com/details.asp?ArticleID=3580#_Processing_of_Natural, (2008).
- 2) it.encarta.msn.com/.../Gomma.html, (2008).
- 3) www.ctseurope.com/dettaglionews.asp?id=24, (2008).
- 4) C. A. Harper, < *Modern Plastics Handbook* >, McGraw-Hill, New York (2000).
- 5) www.lgm.gov.my/images/thomashandcock.gif, (2008).
- 6) www.bouncing-balls.com/.../rubprocess1.gif, (2008).
- 7) <http://z.about.com/d/cleveland/1/0/B/L/-/-/goodyear.jpg>, (2008).
- 8) J. Gordon Cook, < *Your Guide to Plastics* >, Merrow Publishing CO-LTD, England (1964)
- 9) Khairi Nagdi < *Manuale della Gomma* >, Tecniche Nuove, Milano (1987).
- 10) -a) B. Elsener, http://dipcia.unica.it/superf/Degrado/Polimeri_Capitolo1.pdf, (2008).
-b) K. H. Meyer, < *Natural and Synthetic High Polymers* >, Interscience Publishers, Inc., New York (1950).
- 11) E. Martuscelli < *Le fibre di Polimeri Naturali- le Fibre di Seta* >, Monografie Scientifiche, Serie Scienze Chimiche, Consiglio Nazionale delle Ricerche, Roma (1999).
- 12) a-) C. A. Harper, < *Handbook of Plastics and Elastomers* >, McGraw-Hill, New York (1975).
b-) C. V. Horie, < *Materials for Conservation* >, Butterworth-Heinemann, Amsterdam (2005).
- 13) <http://www.chemistryexplained.com/Ru-Sp/Rubber.html>, (2008).
- 14) 1) E. Martuscelli, *La Chimica e L'Industria, RICHMAC Magazine-77*, 538 (1995).
- 15) L. Scacchi Gracco, < *Pensieri di Plastica* > A. Mondatori Editore, Milano (1986).
- 16) <http://www.plastiquarian.com/hancock.htm>, (2008).
- 17) <http://www.plastiquarian.com/vulcanit.htm>, (2008).
- 18) <http://www.morninggloryjewelry.com/victorian-vulcanite-jewelry-c-97.html>, (2008).
- 19) <http://en.mimi.hu/jewelry/vulcanite.html>, (2008).
- 20) <http://www.morninggloryantiques.com/collectVictJet.html>, (2008).
- 21) J. Harry DuBois < *Plastics History USA* > Cahners Books, Boston (1972).
- 22) P. Maggi, G. Negreti, F. Nencini, < *Penne da collezione* >, Wrist Srl - Milano (1990)
- 23) <http://museo.cannon.com/museonew/UKmuseo/reale7UK.asp?Direzione=Indietro&bachecapass=1&salapass=>, (2009).
- 24) < *Plastics, collecting and conserving* >, Edited by A. Quye, C. Williamson, NMS Publishing limited (1999).
- 25) Y. Shashoua, < *Conservation of Plastics* >, Elsevier, Amsterdam (2008).
- 26) -a) M. T. Baker, *Polymer Preprints*, ACS, Volume 39, Number 2, pp-1253-1254, August (1998).
-b) The aging of rubber vulcanised, <http://www.bouncing-balls.com/index2.htm>, (2009).
-c) J. C. Anderson, K. D. Leaver, J. M. Alexander, R. D. Rawilings, < *Materials Science* >, Nelson, Hong Kong (1981).
- 27) I. C. McNeil, < *Fundamental Aspects of Polymer Degradation* >, in “*Polymers in Conservation*”, Edt. by N. S. Allen, M. Edge, C. V. Horie, Royal Society of Chemistry, pp. 15-32 (1992).
- 28) B. Elsener, http://dipcia.unica.it/superf/Degrado/Polimeri_Capitolo2.pdf, (2008).
- 29) R. Scott Williams, < *Waac Newsletter* >, “Care of Plastics: Malignant plastics”, January, Volume 24 Number 1 (2002)
<http://cool-palimpsest.stanford.edu/waac/wn/wn24/wn24-1/wn24-102.html>, (2009)

- 30) J. Morgan < *A Survey of Plastics in Historical Collections* >, Plastics Historical Society and The Conservation Unit of the Museums & Galleries Commission 1994.
<http://www.plastiquarian.com/survey/survey.htm>, (1008).
- 31) C. J. Williamson, < *150 years of plastics degradation* >, in “*Polymers in Conservation*”, Edt. by N. S. Allen, M. Edge, C. V. Horie, Royal Society of Chemistry, pp. 1-13, (1992).
- 32) S. A. Connors et Al., *Polymer Preprints*, ACS, Volume 39, Number 2, pp-1251-1252, August (1998).
- 33) Hunseung Kang, Min Young Kang, and Kyung-Hwan Han, *Plant Physiol.*, 123(3): 1133, July; (2000).
- 34) http://www.bouncing-balls.com/chemistry_tech_conservation/conserved.htm, (2009).
- 35) [http://www.scialert.net/pdfs/biotech/2006/234-,\(2009\).](http://www.scialert.net/pdfs/biotech/2006/234-,(2009).)
- 36) C. O. Byrum, < *Preliminary Review of The Degradation of Cellulosic, Plastic, and Rubber Materials in the Waste Isolation Pilot Plant, and Possible Effects on Magnesium Oxide Safety Factor Calculations* >, Contract Number EP-D-05-002 Work Assignment No. 2-09. Prepared for:U.S. Environmental Protection Agency Office of Radiation and Indoor Air, September 11, (2006).
http://www.epa.gov/radiation/docs/wipp/epa_mgo_report_91107.pdf, (2009).
- 37) K. Rose, A. Steinbüchel, *Applied and Environmental Microbiology*, Vol. 71, p. 2803-2812, No. 6, June (2005).
- 38) T.S. Rao, M. Hireen Joshi, V.P. Venugopalan, S.V. Narasimhan, G. Mohana Krishnan and C. Anand Babu, < *Microfouling Problem In Acid Transfer Unit Of Boron Plant* >, <http://www.barc.ernet.in/publications/nl/2007/200712.pdf>, (2009).
- 39)
 a) www.merl-ltd.co.uk/2003_materials/rubber04.shtml, (2009).
 b) www.bouncing-balls.com/.../ageing.htm, (2009).
 c). Keneghan, *Conservation Journal* October (1996),
http://www.vam.ac.uk/files/file_upload/42730_file.pdf, (2008).
 d) Y. Shashoua, *Conservation of plastics-is it possible?*, lecture presented at giornata Aim dedicata a “Il restauro e la diagnostica degli oggetti d’arte e di design in plastica”, (Napoli), 31/10/ (2008).
- 40) R. Scott Williams, *Canadian Conservation Institute*,
<http://cool-palimpsest.stanford.edu/byform/mailling-lists/cdl/2001/0354.html>, March 23, (2001)
- 41) L. Bacon, *Conservation today*: papers presented at the UKIC 30th Anniversary Conference, , pp. 96-100 (1988).
- 42) www.oldflutes.com/articles/giorgi.htm, (2009).
- 43) <http://www.plastiquarian.com/deterio.htm>, (2009).
- 44) <http://www.bouncing-balls.com/index2.htm>, (2008).
- 45) H. A. Razavi, B. G. Frushour, *Polymer Preprints*, ACS, Volume 35, Number 2, pp-309-310, August (1994).
- 46) E. Martuscelli, *Plastics In Art (In Cultural Heritage) - Plastics For Art (For Cultural Heritage)*, lecture presented at giornata Aim dedicata a “Il restauro e la diagnostica degli oggetti d’arte e di design in plastica”, (Napoli), 31/10/ (2008).
- 47) [rubber-formulation.htm](http://www.rubber-formulation.htm) (2009).

SECTION-2

THIRD-CHAPTER

PLASTICS BASED ON NATURAL PRE-FORMED POLYMERS: PLASTICS FROM CHEMICAL TRANSFORMATION OF CELLULOSE

CELLULOID: PROCESSING, STRUCTURE, COMPOSITION AND PROPERTIES

Celluloid, considered the oldest artificial plastics made by the man, is the trade name of a thermoplastic multi component material whose main constituents are hereafter listed:

- 1) Cellulose nitrate as polymer;
- 2) Camphor as plasticizer and stabilizer(20-40%);
- 3) Zinc oxide as filler and opacifier;
- 4) Pigments;
- 5) Ammonium phosphate, to reduce flammability;
- 6) Impurities related to processing (lignin, sulphuric acid, acids, chlorine, etc.).

The most important historical steps that led to the development of the celluloid, as plastics are hereafter summarized.

--- Christian Friedrich Schönbein (figure 1, [1]), a German professor in chemistry working at the Basle University, on 1846, accidentally discovered that was possible, by treating cotton fibres with a mixture



FIGURE 1: Christian Friedrich Schönbein (1799-1868), the German professor in chemistry that discovered the synthesis of the cellulose-nitrate [1].

of nitric and sulphuric acids, to convert the cellulose in nitro-cellulose and water, a clear, tough, horny material. The sulphuric acid was necessary to prevent the water produced in the reaction from diluting the concentrated nitric acid [2,3].

The scheme of the reaction of nitration of cellulose, main component of cotton fibres, is shown in figure 2 [3].

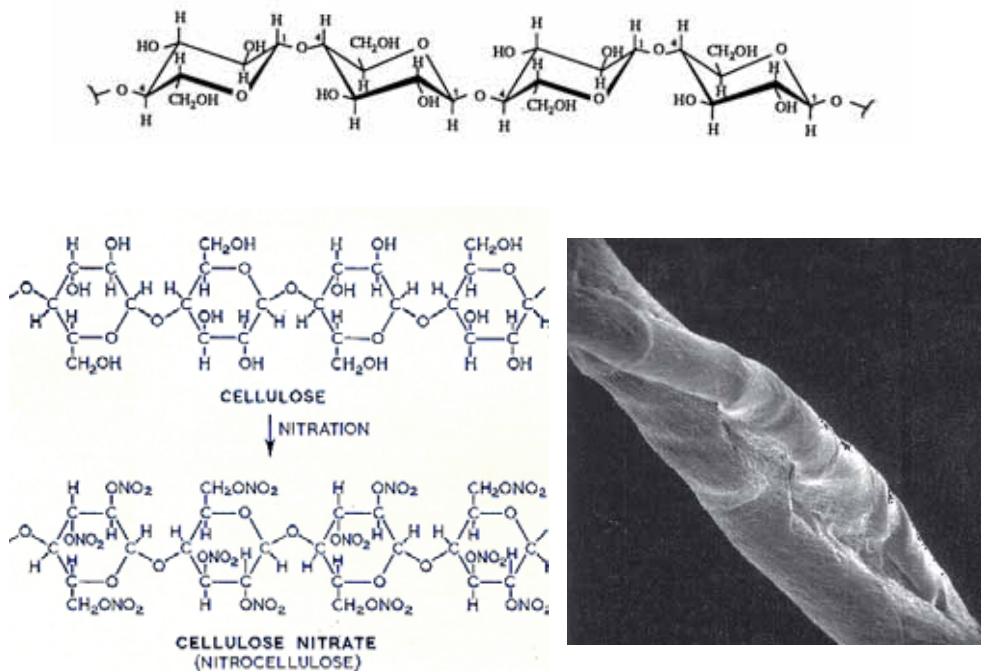


FIGURE 2:

Top: Molecular structure of cellulose macromolecules.

Bottom, right: Morphology of a natural cellulose based cotton fibre.

Bottom, left: Schematic representation of the nitration reaction of cellulose leading to nitro-cellulose.

In practice nitric acid esterifies only part of hydroxyl groups present along the cellulose macromolecules [2-4].

--- Alexander Parkes (see figure 3, [5]), born in 1813 in Birmingham (England), in the course of its experiments, started on 1854, aiming at producing from nitrocellulose a useful mouldable material, discovered that cellulose nitrate is soluble in molten camphor. < *As it cooled, the mixture passed through a putty-like plastic stage during which it could be moulded. Then it set to a flexible horny material* > [3].

Parkes, on 1861, patented this new material, with the name “Parkesine” and exhibited it at the Great International Exhibition in London in 1862. On December 1865 the Parkesine was presented to the Royal Art Society [3,4].

In 1866 Parkes established the *Parkesine Company* in London [5,6,7].

--- In the United States in 1868 John Welsey Hyatt (figure 4) was able to produce billiard balls, in substitution to those made in ivory, by using the following process:

- 1) Nitrocellulose was ground with camphor;
- 2) The mixture was heated until it became fluid forming a mouldable mass;
- 3) The fluid mass was shaped at high temperature and pressure by using a suitable compression moulding device designed for thermoplastics.

< Marketing this tough, flexible material, called celluloid, as a substitute for ivory, tortoiseshell, and horn, Hyatt's Celluloid Manufacturing Company made it into a variety of products, including combs, piano keys, and knife handles. Beginning in the 1880s, celluloid acquired one of its most prominent uses in detachable collars and cuffs for men's clothing, and the development of superior solvents allowed the material to be made into flexible film for photography > [2].

Hyatt patented on 1870 the process invented for making celluloid. Moreover he was also capable to design and build up machineries suitable for processing celluloid mass. For the whole of his activity Hyatt was awarded the Perkin Gold Medal in 1914 [7].

Celluloid was the first commercially successful plastic that come into production, thus its development is generally assumed, from historical point of view, as the milestone that signed the birth of the modern plastics industry.

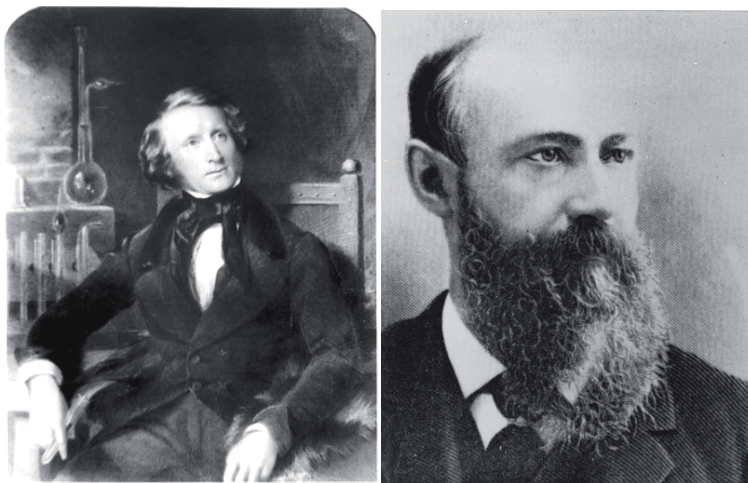


FIGURE 3, left: Portrait, painted from a pencil drawing by Abraham Wivell (1786- 1849), of Alexander Parkes (1813-1890) which produced the first man-made plastics named Parkesine [5].

FIGURE 4, right: John Welsey Hyatt (1837-1920), the inventor of the Celluloid. In his experiments, Hyatt discovered the solvent action of camphor on cellulose nitrate under moderate heat and pressure, and this was the basis of his 1870 patent [6,7,8].

Following the insights of Parkes and Hyatt, celluloid for about twenty years was practically the only plastic produced and commercialised.

In reference [3] the steps of celluloid manufacturing were schematically summarized through the drawings reproduced in figure 5.

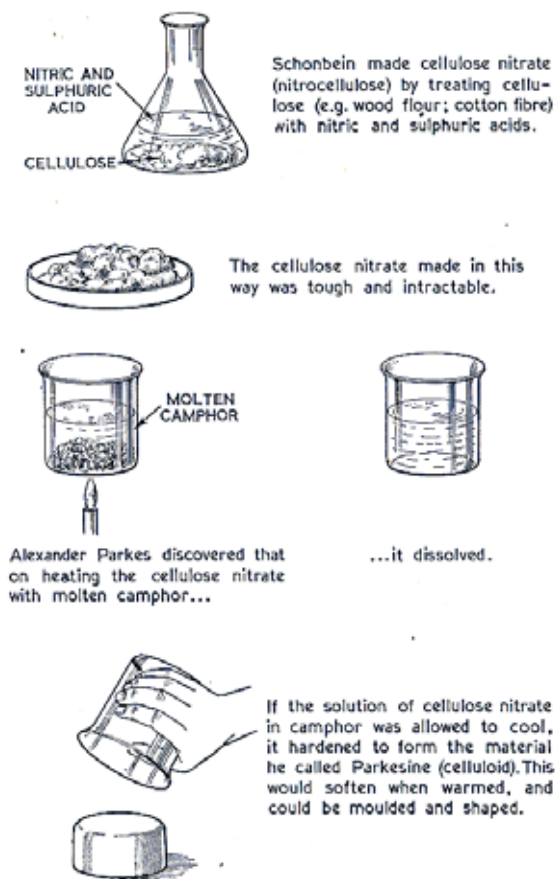


FIGURE 5: The main steps in the manufacturing of celluloid [3].

Camphor, a waxy, white or transparent solid with a strong aromatic odour is a terpenoid with the chemical formula $C_{10}H_{16}O$. The molecular structure of camphor, a bi-cycleketone (IUPAC chemical name: 1,7,7-trimethyl-bicyclo(2,2,1)heptan-2-one), is shown in figure 6. Natural camphor is extracted from the wood of the Camphor laurel (*Cinnamomum camphora*), an evergreen tree growing in Asia, by vapour stream distillation followed by purification by sublimation [9,10].

Some of the main properties of camphor are hereafter reported:

- Molecular weight: 152.24;
- Solubility: 0.12;
- Boiling point: 207.0;
- Melting point: 177.0;
- Density: 0.99 [10].

Camphor molecules, through the formation of hydrogen bonds involving the cellulose hydroxyls, act not only as plasticiser but also as stabiliser of nitro-cellulose.

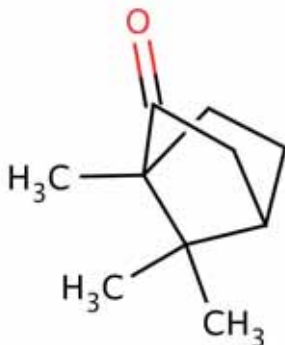


FIGURE 6: Molecular structure of camphor used as plasticiser of nitrocellulose. [9,10].

The effectiveness of camphor as solvent/plasticiser for nitrocellulose, according to Worden, was essentially due to the following set of characteristics:

- < --- *Excellent gelatinising agent of quick and deep penetration, and is an energetic solvent....*
- *Readily soluble in ethyl alcohol ... [methyl alcohol and acetone]*
- *High melting and boiling point, and gives, therefore, a solid celluloid.*
- *Volatility is so low as to make loss from evaporation during storage negligible.*
- *Uncommonly resistant towards chemical agents [nitric acid, acids, alkalis] and does not liberate anything on liquefying which would tend to decompose celluloid....*
- *It reduces the explosibility, but not the inflammability, of cellulose nitrate when mixed with it.*
- *It does not possess a high power of crystallization, and hence does not separate out of celluloid upon heating and subsequent [sic] cooling or upon long storage.*
- *Light has no effect upon it ...> [10].*

The enormous success of celluloid was essentially ascribed to the following factors:

- Easy mouldability into relatively complicated shapes;
- Transparency and lustre;
- Easy colourability;
- Water resistance;
- Relatively low production cost;
- Toughness and flexibility.

The main drawback of celluloid was related to its high inflammability [3].

Initially celluloid found application as substitute for ivory, tortoiseshell, and horn in the production of a variety of products, including combs, piano keys, and knife handles. < *Beginning in the 1880s, celluloid acquired one of its most prominent uses in detachable collars and cuffs for men's clothing, and the development of superior solvents allowed the material to be made into flexible film for photography. In the early 20th century celluloid found new applications as side windows for motorcars and as film for motion pictures.....* > [2].

Artefacts in celluloid usually are obtained by manufacturing semi-finished products (plate, sheet, stick, tube, ribbon, film, etc.). Bulk celluloid is also shaped by using hot water or hot air and by compression moulding.

Some of the first artefacts manufactured in Celluloid (Parkesine), in display at the Science Museum of London (England), are reproduced in figure 7 [3].

Examples of early applications of celluloid in substitution of horn, glass and ivory are shown in figure 8 [11,12,13].

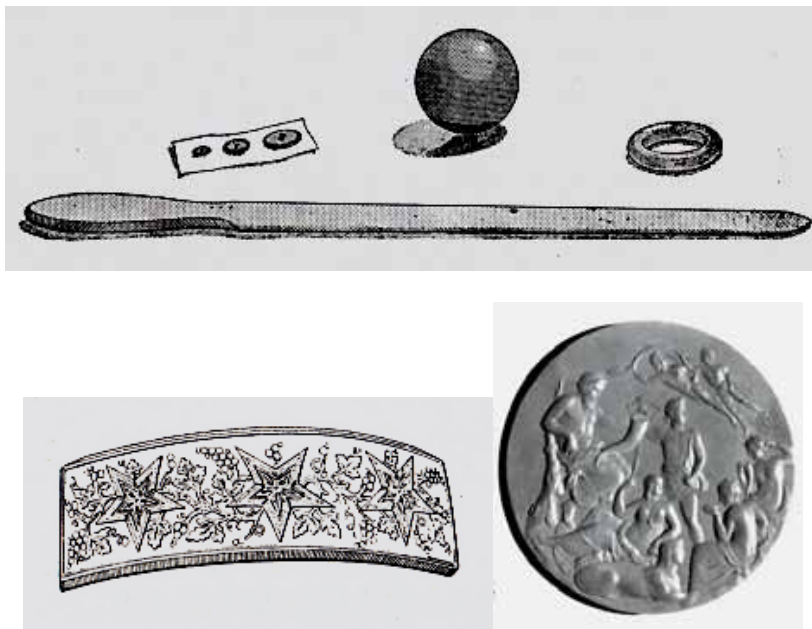


FIGURE 7: Some of the first artefacts manufactured in Celluloid in display at the Science Museum of London.
Top, a billiard ball, buttons, a curtain ring and a paper knife.
Bottom-left, a hair clasp inlaid with brass and mother-of-pearl.
Bottom-right, a moulded plaque [3].

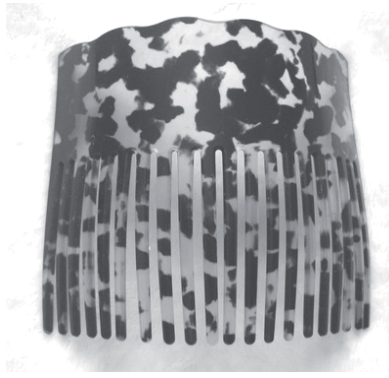


FIGURE 8: Early objects obtained by celluloid mouldings.

Top- Comb in celluloid

Bottom- < On the right is a tortoise-shell patterned puff box...
... moulded by blowing.

On the left is a box having its side, top and lid pressure-moulded,
with bottom and feet fitted and cemented. The lid, handle and feet
are clear and pearl sheet laminated by moulding together.

The toothbrush is of moulded bar stock with the bristles moulded
in >[13].

Celluloid had a relevant role in the development of the industry of photography and cinematography.

The Eastman Kodak, that since 1880 had started the production of photographic plates in nitro-cellulose, in substitution of the more heavy, fragile and slow ones made in glass and collodion, in 1889 developed and commercialised for the first time flexible photographic films in celluloid. Such an innovation represented the milestone that signed the birth of the cinematographic industry that all including passed to the history as “*the world of celluloid*” [14].



FIGURE 10, left: Exemplar of an early toy made in celluloid [11,18].

FIGURE 11, centre-right: Early applications of celluloid in custom jewelry.

Centre, hand made necklace with pearls in celluloid tortoiseshell coloured, years 1950 [19]. Right, brooch, years 1950. The small yellow pearls as well as petals are made in celluloid [20].



FIGURE 12-a): Exemplars of early fountain pens in celluloid produced by Watermans (series: *Patrician*), years, 1929-1938 [21-a]).



FIGURE 12- b), top: coloured rods in celluloid used to obtain fountain pens.

FIGURE 12- c), bottom: turning some Jade green celluloid rods by a foot-powered lathe [21-b).



FIGURE 13: Exemplars of modern sunglasses with frames made in celluloid [22].

A Fragment of an ancient cinematographic film in celluloid is shown in figure 9 [14]
In the 1920s and '30s celluloid began to be replaced in most of its applications by less flammable and more versatile materials as: Cellulose acetate, Bakelite, and the new Vinyl polymers [2].
Since 1952 celluloid was gradually substituted by cellulose acetate in the manufacturing of cinematographic films as this polymers was capable to offer a higher level of safety and stability.
More recently polyethylene terephthalate is substituting cellulose acetate in the production of flexible films to be used in the cinematographic field [15].

The sequence of the happenings above described is an example of the historical processes, concerning a sector of application, which led first to the substitution of more traditional materials with polymers and afterwards to the inter-competition and substitution between different polymer materials [12,16,17].

Some early applications of celluloid in the manufacturing of toys, custom jewelries and fountain pens are evidenced through the reproductions of the exemplars shown in figures 10, 11 and 12 respectively [11,18,19,20,21].



FIGURA 9: Fragment of an ancient cinematographic film in celluloid.

In the manufacturing of toys celluloid substitutes materials as wood, paper pulp, ceramic, etc.
The success of celluloid in the field of *bijouterie* and fountain pens is to be attributed to the easy workability and colourability of the plastic material that allowed the possibility to design and realize elegant, artistic and relatively low-cost artefacts.
Fountain pens still now a day are handmade from celluloid coloured rods as those shown in figure 12-b) by using foot-powered lathe (see figure 12-c) [21-b]].
It is worthwhile to underline that in the case of fabrication of fountain pens celluloid victoriously competed with ebonite and successively had to fight against bakelite. [4,5,16,17].
Celluloid is preferred to other materials (for example tortoiseshell) by many stylists for the manufacturing of glass frames (see examples in figure 13) [22].

Celluloid since the beginning of its history, due to the particular properties (workability, colourability, versatility, low cost, etc.) was used by many artists who wished to experiment for their artefacts a new material.

Of great relevance were the highly innovative works realized by Naum Gabo (1890-1977), an American sculptor and designer born in Russia < *known for his sculptural experiments with constructivism* > [23].

Some significant examples of sculptures, containing elements in celluloid, made by Naum Gabo are reproduced in figure 14 [24,25].

Many types of the artefacts in celluloid, are part of private and public collections and on display in many museums of science, achievements and customs development; some of them have been already shown, other examples are reproduced in figure 15 and 16.

Painting on celluloid sheets was largely used for the representation of sacred history. A rare example is reported in figure 17 where it is reproduced the page in painted celluloid of a Spanish and ancient pocket calendar [21].

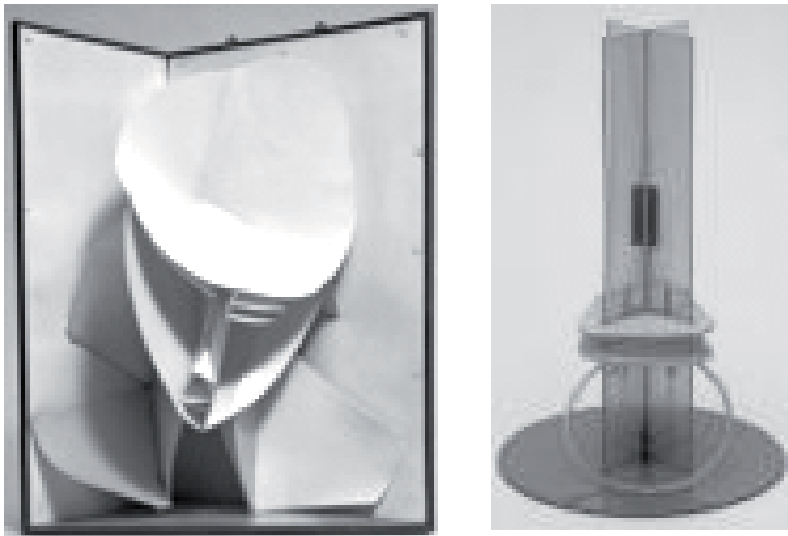


FIGURE 14: Artefacts made by Naum Gabo with elements in celluloid.

Left: *Head of a Woman*, 1917-20, celluloid and metal, Museum of Modern Art, NY [24].

Right: *Model for 'Column'*, 1920-21, Tate Gallery, London [24].



FIGURE 15, left: Antique Edwardian Tapestry and Celluloid Butterfly Frame Evening Bag (≈1910)

< This lovely little antique evening bag has a Pouch style tapestry panelled body. The really spectacular part of this bag is its frame, which is in pearlized Cream celluloid. The frame is further enhanced with a small celluloid Butterfly finial on the flip clasp. This delightful antique evening bag is lined in Cream Crepe >[26].

FIGURE 16, right: Antique Victorian Celluloid Art Nouveau Hair Comb in faux tortoise shell celluloid plastic (≈1885) [27].



FIGURA 17: It is reproduced the page in painted celluloid of a Spanish and ancient pocket calendar (1929) [28].

REFERENCES

- 1) <http://it.wikipedia.org/wiki/Explosions-Polka>, (2009).
- 2) <http://www.britannica.com/EBchecked/topic/1426103/industrial-polymers/76469/Cellulosics>, (2009).
- <http://www.nationmaster.com/encyclopedia/Cellulose-nitrate>, (2009).
- 3) J. Gordon Cook, < *Your guide to Plastics* >, Merrow Publishing Co LTD, England (1964).
- 4) E. Martuscelli, *La Chimica e L'Industria, RICHMACMagazine-77*, 538 (1995).
- 5) <http://www.ssplprints.com/lowres/43/main/6/84929.jpg>, (2009).
- 6) museo.cannon.com/.../storia2.asp?decepass=, (2009).
- 7) www.plasticsacademy.org/swp//imageview.php?im, (2009).
- 8) www.plasticshalloffame.com/articles.php?artic, (2009).
- 9) <http://www.nationmaster.com/encyclopedia/Camphor>, (2009).
- 10) -www.3dchem.com/moremolecules.asp?ID=203&other, (2009).
- Worden, < *Nitrocellulose industry* >, Vols. 1 and 2. New York: Van Nostrand (1911).
- 11) < *Gli anni di plastica* >, Gruppo Montedison, Electa, Milano (1983).
- 12) E. Martuscelli, < *dalla Scoperta di Natta lo Sviluppo dell'Industria e della Ricerca sulle Plastiche in Italia* >, Monografie Scientifiche, Serie Scienze Chimiche, Consiglio Nazionale di Ricerca, Roma (2001).
- 13) H. W. Rowell, < *The Technology of Plastics* >, London: Plastics Press LTD. (1937).
- 14) L. Scacchi Gracco, < *Pensieri di plastica* >, Mondadori Editore, Milano (1986).
- 15) D. Matè, M. C. Sclocchi, D. Ruggiero, < *Kermes* >, **47**, 41 (2002).
- 16) E. Martuscelli, < *le plastiche nel terzo millennio* >, dossier le plastiche, *Ricerca & Futuro*, **23**, 46 (2002).
- 17) E. Martuscelli, < *Le fibre di polimeri naturali nell'evoluzione della civiltà: le fibre di seta* >, Consiglio Nazionale delle Ricerche, Serie Scienze Chimiche, Roma (1999).
- 18) <http://byemylife.com/id24.html>, (2009).
- 19) <http://www.finisilvia.com/girocolli%20nuovo.php>, (2008).
- 20) www.finisilvia.com/spille%20nuovo%20pag.6.php, (2008).
- 21) –a)P. Maggi, G. Negretti, F. Nencini, < *Penne da collezione* >, Wrist Srl - Milano (1990).
–b)www.stutler.cc/pens/nakaya/images/celluloid.jpg, *Nakaya Fountain Pen*, March, (2002).
- 22) picasaweb.google.com/.../wWlBv7Nn29x4s722QLmrkg, (2008).
- 23) M. Derrick, S. Stulik, E. Ordonez, < *Cellulose nitrate deterioration in constructivist sculptures made by Gabo and Pevsner* >, Polymer Preprints, Division of Polymer Chemistry, Inc. , American Chemical Society, **33,N.2**, 637 (1992).
- 24) www.artlex.com/ArtLex/Con.html, (2008).
- 25) <http://fusionanomaly.net/naumgabo.html>, (2008).
- 26) <https://steptoantiques.secured-area.co.uk/a...>,(2009).
- 27) <https://steptoantiques.secured-area.co.uk/a>. (2009).
- 28) www.todocoleccion.net,(2008).

SECTION-2

FOURTH-CHAPTER

PLASTICS BASED ON NATURAL PRE-FORMED POLYMERS: PLASTICS FROM CHEMICAL TRANSFORMATION OF CELLULOSE

CELLULOID: DEGRADATION PHENOMENA IN RELATION TO- --- CHEMICAL COMPOSITION AND PROCESSING --- HISTORY AND USE FUNCTIONS --- EXPOSITION TO THE ENVIRONMENTAL FACTORS OF DEGRADATION

Many artefacts in celluloid, especially those made in early times and kept in unsuitable conditions, deteriorate with age showing heavy symptoms of degradation caused by chemical and physical changes following the action of several types of both internal or environmental external factors.

The type of the damages induced in celluloid objects and their degree are related to the:

- Chemical composition;
- Manufacturing processes;
- Environment in which the objects were used in relation to their use function;
- Temperature and relative humidity fluctuations;
- Exposure to ultraviolet radiation, oxygen and environmental chemical reactive pollutant agents.

Quite often visible signs such as cracking, discoloration or deformation are indication that degradation is occurring on plastic objects. Nevertheless the fact that no evidence of such symptoms is observed doesn't mean that they *< will stay in good shape. Even items that appear fine for long periods can suddenly deteriorate once chemical changes start ... >* [1].

The conservation of celluloid objects in museum collections *< ... has suffered badly from a lack of detailed understanding about the materials and techniques used for the manufacturing, the conservation and the restoration of artefacts that are now in critical condition, ... >* [1].

The application of up to date diagnostics methodologies capable to give details about the composition of celluloid based items and also about the prevailing mechanisms of deterioration, starting from a careful reading and interpretation of symptoms of damages, is necessary to identify the more suitable conservation techniques (including cleaning, restoration and protection and the conditions of displaying) finalized to avoid further degradation processes or at least reduce their rate of propagation [2,3].

--- The degradation of celluloid and the most common symptoms of degradation observed in celluloid artefacts

The most common observed signs of deterioration on celluloid artefacts, due to the actions of both physical and chemical factors are:

- Crazing and cracking;
- Discoloration and change in colour (especially if pigments/colorants sensitive to the action of acids are present) and yellowing;
- Liquid exudates on the surface (aqueous zinc nitrate solution following reaction between ZnO And HNO_3)
- Liquid exudates, from which crystals of CaSO_4 -dihydrate separate;
- formation of surface efflorescence;
- Corrosion of metal components following reaction with acids produced by degradation phenomena [4].

Celluloid objects with clear symptoms of chemical degradation are shown in figures 1-4 [5,6,7].

The degradation behaviour of celluloid is strongly dependent on its composition. Thus the knowledge, through the application of suitable diagnostic methods, preferably non-destructives, of the chemical nature of additives and their relative content in a celluloid item represents the first step to be accomplished. The pattern of degradation of celluloid will be the resultant of the complex phenomena involving not only the main components (cellulose nitrate and camphor) but also several other additives and fillers as well as impurities deriving from the manufacturing processes.

Some of the most relevant degradation phenomena of celluloid involving also the various components are hereafter reviewed.

--- Thermal de-nitration of cellulose nitrate

It is well known that the cellulose nitrate, main component of celluloid, undergoes a spontaneous heat induced thermal degradation process, accelerated by light exposure, that leads to the release of gaseous and toxic vapour of nitrogen oxides (NO_x) which in presence of oxygen and humidity transform in nitrous and nitric acid (HNO_2 and HNO_3). Those acids have the capability to favour the hydrolysis of the polymer; < ...once initiated the process becomes auto catalytic > [4].

Due to the above phenomenon in order to minimize the effects of nitric acid the artefacts in celluloid should be stored in environment where active procedures are able to remove the HNO_3 from their surfaces. Moreover textiles and metal objects, sensitive to the attack by the HNO_3 should be never kept in the proximity of celluloid [10].

--- Degradation effects due to lignin

Cellulose raw materials such as cotton fibres, contain a certain amount of lignin, a water resistant polymer, with a very complex molecular structure (see figure 5), that is present in the cellular walls of all vascular plants where it acts as reinforcing agent to avoid their collapsing [11].

Lignin is unstable to light, thus following a photo-oxidative process, gives rise to the formation of a mixture of acid substances, which favour the degradation of the cellulose nitrate polymer.



FIGURE 1, left: < The series of images... shows the stages of degradation of Antoine Pevsner's 1923 "Head of a Woman," made of nitrocellulose plastic. Courtesy of the hirshhorn museum; John lee/National Museum of Denmark > [5].

FIGURE 2, centre: Setsquare in celluloid [7].

FIGURE 3, right: Handbag comb made in celluloid [7].



FIGURE 4:

Left, heavily degraded shoehorn made in celluloid (1930) [8].

Right, < Decaying cellulose nitrate with active corrosion at the contact points between the metal and plastic. Image by Emily Williams, Colonial Williamsburg > [9].

--- Degradation induced by the presence of residues of the bleaching process of raw cellulose

Before the reaction of nitration the raw cellulose is, as a rule, bleached, < a process in which natural colouring matter is removed from a textile fibre to make it white > [12]. Usually a bleaching agent is < an oxidizing or reducing chemical such as sodium hypochlorite, sulphur dioxide, sodium acid sulphite, or hydrogen peroxide > [12].

Following the bleaching process acid residues as well as derivative of chlorine are left in the cellulose.

It has been demonstrated that such impurities may contribute to the deterioration of cellulose nitrate and then of celluloid plastics.

--- Degradation related to the presence of camphor

As already written camphor is used as plasticiser of cellulose nitrate. It has been observed that the % of added camphor represents crucial factors as far as the overall properties of celluloid are concerned.

As matter of fact if the % is relatively low then celluloid results to be fragile, thus easy to form crazes.

On the contrary a relatively high % of camphor content determines a sublimation phenomenon from the bulk that causes many deleterious effects to the characteristics of artefacts in celluloid.

It is also worthwhile to remind that some impurities contained in the camphor may also be the reasons for the yellowing of the celluloid.

The technique based on the *Fourier transform Infrared Spectroscopy* (FTIR), according to R. Stewart and others, results to be particularly successful in the study of the degradation of celluloid as it allows the determination of the degree of deterioration by monitoring the process of denitration of cellulose that imply first the removal of the NO₂ groups from the backbone chains and second the formation of HNO₃ molecules following reaction with water (see the below scheme) [13].

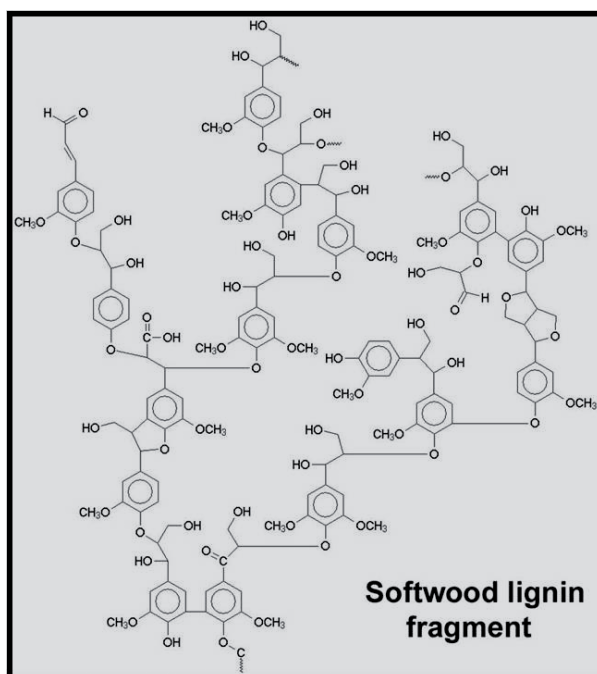
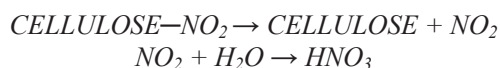


FIGURE 5: Molecular structure of softwood lignin fragment [11].

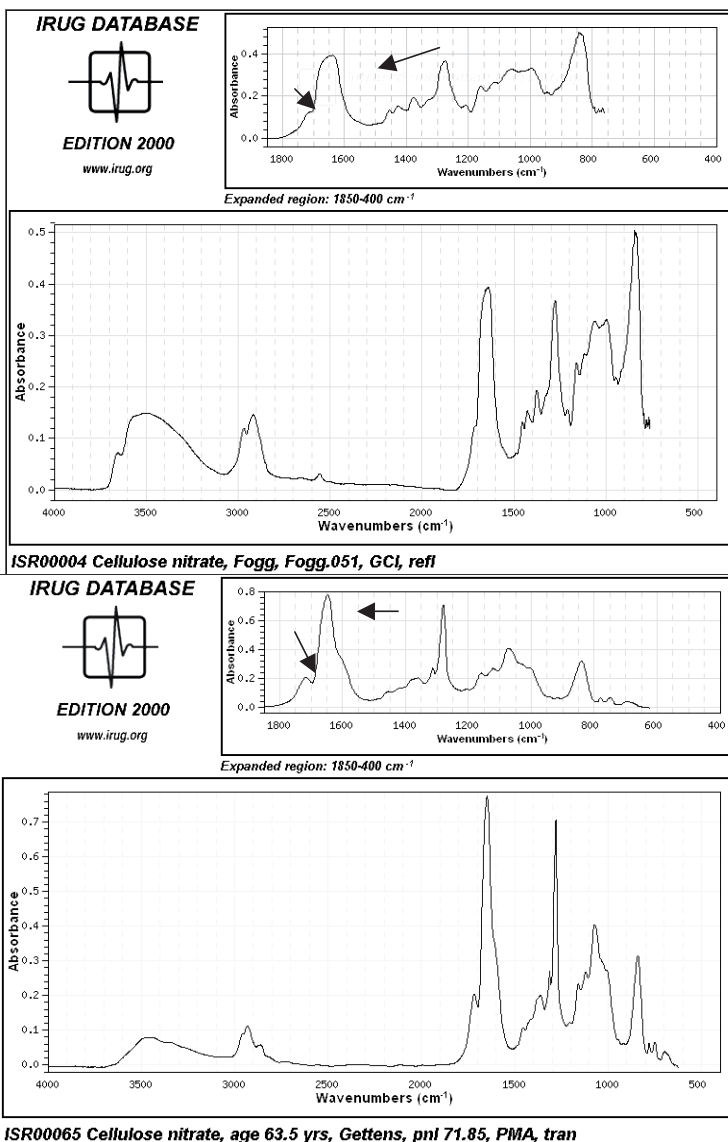


FIGURE 6: Top - FTIR spectrogram in absorbance of un-degraded cellulose nitrate sample.

Bottom - FTIR spectrogram in absorbance of aged cellulose nitrate. The arrows indicate the absorbancies at 1650cm^{-1} and 1733cm^{-1} of cellulose-bonded $-\text{NO}_2$ and carbonyl groups present on additives molecules, respectively [13].

The entity of the reaction of de-nitration, as can be seen by the spectrograms in figure 6 may be qualitatively and quantitatively assessed by measuring the relative lowering of the intensity of the FTIR peak at 1650cm^{-1} , due to the absorbance of the $-\text{NO}_2$ groups bonded to the cellulose chains, taking as reference a unmodified band. Moreover through FTIR it is also possible to quantify the lost of additives from the celluloid mass from the intensity of the band at 1733 cm^{-1} due to the presence of carbonyl groups migrated to the surface of the artefacts(figure 6) [13].

Sulphates and oxalates were found in degraded samples of celluloid by Ion-Exchange Chromatography investigation. According to reference [13] the sulphates derive from molecules of acid residues of the manufacturing processing or from the hydrolysis of cellulose bonded $-\text{SO}_3$ groups, while the oxalate are by-products of the complex degradation pattern of nitro-cellulose.

Some case histories, concerning the application of various diagnostic techniques to assess the chemical composition and the state of conservation of celluloid artefacts, are described in order to verify their effectiveness in determining the nature and origin of the visible symptoms as well as the most dangerous factors active in the degradation processes.

Case-1: Deterioration of celluloid in constructivist sculptures, made by Gabo and Pevsner [10]

The most relevant results of a study performed by M. Derrick, S. Stulik and E. Ordonez, aiming at the identification of the origin and mechanisms of factors leading to the deterioration of some artefacts in celluloid manufactured by *Gabo and Pevsner* (see example in figure 7) are hereafter reported [10-a)].

--- Head of a Woman (Naum Gabo-1917-1920)

The object, stored in the *Museum of Modern Art's* (MoMa), < ..was formed from thermally shaped, cream-colored pieces of cellulose nitrate and cellulose acetate.....When on display, it was hung in a corner with no vitrine > [10-a)].

The sculpture shows as all a rather good state of conservation. Nevertheless crazes are present in some of parties while a yellowing process interests others.

From FTIR analysis it was confirmed that cellulose nitrate is the main structural component of the artefact. By X-rays diffraction it was possible to point out the presence of zinc oxide used as opacifier. The cause of yellowing was unascertainable [10-a)].

--- Head of a Woman (Antoine Pevsner-1923)

From the analyses the artefact, in cellulose nitrate and in a bad state of conservation, kept c/o the *Hirshhorn Museum*, Washington D.C., resulted to be heavily yellowed showing a diffuse phenomenon of crazing. The basement of the sculpture was in nitrate of cellulose opacified with zinc oxide. The oily exudates liquid found on the surface of the object following display in a showcase, resulted to be composed by a basic water solution containing zinc nitrate ($\text{Zn}(\text{NO}_3)_2$). Such a salt was the resultant of a chemical reaction between the zinc oxide-based pigment and nitric acid produce by the de-nitration of the polymer component.

--- Torso (Antoine Pevsner-1923-1924)

Such a sculpture showed a relatively good state of conservation. Nevertheless the following symptoms of degradation were observed:

- Crazes and discolouration of transparent components;
- The presence of a liquid exudates brown in colour;
- Corrosion of metal components.

Moreover it was found that from the exudates crystals separate. Such a crystals, following characterization by FTIR, X-ray diffraction and SEM-EDS (Scanning Electron Microscopy-Energy Dispersive Spectroscopy) resulted to be composed by calcium sulphate bi-hydrate and zinc based salts

--- Torso (Antoine Pevsner-1923-1926)

The artefact consists of several parts made on transparent cellulose nitrate jointed to copper components.

The plastic elements following crazing and discolouration phenomena resulted to be opaque. On the surface the presence of a liquid exudates, containing nitrate salts, was observed.

The component in copper were interested by a corrosion process with formation of a green-blue coloured powder due to the production of copper nitrate.

In all above examined artefacts was assessed, by FTIR, the presence of camphor as plasticiser. The cited Authors found a strict correlation between the camphor content and the degree of degradation of the object in celluloid. As matter of fact items with higher camphor content showed a relatively better state of conservation and an infrared absorbance band at 1340cm^{-1} , characteristic of nitrate, with a lower intensity.



FIGURE 7: Antoine Pevsner, *Torso*, made in celluloid, \approx 1925 [10-b)].

Case-2: Deterioration of celluloid artefacts stored at the Victoria & Albert Museum, London [6]

--- The handle of the Beatrice Lillie fan

The item, shown in figure 8, < shows behaviour typical of cellulose nitrate degradation with the material becoming crystalline and opaque > [6].

--- A cellulose nitrate necklace from the 1922 stage production of Chu Chin Chow

This artefact results to be heavily degraded. The state of conservation was described in reference [6] as follows: < In this case the acidic vapour formed on degradation has caused the textile thread holding the beads to disintegrate completely. A metal component of the necklace has also been attacked, resulting in a bright blue corrosion product >.



FIGURE 8: It is illustrated the degradation of cellulose nitrate observed on the handle of the *Beatrice Lillie fan*, made in celluloid (Theatre Museum collection of the Victoria & Albert Museum, London) [6].

Case-3: Deterioration of boxes in celluloid belonging to the M. P. Incutti collection (Naples)
[14]

The results of an attempt aiming at the characterization of ancient boxes made in celluloid, naturally aged (see figure 9), by using several different techniques of analysis, are reported in reference [14].



FIGURE 9: Boxes in celluloid belonging to the M. P. Incutti collection (Naples) whose state of conservation was investigated in the framework of the project cited in reference [14].

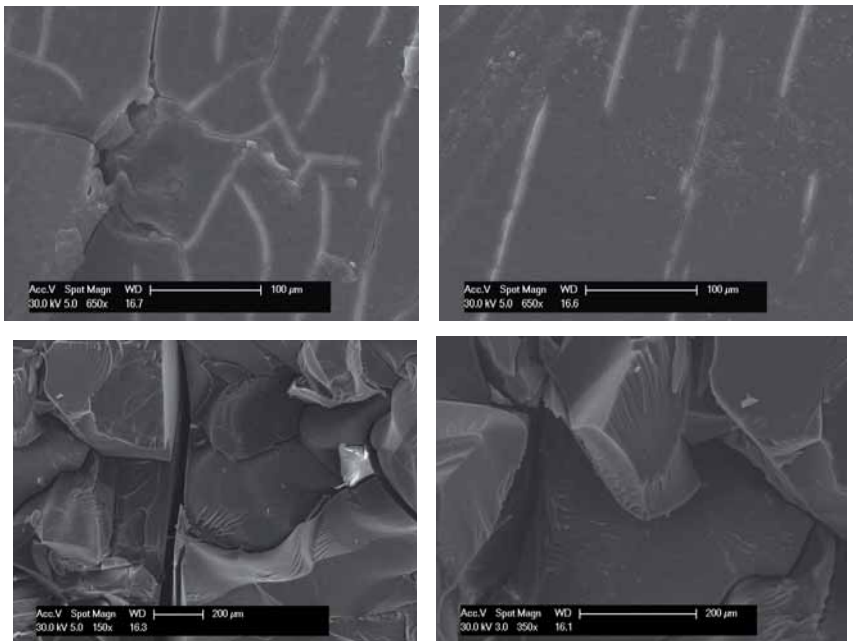


FIGURE 10: Scanning electron micrographs of:
Top, surface of the yellow box with the mother-pearl like motives (figure 9-left);
Bottom, transversal section sample [14].

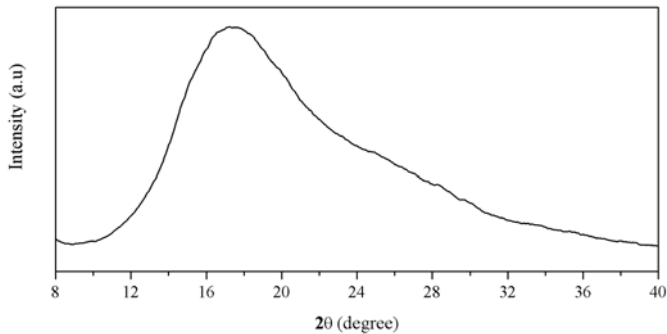
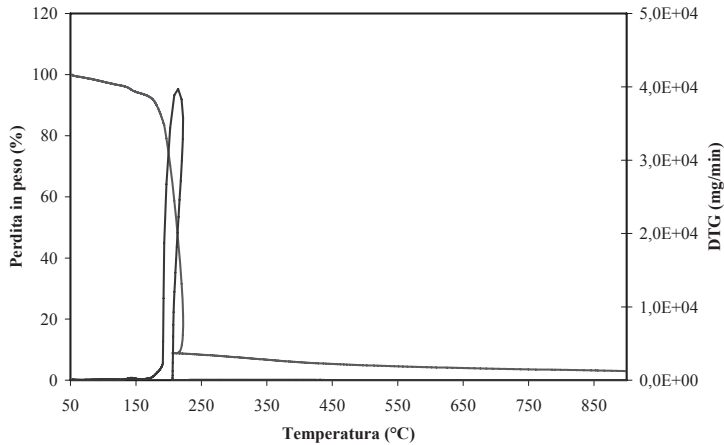


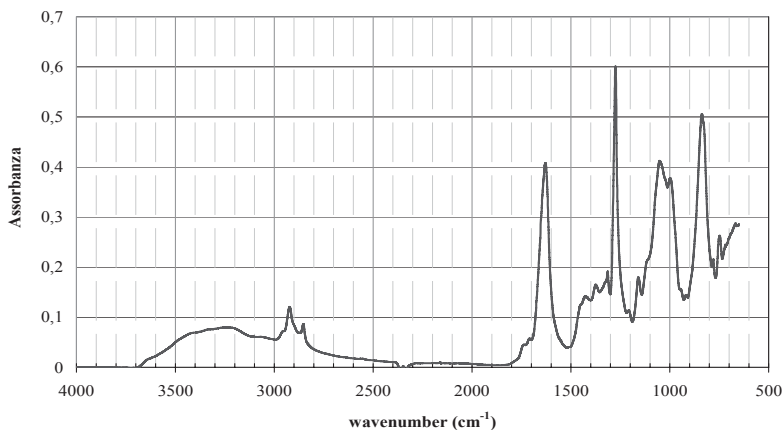
FIGURE 11, Top: Thermogravimetric and Differential Thermogravimetric (DTG) diagrams of samples of the artefacts shown in figure 9-left [14].
FIGURE 12, Bottom: X-ray diffractogram of a sample from the artefacts shown in figure 9-left [14].

From the destructive analyses performed on samples taken away from the box in figure 9-left, by means of Scanning electron micrographs (SEM), Thermogravimetry (TG) and Differential Thermogravimetry (DTG), Wide-angle X-ray diffraction and FTIR-ATR techniques, whose results are shown in figures 10 11, 12, and 13 respectively, the following elements emerge [14]:

- 1) SEM micrographs of the surface of the yellow box with the mother-pearl like motives (see image in figure 9-left) and of the transversal sections, shown in figure 10, evidenced the presence of crazes and detachment phenomena due to natural ageing.
- 2) A sample taken from the box heated from 50 to 900°C at a rate of 20°C/min presents a combustion process at 200°C with almost no residual material (see figure 11).

3) The material used to manufacture the box results to be from X-rays diffraction essentially amorphous (figure 12).

4) The FTIR-ATR spectrogram is typical of nitrocellulose (figure 13) [14].



Assignment ^a	NC IR
Pyranose	543 w
$\gamma_r(\text{NO}_2)$	625 w, 638 w
Pyranose	688 m
$\delta(\text{NO}_2)$	692 m
$\gamma_w(\text{NO}_2)$	747 m
$\nu(\text{NO})$	843 b, s
$\delta(\text{CH})$	915 w, 947 vw
$\nu(\text{CO})$	1000 m, 1020 m
$\nu_a(\text{C-O})$ pyranose	1073 m, 1117 m, 1162 m, 1208 vw
$\nu_s(\text{NO}_2)$	1280 b, s
$\gamma_w(\text{CH}_2)$	1313 sh
$\delta(\text{CH})$	1382 w
$\delta(\text{C-OH})$	1426 w
$\delta(\text{CH}_2)$	1454 w
$\nu_a(\text{NO}_2)$	1660 b s
$\nu(\text{CO})$	1719 m
$\nu(\text{CH})$	2972 b w, 2924 b w

FIGURE 13: FTIR, ATR mode, spectrogram of a sample of the artefacts shown in figure 9-left [14]. Below are reported the assignment of the main bands of absorbance [14].

The above results lead to conclude that, in general, the techniques of diagnostics based on chemical instrumental analysis (FTIR, WAXS, SEM and SEM-EDS (Scanning Electron Microscopy-Energy Dispersive Spectroscopy), DSC, TG and DTG, DTMA, NMR, etc.) can be effective not only for the definition of the composition of objects in plastics and their state of conservation but also for the determination of the chemistry of the most active processes of deterioration and the nature of the degradation products including liquid and solid exudates, and this in agreement with the major apparent symptoms of degradation [15,16].

Several reliable instrumental methods are available, now a days, capable to identify the functional chemical groups characteristics of macromolecules component of a plastic materials as well as related additives molecules (see for example those indicated in table 1). *< Accuracy depends on the technique selected and generally, the more techniques that are used in the identification process, the more reliable the result. Where sampling of an object is restricted, only techniques causing minimal damage should be used for analysis >* [15].

Of the instrumental chemical diagnostic technique listed in table 1 *< Fourier transform infrared spectroscopy offers the most information while demanding the absolute minimum of damage to the object tested >* [15].

TABLE 1: Some of the techniques used for the identification of plastics and their components. On the right column the main information obtained is indicated [15].

Technique	Information obtained
Fourier transform infrared spectroscopy (FTIR)	Characteristic spectrum of the plastic
Differential Scanning Colorimetry (DSC)	Glass transition temperature and melting point
Nuclear magnetic resonance spectroscopy (NMR)	Chemical structure
Dynamic thermal mechanical analysis (DTMA)	Glass transition temperature

By using a correct combination of some of the above techniques, it is possible to get information suitable for defining the type of conservation measures to be applied. Some of the most relevant topics, which have been elucidated in the case of celluloid objects following a proper interpretation of the results obtained by means of these methodologies, are hereafter summarized.

1) The most effective factors of degradation in the case of celluloid artefacts are essentially related to:

- Unsuitable conditions of storage or display;
- Chemical nature, function, reactivity and content of additives;
- Presence of residues of processing as well as impurities;
- Physical geometry and design of the artefacts
- Presence of components in metal [10-a].

2) The thermal degradation of celluloid determines the removal of $-\text{NO}_2$ groups following the scission of the $\text{O}-\text{NO}_2$ bonds. Such a reaction normally occurs at a temperature $> 100^\circ\text{C}$.

3) The physical degradation of celluloid is associated to the migration of the plasticisers as well as to mechanical stresses induced by processing methodologies.

4) The chemical degradation of cellulose nitrate is mainly due to acid or basic hydrolysis. The acid hydrolysis causes the scission of glycoside bonds, which in turn determines the reduction of the degree of polymerisation of the chains. The alkaline chemical degradation, occurring at a higher rate, gives rise to the production of low molecular weight molecules together with oxidized compounds.

The two possible mechanisms of the alkaline hydrolysis of cellulose nitrate, leading to the formation of nitrates and nitrites, are depicted in figure 14 [16]. The first one consists in the hydrolysis of the ester, while the second produces molecules of oxidised cellulose [16].

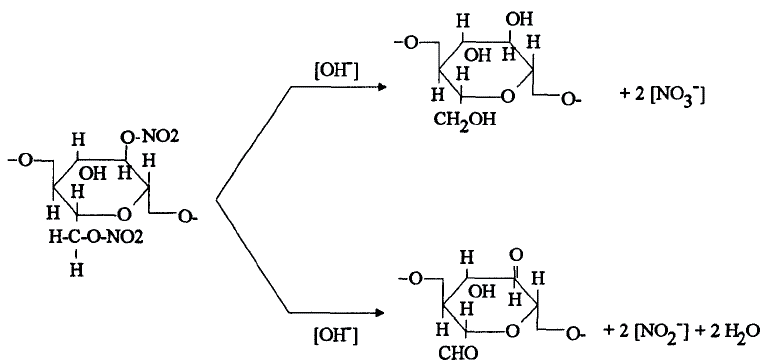


FIGURE 14: The two possible mechanisms of the alkaline hydrolysis of cellulose nitrate, leading to the formation of nitrates and nitrites, The first one (top) consists in the hydrolysis of the ester, while the second one (bottom) produces molecules of oxidised cellulose [16].

M. Avella and others demonstrated that the alkaline chemical degradation of celluloid, induced artificially by treating samples of celluloid with a 2% water solution of NaOH at 70°C for different times (25mins, 1 and 2 hours) may be conveniently studied by FTIR [14].

As matter of fact, as shown in figure 15, in the region between 1800-1300 cm^{-1} the FTIR spectrogram of a sample of celluloid shows the absorbance bands, at 1730 cm^{-1} and at 1640 cm^{-1} , due to the stretching of the camphor C=O groups and to the NO₂ groups present along the cellulose nitrate chains respectively (see arrows in figure 15).

The alkaline ageing, as can be seen by the spectrograms in figure 15, determines a sharp reduction in the intensity of the 1740 cm^{-1} band (see left arrow in figure 15), accounted for by a lost of plasticiser (camphor), and by a gradually diminishing of the intensity of the 1640 cm^{-1} band, due to the de-nitration effect (see right arrow in figure 15) [14].

The process of alkaline induced de-nitration of cellulose nitrate may be also detected by assessing the reduction of the intensity of the band at 1280 cm^{-1} related to the symmetric stretching of the NO₂ groups bonded to the polymer chains (see arrow in figure 16) [14].

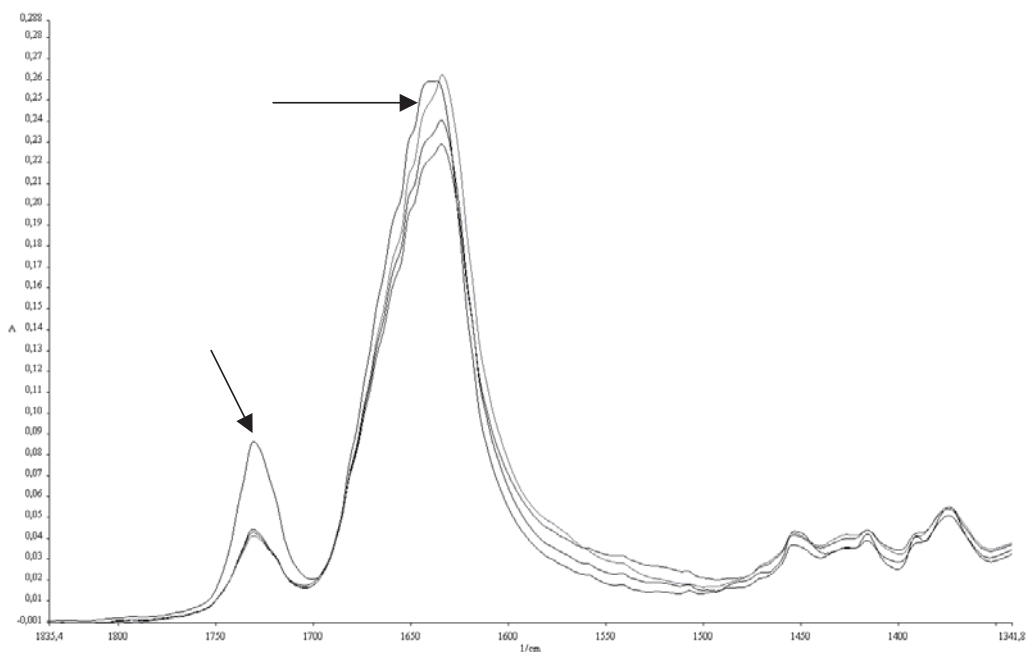


FIGURE 15: FTIR spectrograms, region between 1800-1300- cm^{-1} , of samples of celluloid un-aged (top-line) and alkaline artificially aged in 2% NaOH water solution at increasing times (25mins; 1hour; 2hours), see text [14].

The Raman spectroscopy, as shown by the diagrams in figure 17, turns to be also a suitable technique to follow the chemical degradation of celluloid items [14].

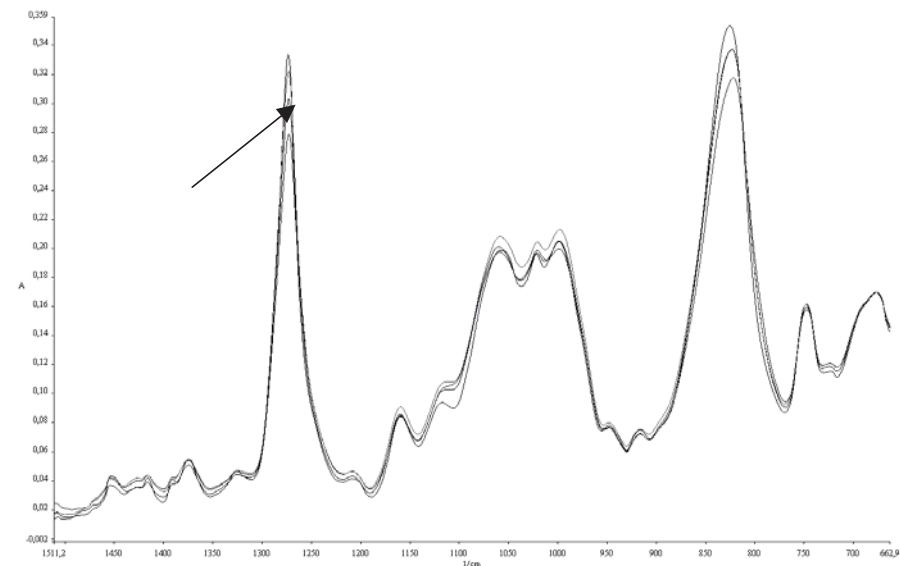


FIGURE 16: FTIR spectrograms, region between $1500\text{-}660\text{-cm}^{-1}$, of samples of un-aged celluloid and alkaline artificially aged in 2% NaOH water solution at increasing times (25mins; 1hour; 2hours), see text [14].

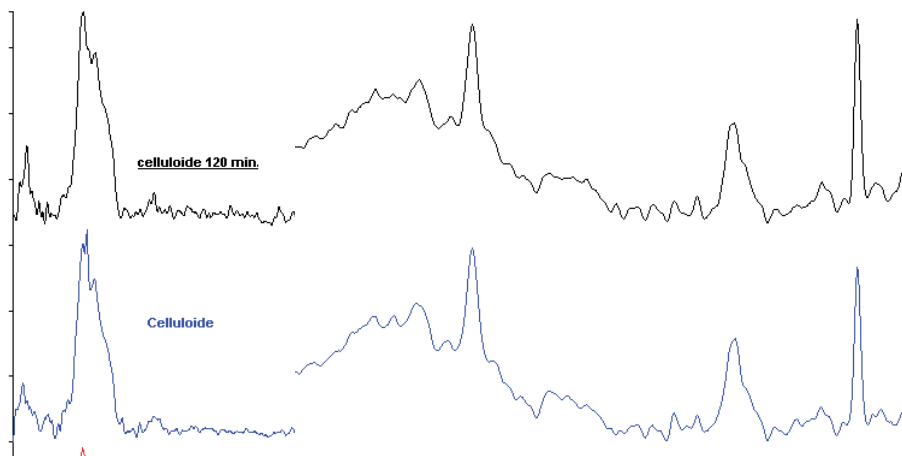


FIGURE 17: Raman spectrograms (only partial view) of samples of un-aged celluloid (bottom) and alkaline artificially aged in 2% NaOH water solution (top, 2hours) [14].

REFERENCES

- 1) Society for Science & the Public 2000 - 2009
www.sciencenews.org/.../title/Long_Live_Plastics, (2009).
- 2) E. Martuscelli, < *le plastiche nel terzo millennio* >, dossier le plastiche, *Ricerca & Futuro*, **23**, 46 (2002).
- 3) E. Martuscelli, < *Le fibre di polimeri naturali nell'evoluzione della civiltà: le fibre di seta* >, Consiglio Nazionale delle Ricerche, Serie Scienze Chimiche, Roma (1999).
- 4) J. Morgan, < *A Survey of Plastics in Historical Collections* >, Plastics Historical Society and The Conservation Unit of the Museums & Galleries Commission.
<http://www.plastiquarian.com/survey/survey.htm>, (1994).
- 5) Society for Science & the Public 2000 – 2009;
www.sciencenews.org/.../title/Long_Live_Plastics, (2009).
- 6) B. Keneghan, < *Plastics? – Not in my collection* >, *Conservation Journal*, October 1996:
http://www.vam.ac.uk/files/file_upload/42730_file.pdf, (2009).
- 7) www.plastiquarian.com/deterio.htm, (2009).
- 8) S. Katz, *Materials World*, Vol. pp. 377-78, August (1995);
www.azom.com/details.asp?ArticleID=1655 (2009).
- 9) C. Brady, M. Gleeson, M. Myers, C. Peachey, B. Seifert, H. Wellman, E. Williams, L. Young, < *Rubber and Plastics* >, Website content ©The Society for Historical Archaeology, 2007.
www.sha.org/.../conservation_faqs/treatment.cfm, (2009).
- 10) –a) M. Derrick, S. Stulik, E. Ordonez, < *Cellulose nitrate deterioration in constructivist sculptures made by Gabo and Pevsner* >, Polymer Preprints, Division of Polymer Chemistry, Inc. , American Chemical Society, **33,N.2**, 637 (1992).
–b) www.dartmouth.edu/.../unit16/unit16.html, (2009).
- 11) sci.waikato.ac.nz/farm/images/lignin%20struct, (2009).
sci.waikato.ac.nz/.../plantstructure.html, (2009).
- 12) < *Dizionario enciclopedico scientifico e tecnico, inglese italiano, italiano inglese* >, McGraw-Hill Zanichelli; Zanichelli (1985).
- 13) R. Stewart et Al., < *Analytical studies of the degradation of nitrate plastics in museums* >, Polymer Preprints, Division of Polymer Chemistry, Inc. , American Chemical Society, **37,N.2**, 168 (1996).
- 14) Conclusions of the Project: < *Sviluppo industriale di procedure semplificate per la caratterizzazione chimica non distruttiva e per il recupero di manufatti in plastica: applicazioni nella catalogazione e restauro di beni culturali e nel controllo qualità di prodotti industriali a base di materiali termoindurenti* >, financed by MIUR (n.: Prot. 915 del 30/01/2004 ammesso al finanziamento con D.D. n°2059 del 21 dicembre 2007 a valere sui contributi del Dlg. n° 297/99 (D.M 8 agosto 2000 n. 593 art. 9)) by AET- CO.BE.CAM. – CNR-ICTP – UNI SALERNO– PERKIN ELMER (2009).
- 15) E. Then, V. Oakley, *Conservation Journal*, N° 6, January (1993).
- 16) M. Edge and others, *European Polymer Journal*, **26**, 623 (1990).

SECTION-2

FIFTH-CHAPTER

PLASTICS BASED ON NATURAL PRE-FORMED POLYMERS: PLASTICS FROM CHEMICAL TRANSFORMATION OF CELLULOSE

CELLULOID:

--- CONSERVATION MEASURES SUGGESTED FOR RELATED ARTEFACTS.

--- PROTECTION MITIGATION AND PREVENTION AGAINST MAIN FACTORS OF DEGRADATION

1) primary and secondary processes of degradation occurring in nitrocellulose

Having in mind the manufacturing cycle of celluloid production, summarized through the scheme in figure 1 [1], hereafter some general recommendations concerning the conservation of celluloid artefacts are presented and discussed also through some literature cited examples.

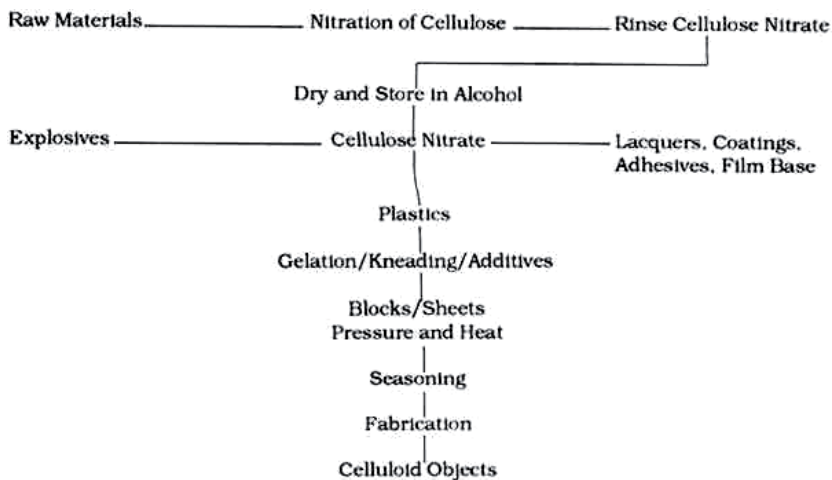


FIGURE 1: Scheme of the manufacturing cycle of celluloid artefacts [1].

The complexity of degradation behaviour of celluloid objects, discussed in details in the previous chapters, is also documented through the example reported in figure 2 where the micrographs of the corrosion products from a degraded cellulose nitrate handbag clasp are shown [2].

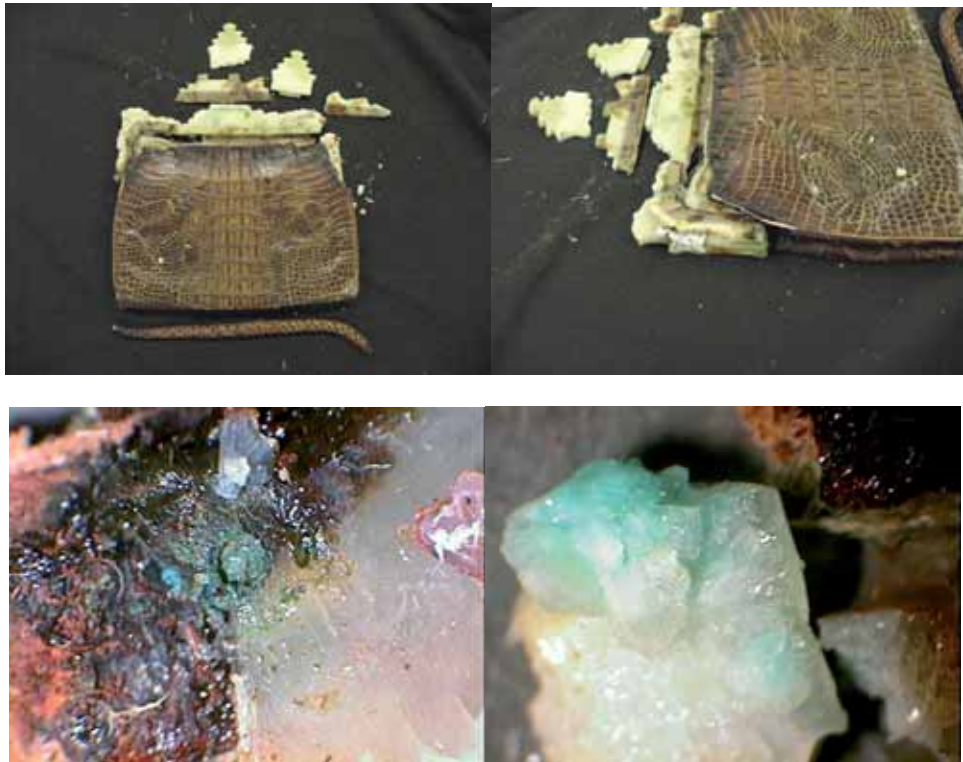


FIGURE 2: Top-left-overall pictures of an alligator purse with degraded cellulose nitrate clasp. Top-right- Side view of the alligator purse. Bottom, micrographs showing the products from degraded celluloid handbag clasp. The data are part of a conservation collection in University of Rhode Island [2].



FIGURE 3: Crystal like growths caused by additives, observed on the surfaces of cellulose nitrate or cellulose acetate objects [3].

The growth of crystals, attributed to migration of additives towards the surface, followed by solidification, as shown by figure 3, has been quite often observed in celluloid objects [3].

The conservation of an object made in celluloid is complicated by the fact that independently of environmental conditions of storage or display, it undergoes important phenomena of ageing following the action of internal factors deriving from the synthesis and manufacturing steps (see figure 1) which, according to reference [1], are mostly linked to the hereafter listed issues:

< --- *Regular deterioration of cellulose molecules; chemical deterioration produced when processing cellulose; range in quality of cellulose used.*
--- *Range in quality of acids, alcohols, and water used.*
--- *Impure camphor, other compounds mixed with camphor.*
--- *Combination of quality and quantity of additives.*
--- *Reversibility of nitration reaction and corrosive power of deterioration products.*
--- *Inhomogeneities of cellulose nitrate fibres.*
--- *Presence of sulphate esters.*
--- *Trapped "free" acids.*
--- *Freedom of movement of camphor.*
--- *Crystallite formation-pressure.*
--- *Seasoning.*
--- *Fabrication technique* > [1].

Thus it comes out that even though an artefact in celluloid was protected from external factors it will anyhow < *deteriorate according to the mechanisms inherent in its own structure.....*
The cellulose nitrate molecules continue to crystallize around the loci created by the pressures used in manufacture. Camphor molecules are squeezed out, often to the surface where they will sublime at room temperature. This sequence of events leaves celluloid very brittle, cracked, shrunken, warped, collapsed, crumbling, discoloured, and crystallized > [1].

When an object made in celluloid is exposed also to the action of adverse external environmental conditions, which in their turn may induce chemical, physical, and biological deterioration effects, then the overall degradation will be the resultant of a synergic combination of the internal/inherent deterioration processes above mentioned. Consequently the apparent symptoms of degradation (discoloration, warping, swelling, softening, the presence of a coating with droplets or a film of nitrate salts and their acids on the surfaces, ecc.) will be much more pronounced.

Quite often in celluloid artefacts are present also component parties manufactured with other materials (metals, glass, textiles, and paper). In such a case the deterioration processes of one of the components may interfere with those of the others (see for example the corrosive effect produced on metal or textile components by the nitric acid deriving from celluloid degradation).

In the degradation of nitrocellulose polymer, main component of celluloid, two distinct types of decomposition processes, usually called as *primary and secondary*, are active. Hydrolytic decomposition via acid catalyzed ester cleavage, thermal, and photochemical degradation are the three primary decomposition processes occurring in nitrocellulose. These processes lead to the formation of breakdown products that may catalytically induce faster and more extensive degradation pathways commonly known as *secondary processes* of degradation [4].

The above processes will be hereafter described and elucidated with some further details.

--- Hydrolytic decomposition via acid catalyzed ester cleavage

It is generally recognized that the presence in the polymer mass of small amounts of free sulphuric acid and sulphate esters of partially nitrated cellulose was responsible for this decomposition process. As matter of fact it was demonstrated that such a type of decomposition is almost absent in the case of acid-free cellulose nitrate samples [4,5].

--- Uncatalyzed, thermal breakdown

As shown by figure 4 at relatively high temperature the uncatalyzed, thermal decomposition pathways are strictly dependent upon the temperature.

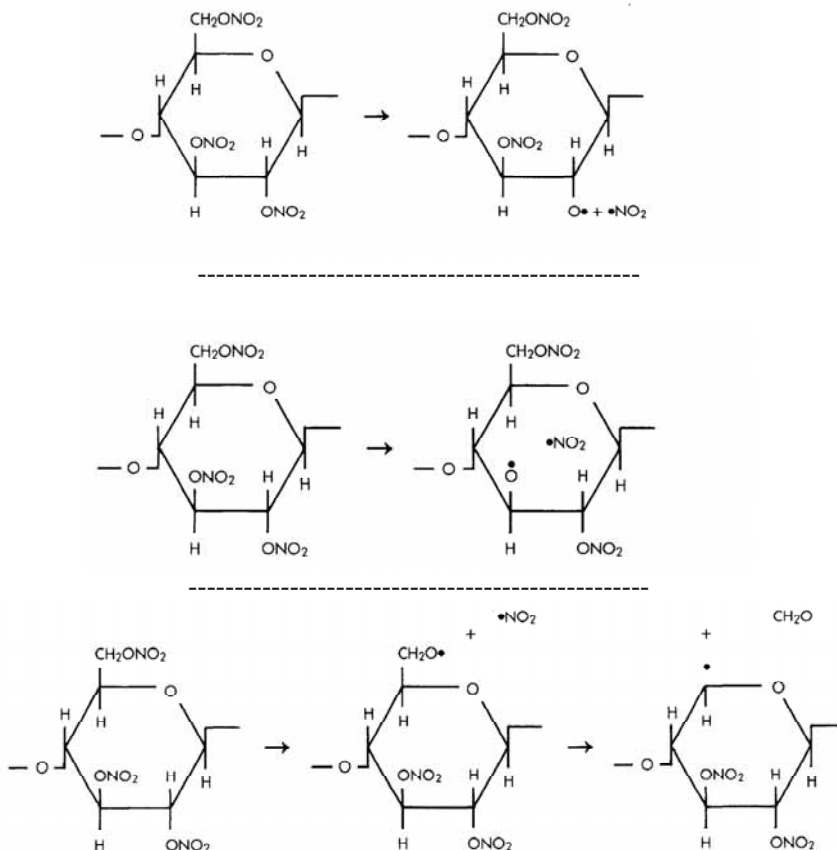
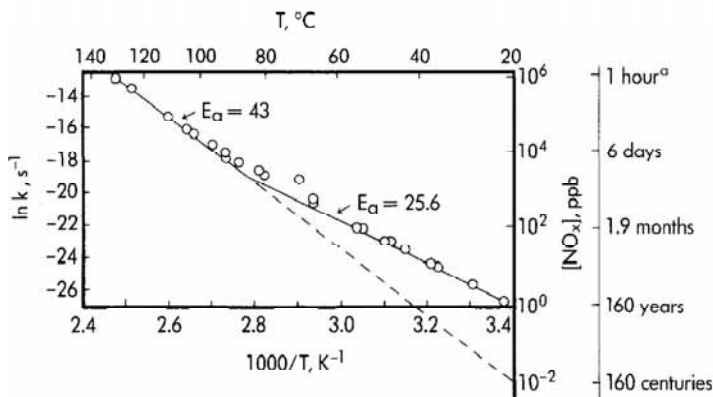


FIGURE 4: Temperature decomposition pathways of nitro-cellulose according to temperature.

Top-Favoured pathway at 120-135°C.

Centre and bottom-Competing pathways at 135-200°C [4].

From the Arrhenius plot, covering the temperature range of 20-135°C, shown in Figure 5, it was possible to assess the effect of temperature on the thermal decomposition of nitrocellulose.



α = Time for cellulose nitrate to degrade to one-third of its original molecular weight.

FIGURE 5: Arrhenius plot covering the temperature range of 20-135°C for the thermal degradation primary process of cellulose nitrate, < The first order rate coefficients are calculated as moles of NOx given off per submole of nitrated glucose anhydride unit, which for 12% nitrogen has a molecular weight of 264 > [6,4].

On the right side of Figure 5 < there is added to the graph published by Fontijn an ordinate that provides the amount of time it would take for 1 gram of cellulose nitrate to form approximately 1 milligram of nitrogen as a function of temperature > [4,6].

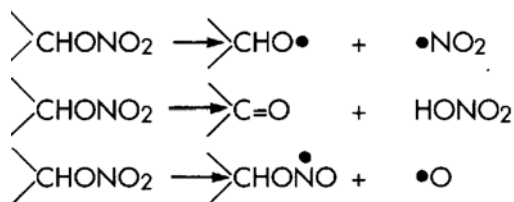
From figure 5 it can be seen that the < experimental points yield a non-linear Arrhenius plot, which, however, can be resolved into two straight lines corresponding to an activation energy of 25.6 Kcal per mole below 80°C and 43 above..... The lower activation energy that prevails over the lower temperature range means that a different reaction mechanism predominates under milder conditions and indicates a mechanism that is much less temperature dependent. > [4].

The above findings indicate that also at relatively low temperature the decomposition process of cellulose nitrate, based on uncatalyzed thermal decomposition, may be active.

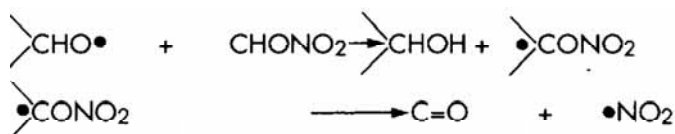
--- Decomposition by Ultraviolet Radiation

It is well known that nitrated cellulose artefacts when exposed, at room temperature, to the action of solar light undergo discoloration (a sample with a water white colour becomes yellow and then brown) contemporaneously a gradual loss of the most important physical properties is observed. For long time of exposure the sample may be completely and irreversibly degraded.

According to the results obtained on model molecules (alkyl nitrates) the following three primary processes occur in the near ultraviolet [4, 7]. The first reaction seems to be favoured.



The reaction then proceeds sequentially according to the following pathway:



This mechanism accounts for the loss of nitrogen but does not for a chain scission process that seems to be active at shorter wavelengths where a viscosity reduction, with little change in nitrogen, was observed. In order to explain also the later process a ring disintegration mechanism for spontaneous decompositions at lower temperatures was postulated [4].

According to the literature data cited in reference [4] *< the ring disintegration mechanism can occur only in rings containing three nitrate esters and cellulose nitrate with a D.S. of 2.6 (the average number of nitrate groups per ring is known as the degree of substitution or D.S.) consists primarily of tri-nitrated rings. In this mechanism there is little change in residual nitrogen content. Their findings provide support for the two different modes of photochemically induced cellulose nitrate decomposition >* [4].

Thus it can be concluded that at low temperature the prevailing primary mechanisms, concerning the degradation of cellulose nitrate, are essentially the following:

- (1) Acid catalysed ester cleavage;
- (2) Homolytic scission of the nitrogen-oxygen bond;
- (3) Ring disintegration [4].

As far as the secondary modes of decomposition at ambient temperatures are concerned the mechanism depicted in figure 6 was proposed [8,4].

< An initially formed oxy radical (Structure A in Fig. 6) converts to a cyclic ketone; this conversion step may be the source of NO formation. The keto-enol structure is relatively stable but in the presence of NO and NO₂ addition reactions occur.

These lead to products that contain multi-nitrated rings, D and E, with di-nitrated carbons. These are structures that should be highly susceptible to ring disintegration. Therefore, tri-nitrated rings can be expected to be less stable than di-nitrated rings by secondary modes of decomposition at ambient conditions > [4].

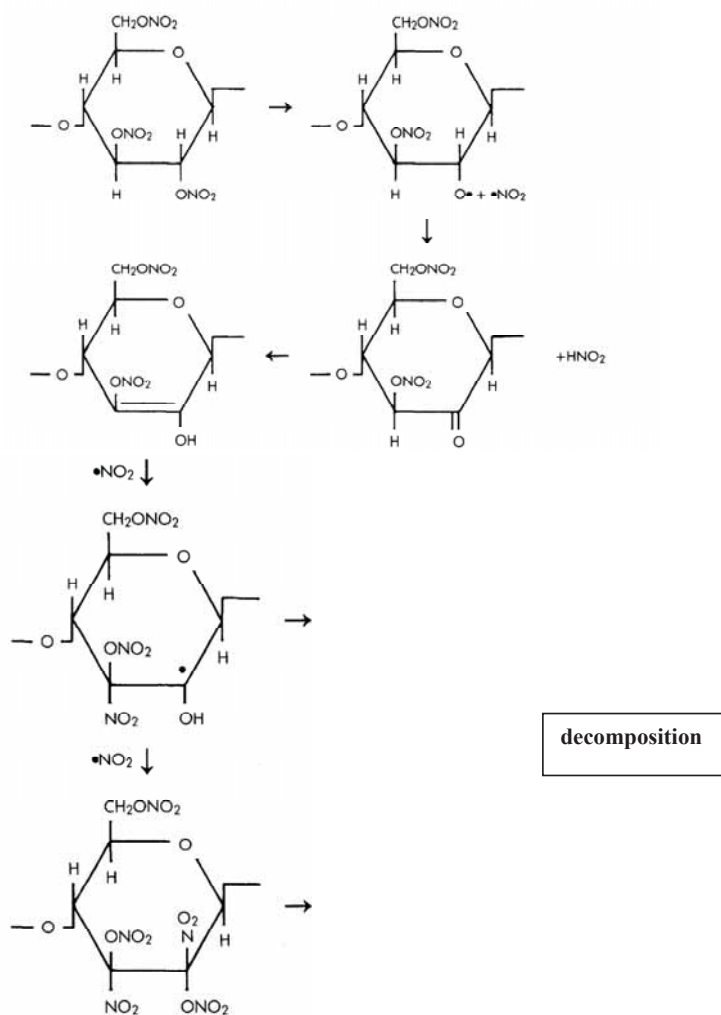
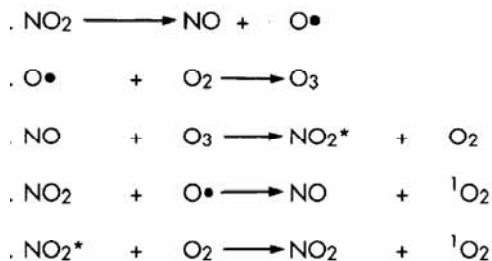


FIGURE 6: Suggested pathways of secondary decomposition for cellulose nitrate [8,4].

The exposure to UV radiations favours the occurring of the hereafter-listed reactions concerning still the secondary modes of decomposition of cellulose nitrate:



< In particular the reaction between ozone and NO is highly exothermic and leads to electronically excited NO₂The destructive effect of this reactant is well known.....

Thus, the effect of UV radiation is to enhance markedly the decomposition caused by secondary reactions particularly where the radiation takes place in the presence of oxygen > [4].

In order to investigate about the influence of several inherent factors (sulphate, filler, iron, and humidity) on the degradation behaviour of celluloid, accelerated ageing experiments were performed by R. Stewart and others on samples ad hoc prepared in laboratory [9].

The ageing was accomplished according the following modalities:

< The samples were placed in glass tank at 75% humidity (using a saturated N_aCl solution) in an oven maintained at 70°C. Samples were taken out at regular intervals and analysed by FTIR spectroscopy, ion chromatography and microanalysis for total % nitrogen > [9].

The results attained are below summarised.

--- Influence of sulphate

Samples of celluloid with different content of sulphate (from 0 to 5mg g⁻¹) were prepared by varying the degree of washing. It was observed that disks of celluloid with higher sulphate content physically degraded become, with time of ageing, brown and brittle. Contemporaneously in the samples a reduction in the nitrogen content (see data in table 1) was found indicating the occurring of a process of chemical degradation.

Under the same ageing conditions celluloid samples free of sulphate practically showed no symptoms of chemical /physical degradation (table 1) [9].

--- Influence of filler

To study the influence of inorganic filler two celluloid samples, one containing 2% zinc oxide and 5mg g⁻¹ sulphate and another just 5mg g⁻¹ sulphate were prepared and aged under the same conditions. The results showed that the sample containing the inorganic filler degraded at a considerably lower rate than that without filler [9].

--- Influence of iron

It was found that, at least under the conditions explored, samples of celluloid containing 10 and 100g g⁻¹ iron showed no signs of degradation after four weeks of artificial ageing [9].

TABLE 1: Change in nitrogen content (%) with the ageing time for two samples of celluloid containing 0 and 5mg g⁻¹ of sulphate (ageing conditions: 70°C and 75% RH) [9].

Time (hours)	0 mg g ⁻¹ sulphate	5 mg g ⁻¹ sulphate
0	10.6	10.1
24	10.4	9.6
72	10.3	9.7
168	10.4	9.1
240	10.5	8.2
336	10.4	7.5

--- *Influence of humidity*

Samples of celluloid with 1 mg g⁻¹ sulphate were exposed to artificial ageing (ageing conditions: 70°C and 11 or 55 or 75% of RH). The humidity seems to play an important role in the degradation behaviour of celluloid. In particular it was found that *< samples in the more humid environment degraded at a far higher rate than those at 11% RH as indicated by a decrease in the % nitrogen (10.5 and 7%) and formation of oxalate (see data in table 2) >* [9].

The above findings lead the Authors to the following comment:

< ...humidity is a major factor in the rate of degradation. Anions such as sulphate and oxalate will become hydrolysed to acids in the plastics and cause increased deterioration > [9].

TABLE 2: Concentration of oxalate (mg g⁻¹) detected in celluloid films artificially degraded at 70°C and 11, 55, and 75% of RH [9].

Time (hours)	11%	55%	75%
0	0	0	0
24	0	0	0.1
48	0	0	2.3
96	0	0	5.2
168	0	0.4	8.0
240	0	2.5	9.8

The above results confirm that techniques capable to detect the decrease of the nitrogen content in celluloid samples, due to de-nitration, as well as the increase of the % of oxalate are effective in to follow the degree of ageing of artefacts made in celluloid. Moreover it comes out that inorganic fillers as ZnO , by neutralising acids are able to reduce the rate of degradation [9].

2) Tests for the identification and characterization of celluloid as component of artefacts

Artefacts in celluloid, a rigid thermoplastic, are usually manufactured by compression or blow moulding, casting, or machining.

For the identification of celluloid and its components several test of chemical, physical or analytic nature have been developed. Some of them are henceforth described.

--- **Solubility test:** Celluloid dissolves in ketones (especially acetone), sulphuric ether, alcohol, oil of turpentine, esters (i.e. amyl acetate), etc., or in various combinations of these agents. Whereas it is insoluble in water, ethanol and hydrocarbons [10,11].

The solubility of cellulose nitrate is determined by its degree of nitration. Samples with lower nitration level (10.2-11.2%) are soluble in alcohol, whereas those with higher degree of nitration (12.4-13.0%) turn to be less soluble in alcohol but result to be soluble in ketones and ester solvents. Solvents as acetone, other ketones, and alkyl acetates preferentially dissolve the amorphous phase of cellulose nitrate, whereas methyl nitrate, alkyl nitrate, are capable also to change the crystalline structure of the cellulose nitrate molecule [1].

The solubility behaviour of celluloid is complicated by the fact this plastic is a two component system (camphor and cellulose nitrate).

Thus < *Some solvents, such as ethanol, primarily affect the camphor portion while others affect both portions (acetone) and some affect only the cellulose nitrate (water)* > (see celluloid components solubility data in table 3) [1].

A solubility test, effective in to differentiate celluloid from ivory, is described as follows in reference [1].

< *It involves taking a very small scraping from the object with a small scalpel blade under low magnification. The sample, visible under microscope, is left on the edge of the scalpel blade and a single drop of acetone is placed on the sample. Ivory flecks do not dissolve and are swirled around in the currents of the acetone drop. These flecks appear to sparkle as they reflect light. Celluloid dissolves instantly, leaving an apparently pure drop of acetone* > [1].

--- **Burning tests:** Celluloid burns rapidly and continually with a bright yellow flame when ignited giving off the odour of camphor while burning [1,10,11].

--- **Rubbing test:** Celluloid when gently rubbed with a soft cloth will give off the characteristic odour of camphor.

--- **Nitrogen test:** The content of nitrogen, it gives also a measure of the degree of nitrate ester substitution, can be determined by using several techniques.

Such a test is not specific for celluloid as it only indicates the presence of nitrogen-containing polymers. The test is useful in to distinguish celluloid from other cellulose derivatives.

TABLE 3: Solubility of celluloid components in various solvents (CN- is for cellulose nitrate) [1].

	CN- soluble	CN- insoluble	camphor- soluble	camphor- insoluble
Water (warm)	x	x		x
Methanol	x		x	
Ethylene glycol	x		x	
Ethanol	x		x	
Other alcohols	x		x	
DMF	x		x	
Acetone	x		x	
MEK	x		x	
THF	x		x	
Pyridene	x		x	
MeCl ₃	x			
1,1,1 trichloroethane	x	x		
Toluene		x	x	
Xylene		x	x	
Turpentine		x	x	
Mineral spirits		x	x	
Naphtha		x	x	
Hexane, heptane		x	x	
Acetic, sulfuric, and nitrate acids	x		x	
Amyl acetone	x	x		
Ether	x	x		
Benzene, benzine		x	x	

---Tests based on stain reactions

Tests based on the fact that some chemicals by reacting with the celluloid components gives rise to the formation of specific and typical stains can also be used to assess the presence of celluloid in artefacts. Some stain reactions used for the identification of celluloid are hereafter described.

--- Diphenylamine Tests [1,12]

Are used to detect nitrogen oxides in cellulose nitrates. Some of them are described in table 4 [1,12].

--- Resorcinol Tests [1]

The procedure of this test is reported in table 5 [1].

--- Carbazole Tests [1]

According to literature data carbazole reacts with cellulose nitrate and with carboxy methyl cellulose giving a deep green colour.

TABLE 4: Diphenylamine tests to assess the celluloid presence in artefacts [1,12]

- A. Dissolve .02 grams of sample in 1 ml of acetone; add, dropwise, a 5% (g/l) solution of diphenylamine in concentrated H₂SO₄. The solution will turn dark blue in the presence of celluloid. With excess diphenylamine solution the mixture will turn brown (Saunders 1966, 27).
- B. Prepare 5% (g/l) solution of diphenylamine in concentrated H₂SO₄. Touch a dissecting needle to acetone, then to the object, then to a drop of the stain solution. A blue color will form in the presence of celluloid (author).
- C. Add a few crystals of diphenylamine to .5 ml of 90% H₂SO₄ and apply on a drop to the sample. A blue color will form in the presence of celluloid (Roff et al. 1971, 161).
- D. Place 20 mg diphenylamine into 1 ml of concentrated H₂SO₄ and apply a drop to the object surface. The color blue indicates celluloid (Haslam et al. 1981, 99).

TABLE 5: Resorcinol test for the identification of celluloid [1]

Wash sample in hot water, digest sample in concentrated H₂O₄; add a small amount of resorcinol. A purplish-blue color indicates the presence of cellulose nitrate.

--- Molisch's test [12].

< *The test is used to detect cellulose as well as modified celluloses such as cellulose acetate and cellulose nitrate, which can be differentiated by the colours of the reaction products. Wood, paper, and cotton give positive reactions* > [12].

The procedure of the Molisch's test is described as follows in reference [12]:

< *Gently rub the frosted end of the microscope slide against the surface of the object. Place a drop of 1-naphthol solution (2% (w/v) 1-Naphthol in ethanol) on the sample. Once the ethanol has evaporated, place a drop of sulfuric acid on the frosted end of the slide and draw it over the sample. Red indicates the presence of cellulose acetate while diffuse yellow-green is characteristic of cellulose nitrate* > (see various steps in figure 7) [12].



FIGURE 7: The various phases of the *Molisch's test* in which two reagents with different volatility (i.e. ethanol (highly volatile and 1-naphthol with low volatility) are used.

Top, a sample is collected by gently rubbing the surface of the artefact over the frosted end of a microscope slide. Once the volatile solvent evaporated, the second reagent can be added.

Centre, a positive result is confirmed by a red colour.

Bottom, this test can also be a confirmation test for a cellulose nitrate if it gives a green colour when positive [12].

The molecular structure of the reagents used in the above-reported tests is described in figure 8.

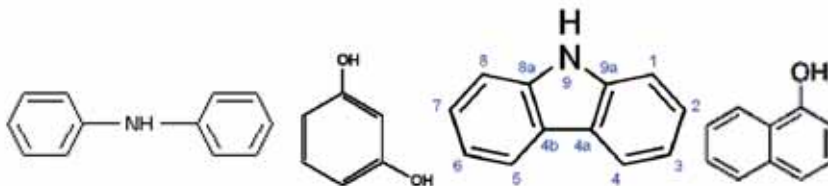


FIGURE 8: The molecular structure of the reagents used in the tests based on stain reactions for the identification of celluloid (see text). From left to right, diphenylamine, resorcinol, carbazole and 1-naphthol.

It must be pointed out that when wood is used as filler then the test can give a false positive answer moreover it cannot distinguish between cellulose nitrate and cellulose acetate photographic films [12].

--- Infrared Spectroscopy Tests

As already reported celluloid may be also identified by FTIR spectroscopy as it gives a spectrum showing a set of absorbance bands that are characteristic of cellulose nitrate and camphor (see diagrams in figure 9) [1].

Usually samples for FTIR investigation are prepared in the form of pellets in KBr or as a thin films. The wave numbers of the most significant absorbance bands of cellulose nitrate, together with the structure of associated chemical groups, are listed in table 6 [1].

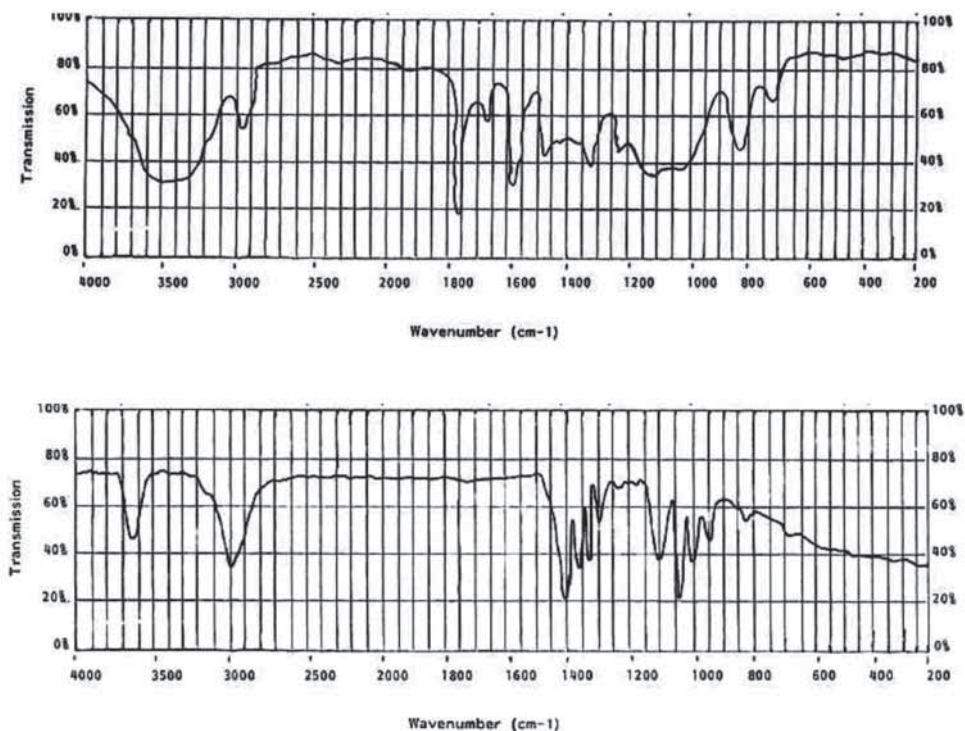


FIGURE 9: Generalized IR-spectra of aged celluloid, (top) and of camphor (bottom) [1].

TABLE 6: Wave numbers of the most significant IR absorbance bands of cellulose nitrate (left-side). The structure of associated chemical groups are indicated on the right-side. [1].

Wavenumber (cm-1)	Structure
3300-3400	(OH); can be indication of esterification (2.87 μ)
2900	(C-H); of CH ₂ , weak (3.42, 3.51 μ)
1670-1750	covalent nitrates, (6.05 μ) (C=O), camphor (5.71 μ) (also cellulosic)
1580 and 1480	-C=C-; aromatic (6.3 and 6.7 μ) (plasticizers) tricresyl phosphate, amyl phenol derivative, acryl diphenyl phosphate.
1250	covalent nitrates; (7.82 μ)
1150	cellulose ring; very broad, (9.4 μ)
820	related to nitrates (11.92 μ)
730	(C-H); rock-(CH ₂) _n ; n 3.(13.87 μ)

TABLE 7: Specific Gravity of Selected Plastics [12].

ABS	1.04-1.10
Casein	1.26 Pure, 1.35 Plastic
Cellulose acetate	1.25-1.35
Cellulose nitrate	1.34-1.38 Plastic, 1.45 Film
Ebonite	1.08-1.25 Unfilled 1.25-1.80 Filled
Nylon	1.01-1.16
Phenol- Formaldehyde	1.27-1.30 Unfilled, 1.36-1.46 Cellulose Filled 1.54-1.75 Mineral Filled 1.75-1.92 Mineral or glass fiber Filled
Polycarbonate	1.20-1.22
Polyethylene	0.91-0.95
Poly (ethylene terephthalate)	1.38-1.41
Poly(methyl methacrylate)	1.16-1.20
Polypropylene	0.85-0.92
Polystyrene	1.04-1.08
Poly(vinyl chloride)	1.19-1.35 Plasticized 1.38-1.41 Rigid

--- **Specific gravity Tests**

As can be seen by the data in table 7, cellulose nitrate differentiates from other polymers also by the values of the specific gravity, thus such a test can be of some practical utility [12].

Other types of tests are used to characterize celluloid samples; some of them with more analytical significance are listed below in table 8 [13]

TABLE 8: Tests used for the characterization of celluloid (NC is for cellulose nitrate) [13].

<u>Test Method</u> -----	<u>Analytical Significance</u>
<u>Nitrogen Content</u> -----	It measures the degree of nitrate ester substitution.
<u>Ether-Alcohol Solubility</u> -----	It assesses low N ₂ NC content and possible contamination.
<u>Acetone Insoluble</u> -----	Purity test.
<u>Ash</u> -----	Accounts for non-combustible.
<u>Viscosity</u> -----	Indirect measurement of degree of polymerisation.
<u>134.5°C Heat Test</u> -----	Direct measurement of NC stability, acidic species.
<u>65.5°C Heat Test</u> -----	Direct measurement of NC stability, neutralization salts.
<u>H₂O and Alcohol Content</u> -----	Quantification of total moisture and volatiles.

3) Active and preventive procedures for the conservation of artefacts in celluloid

It is well understood nowadays that once the degradation of a plastic object is started it cannot be reversed or brought to a halt. Thus the main objective of conservation procedures is to reduce as much as possible the rate of the on going degradation processes in order to extend the useful life of the object under consideration.

Conservation treatments generally may be subdivided in *active/interventive* and *preventive/passive*.

3.1) Preventive/passive or inhibitive procedures for conservation

They essentially consist in minimising the exposure to external deterioration factors (UV and visible radiation, heat, humidity, oxygen, chemical pollutants, etc.); thus providing stable environmental conditions for storage or display which should be tailor to the nature and chemical reactivity of components.

Moreover preventive or passive procedures for conservation must be finalised also to inhibit or mitigate the on going of inherent or internal phenomena of degradation. This can be accomplished through procedures capable to remove harmful products deriving from the inherent degradation of the plastics and/or reducing their emission towards the environment.

The general effect of the above conservation procedures, more opportunely defined by Y. Shashoua as *Inhibitive conservation*, in prolonging the time life of artefacts, is schematically represented through the diagram, taken from reference [15] and reproduced in figure 10 [15].

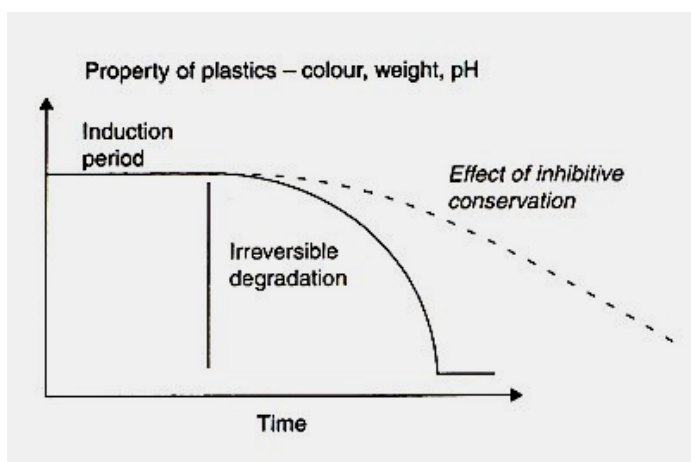


FIGURE 10: < Effect of successful inhibitive (preventive/passive) conservation on rate of degradation > [15].

The trend shown by the diagram in figure 10 is of general value, and is in agreement with the sentence in reference [14] as below reported:

< All plastics materials degrade, some very slowly but others have an expected life-span of less than fifty years. In general, most polymers follow a course of degradation which consists of a long period showing little or no change (induction period) followed by rapid degradation > [14] (figure 10).

As already written celluloid artefacts degrade both for inherent/internal and for environmental factors. Nevertheless through the application of appropriate inhibitive procedures it is possible to extend the life time of artefacts having clear in mind that *< the environmental factors of a celluloid object, in storage or on exhibit may be adequately controlled, deterioration may be slowed but never entirely halted > [1].*

Some inhibitive procedures, recommended to conservationists, being found to be effective in mitigating degradation in case of storage and exhibition of celluloid artefacts are hereafter described [1].

--- Recommendations concerning the environmental conditions for storage/display artefacts in celluloid [1,9,14,15,16]

--- Relative humidity

To slow down processes as de-nitration, hydrolysis, acid formation, and dimensional changes low values of environmental RH are requested (for long time storage/display the suggested values are between 20-30%).

--- Temperature

To reduce the overall rate of degradation, the happening of crystallization phenomena as well as de-nitration low value of the environmental temperature are recommended (2-5°C).

--- ultraviolet and other radiations

Technical systems capable to exclude or at least filter degrading light (for example sheets of Plexiglas UF 3) have to be used. The following values for long range exposure are suggested: maximum illumination, 50 lux; maximum UV, 75 µW/lumen).

--- Air exchange

It is advisable to use devices able to continually exchange air to facilitate the remove of gaseous autocatalytic products of degradation.

--- Boxes, trays, cases and cabinets

Cases and cabinets acid-resistant to protect against rusting as well as containers made of glass, ceramic, or acid-resistant plastics should be used. Containers in metal must be avoided.

--- Near neighbours

Objects in celluloid should be never stored or displayed in proximity of other cellulose materials (textiles, tissues, books, boxes, etc) or metals (i.e. silver, iron copper, etc.) as the degradation products of celluloid may be the cause of their deterioration and corrosion. *< Acid vapours released during degradation were often observed to have attacked other materials in the vicinity, such as fabrics and metals > [16].*

--- Metallic oxides and salts

Artefacts in celluloid have to be protected from contact with the metallic oxides and salts of lead, calcium, arsenic, tin, iron, copper, and zinc in order to avoid the irreversible gel of the softened or dissolved celluloid due to the interactions between solutions of degradation products in water absorbed from the environment and such inorganic substances.

--- gas/vapour adsorbents (molecular traps and scavengers)

Celluloid artefacts, due to their inherent auto-catalytic degradation as well as to their high sensitivity to external factors of degradation should be isolated and stored/displayed in closed container or in display cabinets were, besides the control of the atmosphere composition and temperature, they are also equipped with adsorbents devices (molecular traps and scavengers) capable to inhibit deterioration as well as to reduce the content of harmful vapours and gases.

Several adsorbent systems use as active principle the activated carbon that is a <... carbon that has been treated with oxygen to open up millions of tiny pores between the carbon atoms. There are so many of these that one pound has a surface area of 60 to 150 acres > [17].

< These materials can adsorb a wide variety of substances, i.e. they are able to attract molecules to their internal surface, and are therefore called adsorbents. The volume of pores of the activated carbons is generally greater than 0.2 ml g^{-1} . The internal surface area is generally greater than $400 \text{ m}^2 \text{ g}^{-1}$. The width of the pores ranges from 0.3 to several thousand nm > [18].

The morphology of activated carbon system with a ramified pore structure, is schematically represented in figure 11 [18].

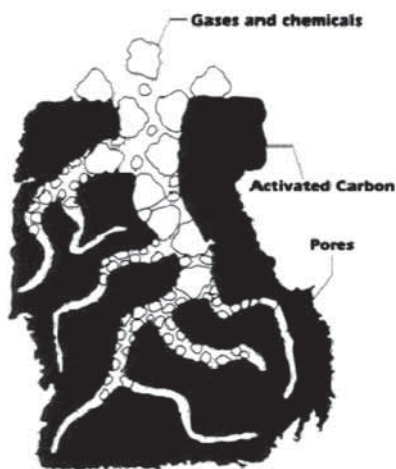


FIGURE 11: Schematic representation showing the complex structure of an activated carbon system < within which various mesopores ($r = 1-25 \text{ nm}$), micropores ($r = 0.4-1.0 \text{ nm}$) and sub micropores ($r < 0.4 \text{ nm}$) branch off from what we call macropores ($r > 25 \text{ nm}$) > [18].

The presence of a very large number of pores provides an enormous surface area where many chemicals are attracted, bonded and trapped (adsorption process). If the internal surfaces are impregnated with suitable chemicals the adsorption efficiency of the activated carbon results to be strongly implemented.

< When these chemicals are deposited, the removal mechanism also changes. The impurities are no longer removed by adsorption but by chemisorption > [18].

The gases that can be trapped by systems based on impregnated activated carbon are listed in the table 9 [18].

TABLE 9: Typical application fields of impregnated activated carbon systems [18].

Gas purification
Hydrogen sulfide
Mercaptan
Mercury
Ammonia
Amine
Acid gases (HCl, SO ₂ , HF, HCN)
Arsine
Phosphine
Aldehyde
Radioactive iodine
Radioactive methyl iodide
Nitrogen oxide

In reference [19] the performance of impregnated activated carbon systems are depicted as follows:

<....., when the boiling point of the vapour is below about 40°C activated carbon is usually impractical as a physical adsorbent..... Examples of such low-boiling point toxic or odorous gases are hydrogen sulphide, methyl mercaptan, trimethylamine, arsine, etc. In such cases, a good

approach is to impregnate the activated carbon with a chemical that converts the gases into products that are more strongly adsorbed or to impregnate it with a catalysts that promotes the oxidation (in air) of the gases to fixed or harmless products >[19].

Products based on Activated Carbon Cloth (ACC) are composed of 100% activated carbon in a textile form (see figure 12-left). ACC, developed and commercialised under the ZORFLEX® brand name by the Chemviron Carbon's Cloth Division, seem to offer many advantages in comparison with activated carbon products [20].

ACC can be cut, sewn and bonded to other materials to allow its integration within display and storage systems (see figure 12, right) [21,22].



FIGURE 12, Left: Activated Carbon Cloth (ACC) are composed of 100% activated carbon in a textile form [21].

Right, activated Carbon Cloth (ACC) is suited to inhibit deterioration of displayed and stored artefacts caused by environmental pollution [22].

Gas/vapour adsorbents devices based on activated carbon, impregnated activated carbon and activated carbon cloth (ACC) resulted to be effective in trapping NO_2 molecules deriving from the de-nitration process of cellulose nitrate avoiding that such a product may take part to inherent phenomena of degradation of celluloid as well as to corrode metal component and or textile and paper items eventually kept in the proximity [15].

Other systems able to adsorb from the environment NO_2 molecules are based on the use of zeolite [15]. According to scientific and technical literature zeolites are a family of hydrated crystalline aluminosilicates (of natural or synthetic source) with a three-dimensional network structure

characterized by the presence of many pores and channels of molecular dimensions. Due to such a structure zeolites find applications in many fields as ion exchange resins, molecular sieves, adsorbents for gases and vapours and as catalysts [23, 24].

The silicates are a large family of minerals characterized by a crystal lattice containing as primary constituting unit $[\text{SiO}_4]$ tetrahedral where in the centre there is a silicon atom that coordinate four oxygen atoms located at the corners (see figure 13) [25].

In the silicates the SiO_4 tetrahedrons by sharing one or more oxygen atoms give rise to the formation of a very large number of three-dimensional structures, which characterize the various families existing in natural rocks. In these structures the oxygen atoms may exist in two different states: terminal with a negative charge or bridged between two silicon atoms without electrical charge [26].

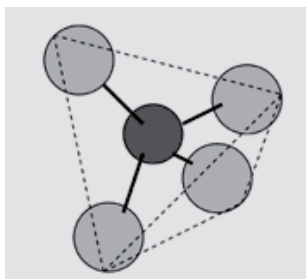


FIGURE 13: The primary unit building (PBU) in zeolites is constituted by (SiO_4) or (AlO_4) tetrahedrons where in the centre there is a Si or Al atoms while at the four corners are located 4 oxygen [25].

The Zeolites (the general chemical formula is: $\text{Na}_x(\text{AlO}_2)_x(\text{SiO}_2)_y \cdot n\text{H}_2\text{O}$ belong to the family of “Tectosilicate” or “framework silicates” whose crystalline structure is characterized by the fact that all four oxygen atoms of the $[\text{SiO}_4]$ tetrahedrons are shared with neighbouring tetrahedrons (each oxygen is then linked to two silicon atoms). Moreover in such a minerals silicon atoms may be replaced by aluminium. In some cases the Si or Al in the middle of the tetrahedrons may also be substituted by P, Ga, B, Be etc. atoms.

According to reference [25] in zeolites

< the tetrahedrons combine to form three-dimensional, strictly periodical components via common oxygen bridges. These represent rings of 4, 6 and 8 and form secondary components. A micro-porous tetrahedron matrix with empty spaces of pores, canals and cages throughout results from the linkage in three-dimensional space. Large cations and crystal water in these empty spaces can equalize the negative charge of the matrix > [25].

The typical highly porous three-dimensional micro-structure of zeolites is schematically represented by figure 14 where the metallic ions (K^+ , Na^+ , Ca^{++} , etc.), necessary to neutralize the negative charge created by the substitution of Si with Al atoms, are at the interstitial positions or in cavities within the crystal network.

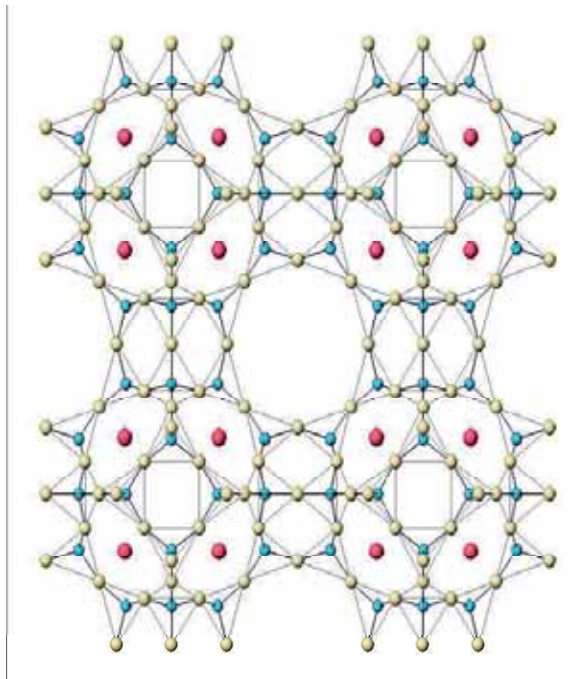


FIGURE 14: The highly porous three-dimensional microstructure of zeolites. The metallic ions (K^+ , Na^+ , Ca^{++} , ecc.) are at the interstitial positions in the crystal network.

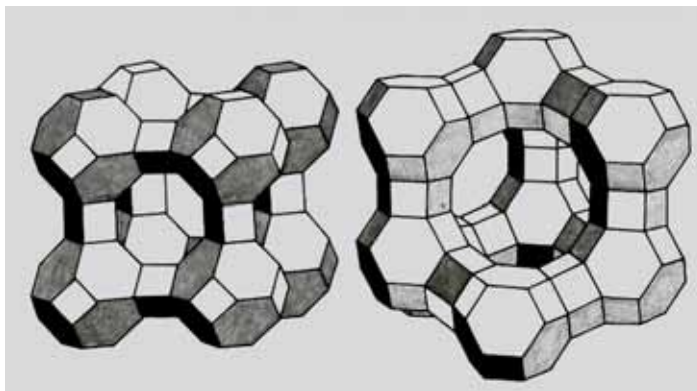


FIGURE 15: Model describing the structures of two crystalline zeolites belonging to the family of *Sodalite*. **Left**, *Zeolite-A*. **Right**, *Faujasite*. Bridging oxygen atoms are left out for clarity [23].

The model of the three-dimensional crystalline structure of two important, from practical point of view, zeolites, belonging to the family of *Sodalite*, as the *zeolite-A* (general formula: $\text{Na}_{12}(\text{AlO}_2)_{12}(\text{SiO}_2)_{12} \cdot 27\text{H}_2\text{O}$) and the *Faujasite* (general formula: $\text{Na}_{86}(\text{AlO}_2)_{86}(\text{SiO}_2)_{106} \cdot 264\text{H}_2\text{O}$), are represented in figure 15, left and right side respectively. In such a model, for clarity, the bridging oxygen atoms are left out.

< The corners of the polyhedrons represent Si or Al atoms and the connecting lines represent the shared oxygen atoms > [27].

Both structure are characterized by the presence of central cavities with a diameter of ≈ 11 and 12 \AA , connected with orifices having diameter of ≈ 4.2 and 8 \AA [23].

Zeolites (naturals or synthetics) due to their chemical composition and porous crystal structure (cavities and channels may occupy up to 50% of overall volume, see figure 15) are very effective in:

- Adsorbing and absorbing many different types of substances such as ions, gas molecules, moisture, petrochemicals, heavy metals, etc.;
- Providing large surface areas on which chemical reactions can occur;
- Acting as desiccants due to their high affinity for water;
- Gas separation for molecular sieving applications [28,29].

For the above-cited properties some zeolites, capable to adsorb selectively nitrogen dioxide molecules find application as adsorbents in the field of conservation of celluloid objects.

--- *Oxygen absorbers*

Oxygen absorbers are used to create an oxygen free microclimate assuming that by reducing the presence of such reactive gas in the environment the degradation of the items to be conserved is inhibited.

< Oxygen absorbers perform their action through a chemical reaction process. They contain iron powder and salt, which reacts with the oxygen in the air causing the iron powder to rust. When all the iron powder has oxidized, the oxygen absorbers are "loaded" and the absorbing action stops > [30] (see Ageless® Oxygen Absorber by Mitsubishi).

The various advantages in using oxygen absorbers, available in individual sealed container, may be summarized as follows:

- Lowering the oxygen in a sealed container to less than 0.01%;
- Preventing mold, mildew and bacteria from forming;
- Not-producing excessively high temperatures.

Moreover they are safe & easy to be used [30].

Eye Oxygen Detector, available in two forms, tablets and thin sheets, have been developed and commercialised to signal when oxygen in a package is depleted. As shown by figure 16 the colour of such device changes from blue (oxygen present 0.5% or more) to pink (oxygen present 0.1% or less) (see also figure 17-a) [31,32].

The oxygen scavengers commercialised by ATCO or Ageless contain fine iron powder covered with sea salt and a natural zeolite impregnated with a NaCl-solution (figure 17-b,c)). According to reference [32]

< One sachet of Ageless Z 2000 absorbs 2000 ml of oxygen (the oxygen from 10 l air) and contains 7,5 g water which can be controlled by a humidity buffer. Ageless should be used at humidities above 55% RH. Below 55% RH, oxygen absorption is slower and activity is reduced. In

dry conditions, the oxygen scavengers RP should be used.....The new type ATCO FTM 2000-S contains sulphur-free iron since it has been demonstrated that the normal types of ATCO and Ageless release sulphurous gases, tarnishing silver and other metals > [32].

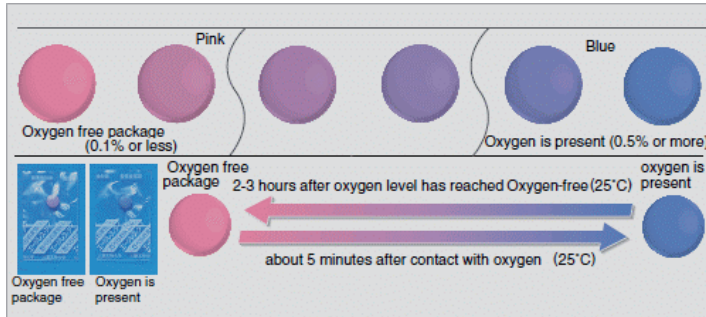


FIGURE 16: Eye Oxygen Detector, available in two forms, tablets and thin sheets, have been developed and commercialised to signal when oxygen in a package is depleted [31].

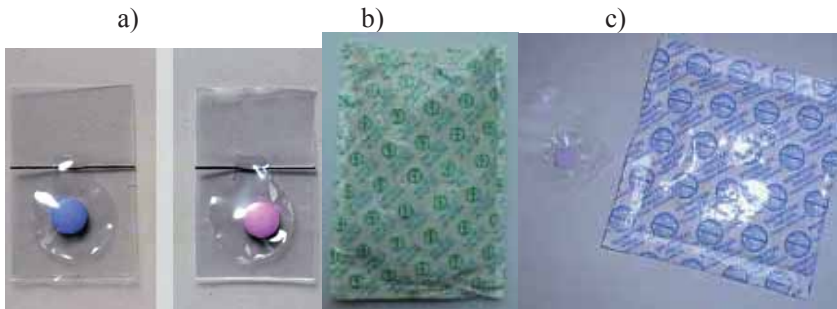


FIGURE 17: a)- Ageless-eye is a small oxygen indicator tablet turning pink below 0,1% oxygen and returning to blue above 0,5% oxygen [32]. b), c)- Oxygen absorber packets commercialised by ATCO or Ageless contain fine iron powder covered with sea salt and a natural zeolite impregnated with a NaCl-solution [32].

In the technical literature is reported that the product named as Ageless-Z is suitable to be used for application in conservation. Ageless-Z is commercialised as Z-100, Z-1000, etc., to indicate the millilitres of oxygen with which a single packet will react [33].

< For example, 12 packets of Ageless Z-2000 can maintain an equilibrium oxygen concentration of less than 0.1% in a 1000-liter case leaking 300 ppm (03%) per day >[33].

--- *Adsorbers based on silica gel (humidity control)*

Commercial devices (for example those commercialised as “ART SORB”) suitable to control the humidity content in storage or display cases are composed of silica gel and lithium chloride.

The main characteristics of ART SORB are described as follows in reference [34].

< It is a moisture-sensitive silica material which adsorbs and desorbs moisture in order to offset changes in relative humidity. Its main use is to create a suitable microclimate inside showcases placed in rooms which are either too dry or too wet or subject to a fluctuating climate.

ART SORB represents a solution in passive buffering systems for conservation of certain works which have to be maintained between 60 - 75 % RH > [34].

ART SORB is commercialised as beads and cassettes, made of PP and polyester non-woven, easy to be collocated into sealed display case or storage cabinet as those shown in figure 18 [34].



FIGURE 18: Acrylic display cube suitable for the display of art objects under controlled environment.

As shown by the data in table 10 the efficiency of the various type of humidity adsorbers based on silica gel depends upon the kind of formulation used. In table 10 are reported the values of the Equilibrium Moisture Content (EMC) (i.e. the amount of water adsorbed by the silica gel when its vapour pressure is at equilibrium with a given relative humidity (RH)) and of M (the amount of water in grams that is gained or lost by one kilogram of gel when the RH changes by 1%).

High value M and EMC means a greater capacity to buffer RH changes. It can be seen by the data reported in the table 10 that *< ART SORB has a unique high adsorption / desorption capability throughout the entire range of RHs. ART SORB outperforms ordinary silica gels, actually increasing its M-value > [34].*

Quite recently a new silica gel device, commercialised as “PROSorB”, having an unique and exceptional adsorption capacity within the 40 - 60% RH range (see figure 19-top) has been developed. Such a system results to be *< ideally suited for stabilizing relative humidity inside museum display cases and storage cabinets > [35].* As matter of fact it is well known that the *< ideal level of humidity for most museum display cases and storage cabinets is between 40 - 60% RH (Relative Humidity) > [35].*

TABLE 10: Values of the Equilibrium Moisture Content (EMC) and of M (the amount of water in grams that is gained or lost by one kilogram of gel when the RH changes by 1%) as function of RH and type of adsorber [34].

% RH	regular density silica gel		medium density silica gel		ART SORB	
	EMC	M	EMC	M	EMC	M
0	0	7.0	0	2.0	0	6.5
10	7.0	7.0	2.0	1.0	6.5	5.0
20	14.0	6.5	3.0	1.0	11.5	4.5
30	20.5	4.5	4.0	1.0	16.0	6.0
40	25.0	3.5	5.0	1.5	22.0	4.0
50	28.5	2.0	6.5	1.5	26.0	9.0
60	30.5	1.5	8.0	1.5	35.0	19.0
70	32.0	1.0	11.0	6.0	54.0	13.0
80	33.0	1.0	17.0	15.5	67.0	7.0
90	34.0	1.0	32.5	61.0	74.0	6.0
100	35.0		93.5		80.0	

From the trend of the diagrams in figure 19- bottom, it emerges that the adsorption capacity of the silica gel based humidity adsorbers depends from the formulation type and by the range of RH to be considered [35].

In order to monitor the humidity content inside an enclosed showcase or display-cabinet color changing “*Humidity Indicating Cards*” (HIC) may be used.

The advantages of such device are below outlined:

--- These HIC cards (see exemplars in figure 20) provide a low cost method of indicating humidity conditions for various types of military, electronic and barrier packaging requirements.

--- HIC cards are capable to turn from blue to pink to indicate the humidity level within a given environment.

--- A full range of cards that indicate humidity levels from 5% to 60% are commercially available [36].

--- *Filters against environmental particulate and systems to keep air free of airborne contaminants*

To isolate objects from the actions of aggressive particulate and to eliminate or reduce the deleterious effects of airborne contaminants special filter systems, see those commercialised as HEPA (High Efficiency Particulate Arrestance) have been developed. This systems are capable to create an atmosphere inside a sealed rooms or showcases 99.97% free of all particulate down to 0.3 microns (including bacteria, fungi and other minute airborne contaminants).

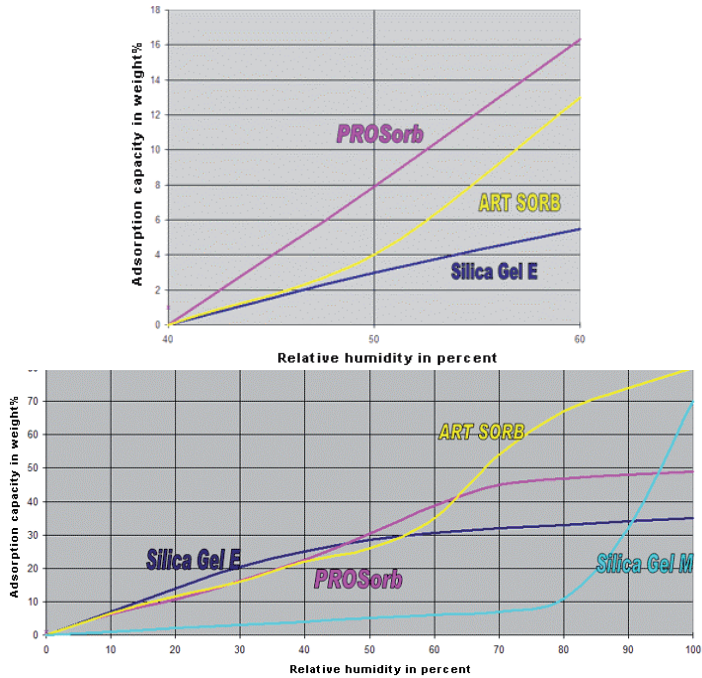


FIGURE 19: Adsorption capacity of various silica gel based humidity adsorbers. **Top**, within the medium humidity range (40-60% RH). **Bottom**, within the medium humidity range (0-100% RH) [35].



FIGURE 20: Exemplars of color changing “Humidity Indicating Cards” (HIC) used to monitor the humidity content inside an enclosed show case or display cabinet [36].

HEPA Filters, part of the 'interception' family of filters < have a deep bed of randomly positioned micro glass fibres, in which the total bed depth (thickness of media) is very large in comparison to the average fibre diameter and effective pore of free path cross section > [37].

Recently the AllerAir Industry developed a new air filtration system (air purifier, air cleaner, and air scrubber) where activated carbon, HEPA filters and UV filtration components are assembled together (see figure 21) [38].

The advantages in using this AllerAir unit are hereafter described:

< The enhanced activated carbon filter will work on removing gases, fumes, and odours, such as formaldehyde, radon, fluorine gas, to name but a few. The HEPA filter will remove, dust, dust mites, mold, asbestos particles among others. What makes this unit truly special is the UV filtration component. AllerAir's UV model units will lower bacterial count more than if it were done through ventilating a room at a rate of 100 air exchanges per hour. The general normal rate of air exchanges for most homes, over the same period of time, is no more than a half dozen times > [38].

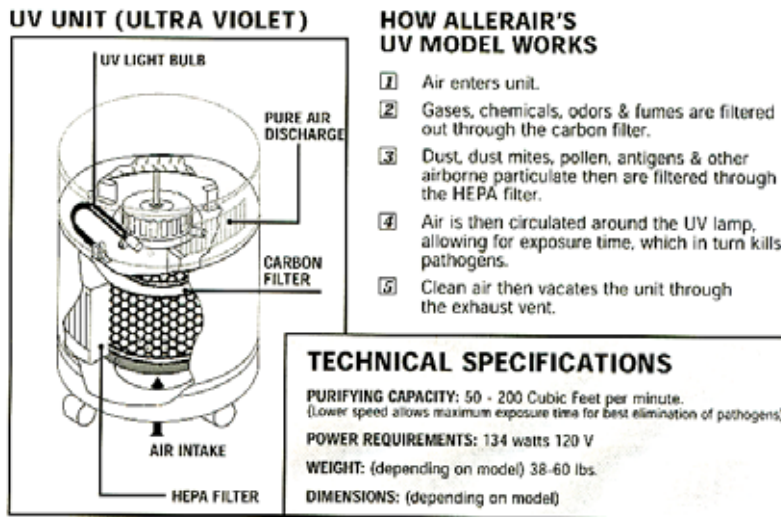


FIGURE 21: Allerair air cleaners, air purifiers, air scrubbers, air filtration systems where activated carbon, HEPA filters and UV filtration components are assembled together (see notes on the figure and the text) [38].

--- acid-absorbing systems

In the case of conservation of celluloid objects in the storage or exhibition space quite often an acid-absorbing material located in the proximity but not in contact with the artefacts is used. Such a material, for example CaCO₃, must be capable to react with the acids formed during deterioration.

--- Indicators and sensors able to detect and calling attention to the first signs of degradation.

Chemical sensors and indicators suitable to detect the presence of a wide range of toxic pollutants characterised by high sensitivity and/or selectivity, and/or fast sampling time may be used for the conservation of artefacts, also those made in celluloid.

A chemical sensor, see the simplified scheme in figure 22, is a self contained probe that provides in real time information about the chemical composition of its surroundings. As reported in reference [39] it is essentially

< ...composed of an active layer and a transducer. The active layer represents the main part of the sensor. Many materials such as organic, inorganic or hybrid organic-inorganic polymers can be used as active layers, providing that pollutants can diffuse into the matrix and be trapped, thus modifying the physical or/and chemical properties of the material. The active layer can also be doped with specific probe-molecules able to react selectively with the targeted pollutants, thus providing the selectivity of the sensor. The transducer role is to convert the variation of a physical property (i.e. refraction index...), or a chemical interaction (i.e. H-bond formation, electrostatic interaction...) or a chemical reaction (covalent bond formation) into a measurable signal (optical, electrical, electrochemical, piezoelectrical, etc...) proportional to the pollutant concentration > [39].

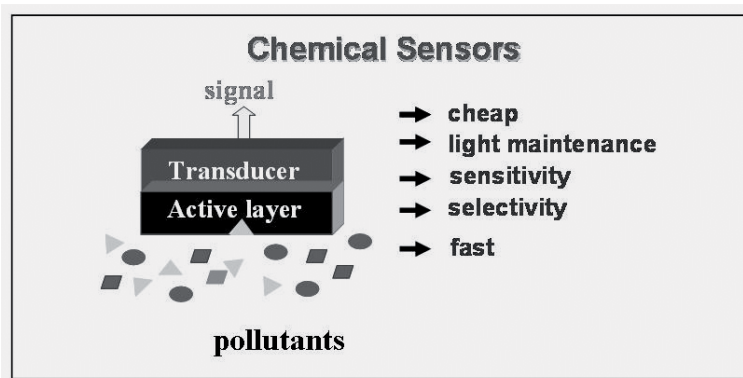


FIGURE 22: Scheme of a typical chemical sensors of air pollutants [39].

Electrically controlled nanowire-based chemical sensors which resulted to be very effective in detecting the presence of NO_2 molecules in a selected environment have been recently developed [40]. The details of construction and the performances of such a device, based on zinc oxide (ZnO) nanowires configured as field-effect transistors FETs are described in reference [40] as follows:

< Single crystalline nanowires (with a typical diameter of about 50nm) were synthesized via a chemical vapor deposition..... Electrical measurements show that the ZnO nanowires are n-type semiconductors..... The metal oxide sensing mechanism originates from the charge transfer between the semiconductor and the chemical species adsorbed at the surface oxygen-vacancy sites. The relative change of conductance after exposure to a target gas determines the sensitivity. For example, the conductance of ZnO decreases with the introduction of NO_2 . At room temperature, with the ZnO in the form of a nanowire, more than 50% of the conductance change was observed under an exposure of 0.6ppm NO_2 . In comparison, doped ZnO thin films achieved less than 2% conductance change when exposed to 1.5ppm NO_2 . This demonstrates a high potential for nanowire sensors with superior sensitivity > [40]. The effectiveness of this device against NO_2 and NH_3 pollutants is demonstrated by the trend of the diagrams presented in figure 23 [40].

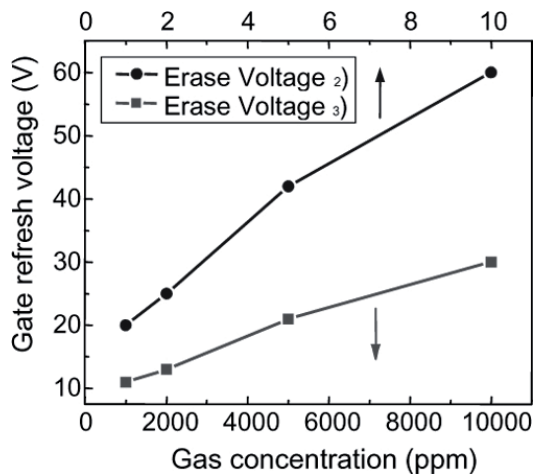


FIGURE 23: Electrically controlled nanowire-based chemical sensors. Gate refresh voltage magnitude as a function of NO_2 (●curve) and NH_3 (■ curve) concentrations (see text) [40].

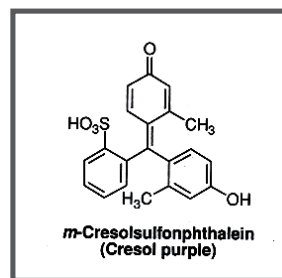


FIGURE 24, Right: The molecular structure of the *Cresol Purple* (*m-cresolsulfonphthalein*), a yellow colouring agent that in presence of acids change its colour to red [41,42].

FIGURE 25, Left: Strips of filter paper soaked with a solution of *Cresol Purple* are good detector of offgasing nitrogen dioxide from a celluloid items. The paper strips turns from yellow to red as pH decreases from 2.8 to 1.2. The sensor in figure indicates that one knob (right) is decomposing but the other is not [41,42].

Strips of filter paper impregnated with *Cresol Purple* (*m-cresolsulfonphthalein*) are an example of an **indicator** useful to detect the offgasing of nitrogen dioxide (NO_2) from a degrading celluloid items. As matter of fact the *Cresol Purple* (figure 24) is a yellow colouring agent that in presence of acids change its colour to red (a paper strip soaked in a solution of *m-cresolsulfonphthalein* turns from yellow to red as pH decreases from 2.8 to 1.2).

An example of application of the above indicator in the case of a radio case in celluloid is illustrated in figure 25 where it can be seen as the paper strip soaked in a solution of *Cresol Purple* applied on the right knob becomes red in colour, while the strip placed on the left knob remain of yellow colour. This indicates that one knob (right) is decomposing but the other is not. This indicates that the degradation is active only on one side of the artefacts.

3.2) Active/interventive procedures for conservation of celluloid artefacts (case history)

Treatments of active conservation, generally, are based on practical procedures finalised to the stabilization, consolidation and protection of heavily damaged artefacts.

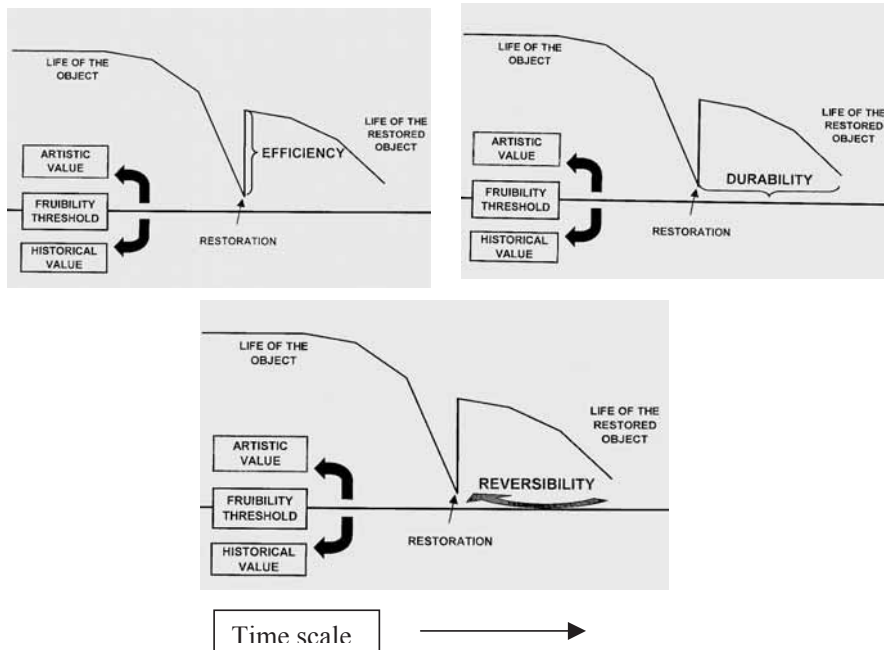


FIGURE 26: Efficiency, durability and reversibility are the pre-requisite of any direct restoration treatment [43]. **Top-left:** Concept of *Efficiency*. **Top-right:** Concept of *Durability*. **Bottom:** Concept of *Reversibility*.

In the case of object made in plastics the practical execution of active treatments find difficulties in the high sensitivity of such materials, especially when degraded, to the action of organic liquids, aqueous solutions and in some circumstances also water.

< In addition, coatings or adhesives which adhere successfully to plastics' surfaces must either soften the substrate by dissolution or melting to achieve bonding. Such treatments are usually irreversible, frequently change the appearance of the original and may not be acceptable in a museum collection > [14].

As general rule any restoration treatment has to be characterized by efficiency, durability and reversibility. The meanings of those requisites are clearly deducible from the diagrams in figure 26 [43].

Moreover it should be underlined that the materials used for active restoration should be compatible with the substrate and stable against thermo/photo oxidation as well as other environmental factors of degradation.

Active treatments (cleaning, repairing, mending, consolidating and protecting) should be undertaken only when the chemical/physical interactions between celluloid components and materials to be used have been assessed. For example the use of alkaline substances may be the origin of irreversible chemical and structural damage to celluloid.

Thus *< any experimentation using alkaline-neutralizing steps must be cautiously pursued and investigated with every available analytic tool > [1].*

--- Cleaning treatments of celluloid manufactured artefacts

Cleaning procedures must be capable to remove from the surface of plastic objects harmful products deriving from inherent and external degradation processes. Moreover cleaning is also practiced to enhance the appearance of the artefacts.

As previously reported the inherent deterioration of celluloid leads to the formation on the surface of related objects of film or droplets of acidic nature that have to be removed otherwise they will speed up the degradation of the plastic.

Concerning such aspect in reference [1] the following recommendation are mentioned:

< The deterioration products are usually readily soluble in water. However, water should be used sparingly as deteriorated celluloid can be water-soluble. Cleaning with a barely dampened swab can be effective but can also be abrasive. If water is used it should be removed immediately with a dry swab > [1].

Quite often it has been found on the surface of artefacts in celluloid the presence of residues deriving from the use of adhesive tapes and glues, which may be strongly bonded to the plastic through chemical reactions causing local degradation. Such kind of material can be only removed mechanically taking into consideration the fact that the substrate may be softer than the adhesive accretions [1].

Very recently J. Lee Kaplan and R. Namiat developed a novel methodology designed to safely control and remove foxing stains from paper & celluloid items using distilled water, sodium hypochlorite, acetic acid, sodium bicarbonate and glue size [44].

The advantages of such a method, as reported in the patent text, are hereafter listed:

- Not to harm or destroy the paper or celluloid item.
- Leaves no residue which will harm the paper or cellulose items.
- Safe to use by humans.
- Low cost to manufacture and to use [44].

The procedure, as described by the authors, is below reported:

- < 1) Soak the paper or celluloid item completely in a warm bath of distilled water;*
- 2) Remove the paper or celluloid item and blot all excess water;*
- 3) Soak the paper or celluloid item completely in a warm bath of household bleach, less than 5% concentration;*
- 4) Soak and rinse the paper or celluloid item completely with warm distilled water;*
- 5) Remove the paper or celluloid item and blot all excess water;*
- 6) Soak the paper or celluloid item completely in a warm bath of vinegar, no less than 75% concentration;*
- 7) Soak and rinse the paper or celluloid completely item in a bath of cold distilled water;*
- 8) Remove the paper or celluloid item and blot all excess water;*
- 9) Soak the paper or celluloid item completely in a bath of sodium bicarbonate (baking soda) and distilled water;*

- 10) Soak and rinse the paper or celluloid item completely with distilled room temperature water;
- 11) Remove the paper or celluloid item and blot all excess water;
- 12) Soak the paper or celluloid item completely in a bath of glue size.
- 13) Soak and rinse the paper or celluloid item completely in a bath of cold distilled water;
- 14) Remove the paper or celluloid item and blot all excess water.
- 15) Air Dry the paper or celluloid item without the use of a heat blower > [44].

--- Repairing/joining treatments for celluloid objects

In general adhesives are used for repairing fractured celluloid artefacts. In selecting the most effective and suitable adhesive systems for a structural plastic manufactured object the following general elements should be taken into considerations [15].

--- The thermal coefficient of expansion of solidified adhesive and plastic item which values should be as much as the closer it is possible, to avoid stresses at the connected interfaces.

--- The influence that products of plastic degradation may have on the properties of adhesive effectiveness.

--- The refractive index of the sealant, especially for transparent items, that must be similar to that of plastic.

In reference [15] as cleaning pre-treatment/preparation of celluloid surfaces it is suggested the use of isopropanol, while epoxies, polyurethanes, acrylics and cyanoacrylates are recommended as adhesive based systems.

--- Case history of conservation of celluloid artefacts

1) advanced treatments for a doll conservation

As case history the procedure and the results of recent advanced conservation treatments, performed c/o the Daniels Objects Conservation Laboratory, Minnesota Historical Society, finalised to the restoration of a heavily damaged head in celluloid of an ancient doll are hereafter summarized [45]. The state of conservation of the doll head was described as follows:

< *By the time she (the doll) reached conservators, her head was broken in many places, held only together by the plaster of her eye rockers and a wooden bar that spanned the interior of her head, nailed through the temple areas.....* > [45] (see figure 27).

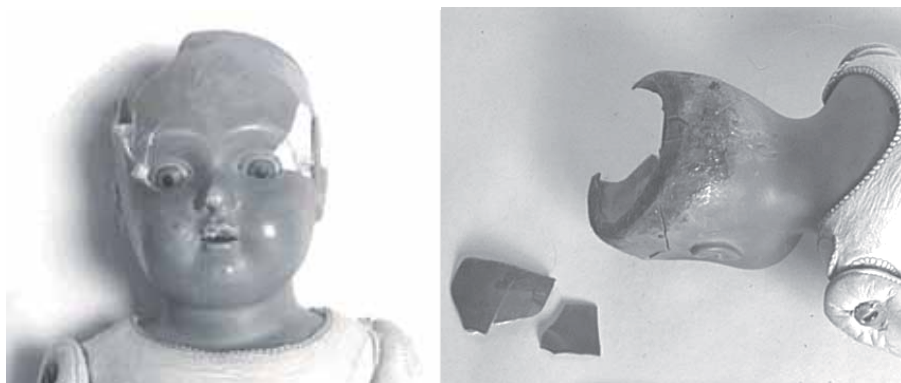


FIGURE 27: Condition of the head doll, manufactured in celluloid, before the conservation treatment [45].

The procedure of active conservation forecasted the following steps:

i) Removal of the eyes to give access to all cracks. < Pieces of cotton padding were dampened and placed on the rockers until they softened the plaster enough to carefully pull them out of the head > [45].

ii) < The unbroken portions of ...head were stabilized by applying a layer of an emulsion called Lascaux 498 (Lascaux Acrylic Adhesive 498 HV is a pure acrylic resin-based emulsion adhesive which can be thinned with water, thickened with acrylic butyl ester, has a pH 8-9 and is biocide stabilized. It is water-thinnable, insoluble in water after drying. Permanently soluble in acetone and toluene, insoluble in white spirit. It has a strong elongation at break, and is suitable for wet and dry applications, reactivation with solvents. Note from the Author) and spreading Japanese paper, a flexible and porous grade, over the Lascaux. As the Lascaux penetrated the paper, it adhered to the inside wall of the doll's head. Due to the brittle condition of the celluloid, some additional cracks developed....., but he (the conservator) carefully replaced each until the head was intact again. Further paper patches were added to newly glued pieces and fillers were placed in areas of loss. The eyes could now be reinserted > [45].

iii) < Due to the heat generated by plaster as it cures, it was decided that a normal process of creating eye rockers would be too dangerous for the celluloid. (Celluloid is extremely heat sensitive and will spontaneously combust or deteriorate). An alternative technique was devised which used a two-part epoxy putty, called Abatron Wood Epox. The putty compounds were combined, molded around the eyes and allowed to cure. Once set, the new rockers were carved to fine-tune their shape and allow appropriate sleep movement for the eyes. The rockers were then glued into proper position to maintain the sleep eye motion. To complete the head repair, .. the conservator used acrylic paints to "inpaint" cracks or loss areas to match adjacent, unbroken edges > [45].

Details of the face of the doll during the conservation treatment after patching from the interior and of doll head repairs at the end of restoration procedure are shown in figure 28 [45].

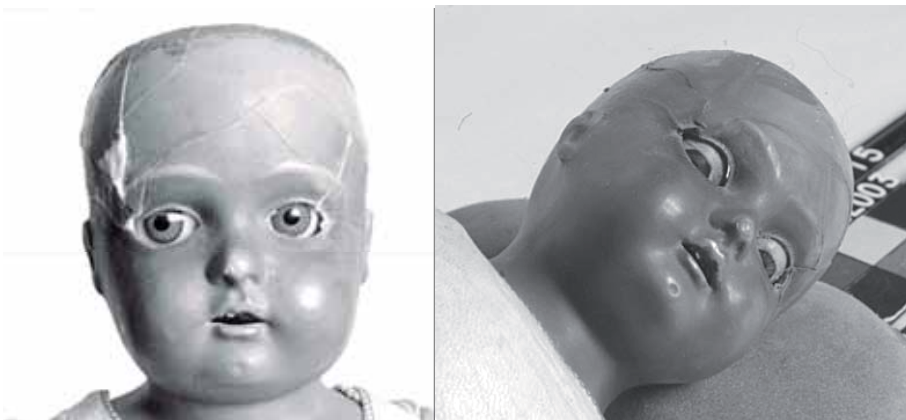


FIGURE 28: Left, details of the doll face during treatment after patching from the interior. Right, details of head repairs after treatments [45].

Finally to prevent that gases given off by celluloid nitrate may cause damages to other plastic dolls in close proximity it was recognized the necessity to keep the restored doll in a separate environment [45].

2) Active conservation of a celluloid mirror back from 1920s

For the consolidation and stabilization of the artefact (\approx 3cm thick), showing a diffuse crazing pattern, an impregnation technique was followed. The procedure was based on the use of an epoxidized soya bean oil (ESBO). Such a compound, a viscous-yellow liquid, acts as anti-ageing additive being capable, after deep penetration into the celluloid artefact < *to limit the build up of acid thus delaying the onset of autocatalysis* > [15]. According to what reported in the literature the treated sample, after 2 years, showed no worsening signs of the state of deterioration.

--- Some further remarks concerning the conservation of celluloid artefacts

The conservation of artefacts where celluloid components coexist with metallic ones (see examples in figure 29) represents one of the still unsolved issues as at the moment no certain and documented solutions are available.

In general in accomplishing conservation treatments one must keeps in mind that:

- The conservation treatments, as shown by the diagrams of figure 26, do not remain stable over time.
- Previous preservation procedure should remain unaffected unless they compromise the stability of the artefact.
- Adhesives, fillers and materials used for consolidation, stabilization and protection have to be selected in order to be sure that long-term, negative chemical reactions with the medium from which the artefact is manufactured are unlikely occurring.
- Any effort must be undertaken to save the original design and appearance of the object [45].

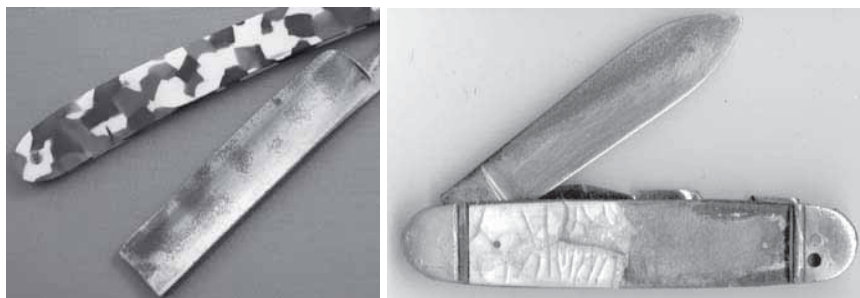


FIGURE 29: Examples showing the corrosion caused by the acidic gas emitted by the celluloid, component, following its inherent degradation, on the steel blades of a razor (left) and a knife (right). In the figure are clearly visible rusting stains from the leeching effect of the celluloid on the blades surfaces [46,47].

Finally it must be underlined that artefacts in celluloid due to the fact that by degrading they give off acidic gases, cannot be encapsulated and stored in sealed impermeable plastic bag with a stagnant atmosphere. As already written they need to be stored/displayed in a confined space with an active circulating/ exchanging air device and in presence of effective and specific adsorbents, scavengers and indicators systems [48].



FIGURE 30: Ancient artistic artefact manufactured in celluloid worthy to be collected. An ornate comb with red rhinestones [51].

Celluloid, invented by John Wesley Hyatt in 1869, due to its characteristics (thermoplasticity, easy to be molded, shaped and coloured) found application in many different fields for the manufacturing of a large variety of products:

- Billiard balls, bracelets, brooches, toys, buttons, hair combs and match safes, handles for scissors or eating utensils;
- Beautifully and artistic decorated wedding albums, postcard albums and boxes;
- Dolls and toys;
- Film components in photograph and early movie industry.
- Jewellery artistic components [49].

Moreover celluloid was widely used, all through the Victorian Era (1890-1917), in the manufacturing of artefacts of the Art Nouveau and parts of the Art Deco Period (1920-1935).

Most of the above mentioned objects (see examples in figure 30) are nowadays considered to be highly collectible and then they deserve attention to be preserved for the future generation as they represent part of the humanity history [50, 51].

REFERENCES

- 1) J. A. Reilly, *Journal of the American Institute for Conservation*, **30**, N° 2, 145 (1991).
- 2) R. Walker “*Conserving Plastics in Nineteenth and Twentieth-Century, Costume Collections*”, Department of Textiles, Fashion Merchandising and Design, University of Rhode Island, <http://www.uri.edu/hss/tmd/20th%20Century%20Plastics.pdf>, (2009).
- 3) R. Walker “*Conserving Plastics in Nineteenth and Twentieth-Century, Costume Collections*”, pdf Adobe Reader (2009).
- 4) C. Selwitz, < *Cellulose nitrate in Conservation* >, Research in Conservation, the Getty Conservation Institute, (1988)
- 5) J. Urbanski, R. Kukulka, *Przemysl Chemiczny*, **62**: 98-101. In *Chemical Abstracts* **98**:(217420) (1983).
- 6) A. Fontijn, H.N. Volltrauer, *Combustion and Flame* **41**, 313, (1981).
- 7) L. Phillips, *Nature*, **165**, 564, (1950).
- 8) D.N.S Hon, T.L. Gui, *Polymer Photochemistry*, **7**, 299, (1986).
- 9) R. Stewart and others, *Polymer Preprints*, **37**, N°2, 168, (1996).
- 10) http://cameo.mfa.org/dynamic/downloads/download_file_377.pdf, (2009).
- 11) <http://chestofbooks.com/reference/Henley-s-20th-Century-Formulas-Recipes-Processes-Vol1/Solvents-for-Celluloid.html>, (2009).
- 12) F. Rémillard, < *Identification of plastics and elastomers by miniaturized tests* >, Centre de Conservation du Québec, (2007).
- 13) http://proceedings.ndia.org/5550/tues_and_wed_briefings/paquet-williams.pdf, (2009).
- 14) B. Keneghan, < *Degradation & Conservation of Plastics* >. The newsletter of the Plastics Historical Society, Number 89 July (2008).
- 15) Y. Shashoua, < *Conservation of Plastics* >, ELSEVIER, Paris, (2008).
- 16) J. Morgan, < *A Survey of Plastics in Historical Collections* >, <http://www.plastiquarian.com/survey/survey.htm>. (1994).
- 17) pages.total.net/~espitech/carbonpower.html, (2009).
- 18) K.-D. Henning and S. Schäfer, < *Impregnated activated carbon for environmental protection* > www.activated-carbon.com/enviro.html, (2009).
- 19) Advanced Materials Laboratory, www.ua.es/.../ingles/technological%20offer.htm, (2009)
- 20) < *Applications for Zorflex® Activated Carbon Cloth* >, www.chemvironcarbon.com/en/activated-carbon-cloth, (2009).
- 21) www.sovereign-publications.com/chemvironca, (2009).
- 22) www.archivalsuppliers.com/prodinfo.asp?number, (2009).
- 23) S. Carra', M. Morbidelli, < *Chimica Fisica Applicata* >, HOEPLI, Milano (1983).
- 24) P. Gillet, J-M Malezleux, J-P. Itie, *American Mineralogist*, **81**, 651 (1996).
- 25) B.Tesche, C. Schrand, M. Kässens, < *Structural analysis of zeolites using a combination of highly resolving electron microscopy and digital image processing* >, ftp://ftp.soft-imaging.de/application_reports/EM/ApplicationNote_zeolithe.pdf, (2009).
- 26) www.a-m.de/englisch/lexikon/mineral/silicate.htm, (2009).
- 27) Siti Aida Binti Ibrahim < *Synthesis and Characterization of Zeolites from Sodium Aluminosilicate Solution* >, Thesis submitted in fulfilment of the requirements for the degree of Master of Science, Pdf, August (2007).
- 28) M.A.S.D. de Barros, N.R.C.F. Machado, F.V. Alves, E.F. Sousa-Aguiar, *Braz. J. Chem. Eng.*, **14**. N°3, São Paulo, Sept. (1997).
- 29) http://www.zeoder.org.tr/en/zeolit_yapisi.php, (2009).

- 30) http://www.nitro-pak.com/product_info.php?products_id=1671, (2009)
www.drypak.com/oxygenAbsorbers.html, (2009).
- 31) <http://www.mgc.co.jp/eng/products/abc/ageless/eye.html>, (2009):
- 32) C. Waller, *Long Life for Art*, [Long Life for Art.htm](http://www.mgc.co.jp/eng/products/abc/ageless/eye.html),
<http://www.mgc.co.jp/eng/products/abc/ageless/eye.html>, (2009).
- 33) V. Daniel, G. Hanlon, S. Maekawa, *Waac-Newsletter*, **15**, N° 3, 15, Sept (1993),
www.keepsafe.ca/Eradication.htm, (2009).
- 34) C. Waller, < *Long Life for Art* > *ART Sorb* directions (2009).
- 35) C. Waller, < *Long Life for Art* > *PRO Sorb* directions (2009).
- 36) www.drypak.com/oxygenAbsorbers.html, (2009).
- 37) http://www.allerairpurifiers.com/pdf/what_is_hepa.pdf, (2009).
- 38) http://www.allerairpurifiers.com/pdf/uv_models.pdf, (2009).
- 39) Chemical sensors of air pollutants,
www-llb.cea.fr/.../Ast/ast_visu.php?id_ast=1168, (2009).
- 40) Jia Grace Lu, < *Electrically controlled nanowire-based chemical sensors* >,
 Industrial Sensing & Measurement, SPIE Newsroom. DOI: 10.1117/2.1200604.0194, 8, June,
 (2006)
- 41) 4) S. C. Stinson, *Chemical & Engineering News* , September **9**, 34, (1996).
- 42) J. Fenn, *Polymer Preprints, Division of Polymer Chemistry, Inc.*, American Chemical Society,
37, N.2, 170 (1996).
- 43) E. Martuscelli, < *Plastics in art (in cultural heritage)*, *Plastics for art (for cultural heritage*
 >, Power Point presentation at the Programma Giornata AIM del 31/10/2008dedicata a “Il restauro
 e la diagnostica degli oggetti d’arte e di design inplastica” c/o PLART-31-10, (2008).44) J. Lee
 Kaplan, R. Namiat, < *Method to remove foxing stains from paper & celluloid items* > United States
 Patent 7462202, Application Number: 11/188814, Publication Date:
 12/09/(2008).
- 45) P. S. Storch, T. Schmitz, < *Doll Conservation: Advanced Treatments* >
 Daniels Objects Conservation Laboratory Minnesota Historical Society. The Minnesota Historical
 Society, in St. Paul, MN, pdf, www.mnhs.org. (2009).
- 46) razortips.blogspot.com/2007/05/celluloid-rot.html, (2009).
- 47) www.knifeworld.com/cefimabydeel.html, (2009).
- 48) < *Plastics, collecting and conserving* >, Edited by A. Quye, C. Williamson, NMS Publishing
 Limited, Edinburgh (1999).
- 49) L. Evans, <http://www.life123.com/hobbies/antiques-collectibles/collectibles/what-is-celluloid.shtml#STS=g06v0fy7.yql>, (2009).
- 50) <http://www.vintagejewelrylane.com/information/vintageplastics.htm>, (2009).
- 51) <http://www.michellesvintagejewelry.com/products/bakelite4.html>, (2009).

SECTION-2

SIXTH-CHAPTER

PLASTICS BASED ON NATURAL PRE-FORMED POLYMERS: PLASTICS FROM CHEMICAL TRANSFORMATION OF CELLULOSE

CELLULOSE ACETATE: SYNTHESIS, STRUCTURE, COMPOSITION, PROCESSING, AND PROPERTIES

The mile stones that led to the synthesis, processing, industrial development and commercialisation, especially as plastic mouldable material and films, of cellulose acetate (CA) are hereafter listed [1-9].

--- 1865-1869- Paul Schutzenberger and his co-workers first synthesised the CA, but at that time the acetylation of cotton resulted not easy to be accomplished at industrial level. Thus for many years the discovery did not found practical application.

--- 1894- Charles Cross and Edward Beavan, got ready the first industrial process for the manufacture of CA. Unfortunately the products showed difficulties in to be practically used as they resulted to be soluble only in toxic solvent (i.e chloroform).

--- 1903-1904- *< Plastic solid CA products became commercial around 1903-4 for use as a textile fiber in both France and Switzerland. The Dreyfus brothers (France) are generally credited with the first successful spun fiber; later they developed a transparent film > [9].*

--- 1905- G. W. Miles (see figure 1) in USA *< discovered that mild acid hydrolysis of cellulose triacetate produced a product which, at about the equivalent of a diacetate (i.e. with 52-52% acetyl value) was soluble in acetone, a solvent which was available on a reasonable industrial scale > [1].*

This CA resulted to be suitable for the production of fibres and clear, though and non-flammable films.

--- 1908- Eastman (Kodak) developed its own cellulose acetate base for application in photography and opened a manufacturing plant in Australia in 1908.

--- 1910- Swiss brothers Camille and Henri Dreyfus (see figure 2) developed a commercial process to manufacture CA. Non-flammable acetate films were produced in Basle.

--- 1912- CA was first introduced for the manufacturing of photographic plates.

--- 1913- Camille and Henri Dreyfus started producing acetate fibres. The Cellonit Gesellschaft Dreyfus & Company was established.

--- 1914-1918- CA developed rapidly in UK during the war following the discovery that a solution of CA applied to airplane fabric caused a tautening effect as it dried (see figure 3). *< In those days of fabric-covered planes, this was a most important property. Large-scale production was carried through under the guidance of Henri and Camille Dreyfus > [2].* The two brothers established in England the British Cellulose and Chemical Manufacturing Company, Ltd [4].

--- 1918-1922- The new company named Celanese was established in USA. A dry spinning technique that allowed the production of CA fibre to be knit and woven for apparel was developed by the two Dreyfus brothers.

--- 1923-1927- the first acetate yarn is spun in the United States. Celanese as “Artificial Silk”

introduced CA fibres. A weaving mill (integrated with dyeing and weaving equipments) was set up to produce a commercial acetate-containing fabrics. The Celanese Corporation of America was established. In the same period the *< cellulose acetate was being used as lacquer-coloured solutions capable to form a tough resilient film when sprayed or brushed on to a surface >* [2].

Furthermore CA found another important application in the production of safety glass where layer of the plastic sandwiched between two sheets of glass started to be used in the field of the car industry [2].

--- 1927-1929- Processing methods were developed capable to produce rods, sheets and blocks in CA.

Pellets suitable to be used as mouldable materials appeared for the first time on the market [2,5]. The discoveries of such new technologies gave a tremendous impulse to the development of CA as mouldable thermoplastic material.



FIGURE 1: The British chemist George W. Miles who discovered that by hydrolysis the highly acetylated cellulose is transformed to a less highly acetylated compound (cellulose diacetate) soluble in acetone [1-a].

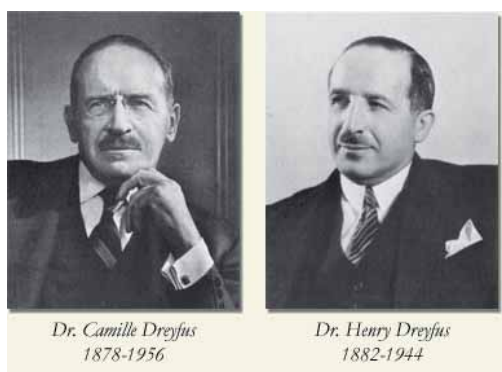


FIGURE 2, right: The brothers Henry and Camille Dreyfus (born in Basel, Switzerland) who devoted a lifetime to the scientific and commercial development of cellulose acetate [1-b].

--- *1930s*- The CA, being heat resist, contrary to cellulose nitrate, became the first thermoplastic, to be processed by injection moulding [5]. This technique < *has enabled the manufacturer to mass-produce moulded articles automatically and at great speed without the time absorbing heating and cooling of the mould required in compression moulding* > [2].

In the early 1930s mixed esters, such as cellulose acetate propionate and butyrate, were used to produce 16mm and 8mm motion picture film, sheet film and x-ray film.

--- *1940s*- 35mm film and microfilm were produced on cellulose triacetate.

--- *1954*- Triacetate cellulose was produced commercially in the USA by Celanese Corporation.

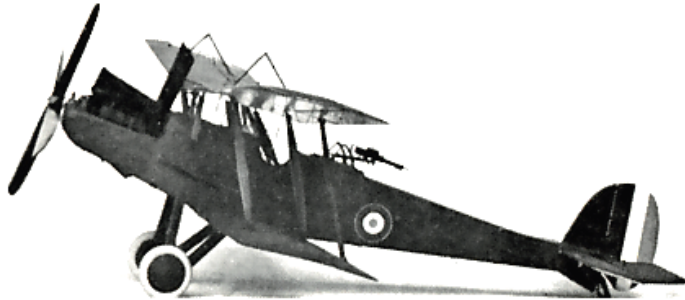


FIGURE 3: The fabric wings of this early military airplane, employed in the course of the 1914-18 war, were stiffened with a dope made of cellulose acetate [1].

Injection moulding was developed in USA and Germany mostly in the years 1930s; the main working principles are schematically evidenced through the diagrams reported in figure 4 [2,6].

The finding that CA was suitable for injection moulding determined, together with its toughness and low thermal conductivity, the great success of this material as thermoplastic in many different sectors (extruded tapes, packaging films, rigid transparent containers, electrical insulation, etc.), that is in sectors totally different from those where CA was traditionally already used as fibre (i.e. textiles and clothing industries). The CA to be used as moulding plastic was first mixed with plasticisers, colorants and other additives by using hot steel roller mill to produce coarse sheets or bars which were dried and chopped into small pieces to form the moulding powders [2].

< *Injection moulding certainly put CA on the industrial map as far as non rayon-users were concerned, and it remained the injection material “maid-of-all-work” until polyethylene and polystyrene appeared after the 1939-45 war* > [1].

Injection moulding processes essentially consist in transporting a melt polymer at relatively high rate into a cold mould where the material by cooling to a temperature below that corresponding to the rubbery state is allowed to solidify. Generally in the first stage operations as feeding, melting and homogenisation are performed by using an Archimedean screw, while the injection by pressure is carried out through the same screw only in a second step [2,6,7,8].

The various phases of the injection moulding process for thermoplastic polymers, with reference to figure 4, may be summarized as follows [2,6,7,8]:

- 1) The polymer powder melts inside the chamber of the injection.
- 2) The molten plastic is forced into the mould by pressure from a plunger.

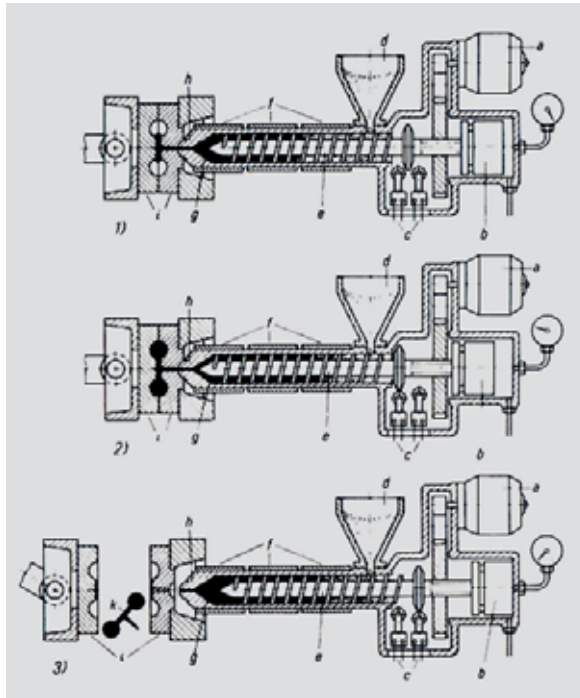


FIGURE 4: Schematic diagram of a modern automatic injection moulding machine. From top to bottom are represented the main phases of the process (see description in the text) [7].

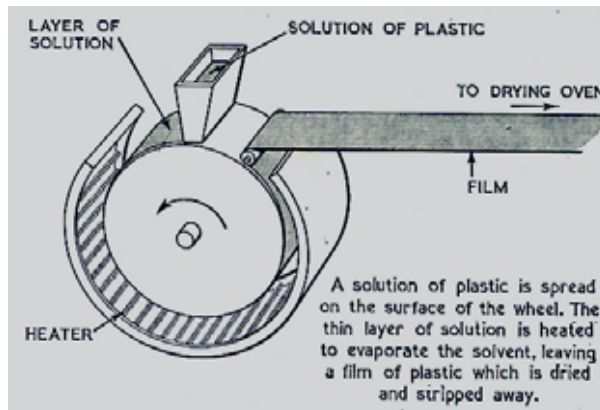


FIGURE 5: Wheel casting process used to make thin films of cellulose acetate to be used in the field of photography and cinematography (explanation on the figure) [2].

TABLE 1: Main characteristics of cellulose acetate as thermoplastic polymer [2].

Colour: Good.

General Physical Properties:
Odourless; tasteless.
Tough and durable.
Good impact strength.
Easily machined and moulded.
Heavier than water (S.G. 1.20 – 1.40).

Water: High water absorption affects dimensional stability.

Heat: Thermoplastic. Softens in boiling water. Loses strength on heating.
Withstands normal usage below freezing point.
Burns slowly.

Solvents and chemicals: Resistant to most household chemicals, oil, gasoline (petrol) and cleaning fluids.
Attacked by acids and alkalies; alcohol.

Light: Good stability.

Age: Shrinks very slightly. Not suitable for continuous exposure outdoors.

Electrical: Good insulator. Suitable for general domestic and industrial use.

TABLE 2: Applications and uses of cellulose acetate as thermoplastic polymer [2].

- (1) *Sheet.*
Produced in a wide range of colours; transparent, translucent or opaque. Special effects include metallized, pearl and mottled.
Examples of Uses: Toys; containers; lampshades; machine guards; advertising displays; brush handles; spectacle frames.
- (2) *Film.*
Produced as continuous rolls in wide range of thicknesses.
Examples of Uses: Photographic film base; packaging; book covers.
- (3) *Rod; tube; sections.*
Produced in a wide variety of sizes and profiles.
Examples of Uses: Beading; insulation; handle and rail covering.
- (4) *Moulding Powders.*
Produced in a variety of colours for injection moulding.
Examples of Uses: Combs; toilet articles; brushes; steering wheels; industrial equipment, e.g. oil pumps; textile bobbins; buttons and buckles; radio cabinets; telephones; door handles.

- 3) The fluid mass after assuming the shape of the mould is allowed to solidify.
- 4) The mould then separates into two halves and the object is removed or ejected.
- 5) The two parts of the mould are again closed together and the cycle is repeated [2,6,7,8].

The main relevant characteristics of CA, including advantages and disadvantages, are listed in table 1 [2]. Plastic-CA, as reported in table 2, was used as component for the manufacturing of a very large variety of consumer goods.

It was previously underlined as CA films, manufactured by using wheel casting processes, already applied for celluloid (see figure 5), due to their low flammability and performances replaced highly flammable films in celluloid for applications in the field of photography and cinematography (see examples in figure 6) [9].

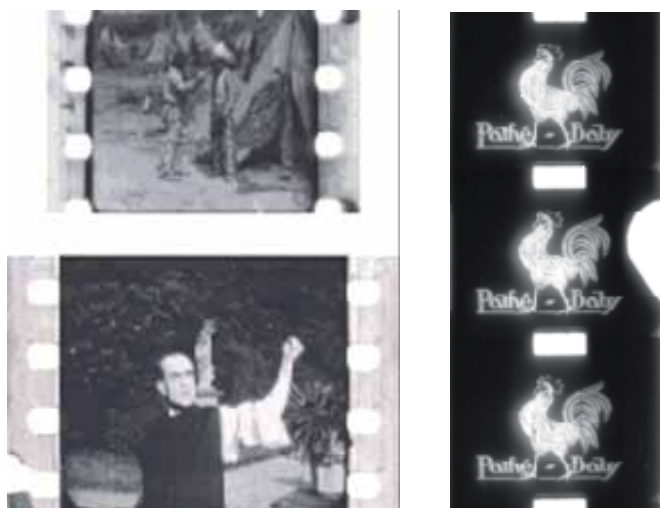


FIGURE 6: *Left*, < comparison of early professional motion picture (MP) films: (top) Pathéscope 28 mm on acetate base and (bottom). Eastman 35 mm on nitrate base; both in a good state of preservation > [9].

Right, < Pathé-Baby amateur film on acetate base with center sprocket holes (1922) > [9].

--- Cellulose Acetate: The Chemistry of syntheses and processing. Additives and related functions

As schematically shown in figure 7 during the synthesis of CA the hydroxyl groups [-OH] are substituted with [-O(C=O)CH₃] groups. The reaction of esterification is usually accomplished by treating at $\approx 0^{\circ}\text{C}$ the insoluble raw cellulose with a mixture of acetic acid and sulphuric acid that acts as catalyst.

From conservation point of view it is worthwhile to note that in the earlier processes part of non-reacted acetic and sulphuric acids remained in the solid polymer even after processing, as “*inherent vice*”. Only lately the process was implemented introducing innovations leading to the removal of most of residual acids [9].

The details of an early procedure of CA synthesis, as described in reference [10], are below textually reported.

< Cellulose acetate is manufactured from cotton linters which have been purified and dried to about 2% water content. In order to obtain an even reaction...the cotton structure is first opened or "swelled" by soaking in glacial acetic acid and is then acetylated with acetic anhydride, using a small quantity of sulphuric acid as catalyst and glacial acetic acid as diluent to reduce the violence of the reaction. The reaction is made in a jacketed dough mixer using refrigerated brine in the jacket to keep the temperature of the mixture near freezing point. After several hours the cellulose fibres are no longer visible...having been changed to cellulose tri-acetate, $C_6H_7O_2 \cdot 3[OCOCH_3]$ containing 62% acetic acid.

As this product is not easy soluble, the excess of anhydride is changed to acetic acid and the triacetate partly saponified to the secondary acetate by adding water to the mixture and allowing it to stand for two or two days...and a washed acetate sample tests 53/54 % acetic. Further dilution with water precipitates the acetate which is washed with water, and then with very diluted boiling mineral acid to stabilize it. The product is then dried carefully and several batches are blended > [10].

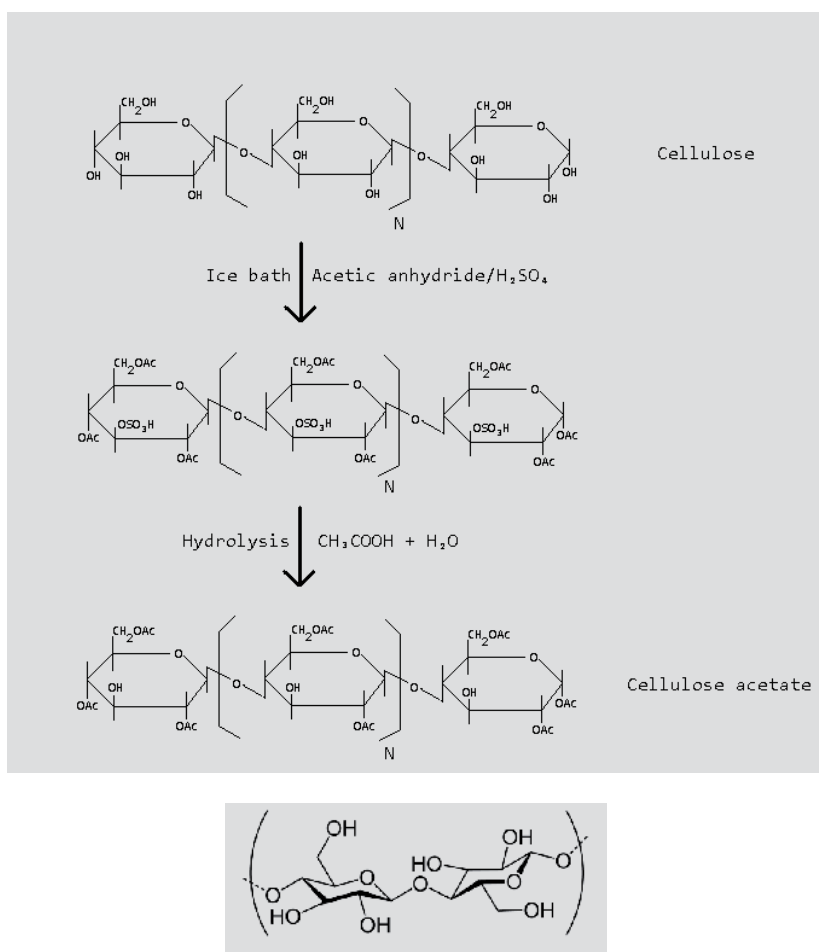
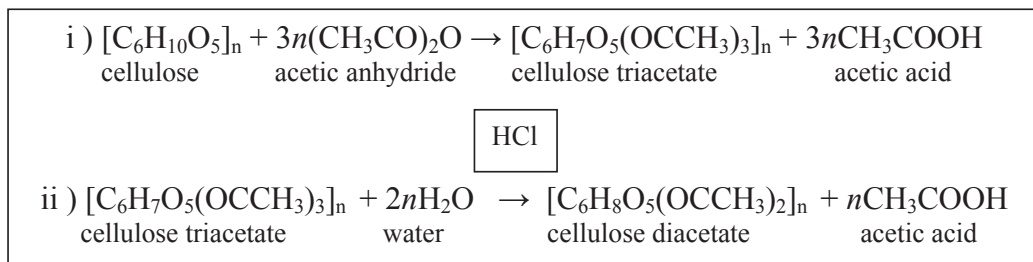


FIGURE 7: The scheme of the reactions that through chemical modification of cellulose chains lead to the production of cellulose acetate (see text for details). The bottom molecular structure represents the cellobiose repeat unit of cellulose.

In the modern standard processes the cellulose diacetate is obtained from the tri-ester (cellulose triacetate) after removing, by acid hydrolysis, some of the acetyl groups. The scheme of the main chemical reactions involved is below represented:



The pure CA, as above produced, to be usefully transformed must be compounded in dough mixers (see figure 8) with plasticisers, dyes or pigments, heat stabilisers, ultraviolet inhibitors, etc. The mixing is accomplished with the help of a volatile solvent, especially acetone.

The formulation (CA plus additives) after homogenisation is ready to be moulded into large blocks by means of an hydraulic press. From these blocks sheets of any thickness can be cut. Tubes and rods are manufactured alternatively by extrusion machines [10]. Moulding powders suitable for injection moulding are produced from sheets or rods, in such a case the amount of plasticiser in the formulation must be higher to lower the value of the soften temperature. Early objects in CA obtained by injection moulding and extrusion are reproduced in figures 9, 10 and 11 [10,2,11]. CA, as shown in figure 12, 13 and 14 was also used for the production of artistic objects characterized by a very innovative and original design [12,13].

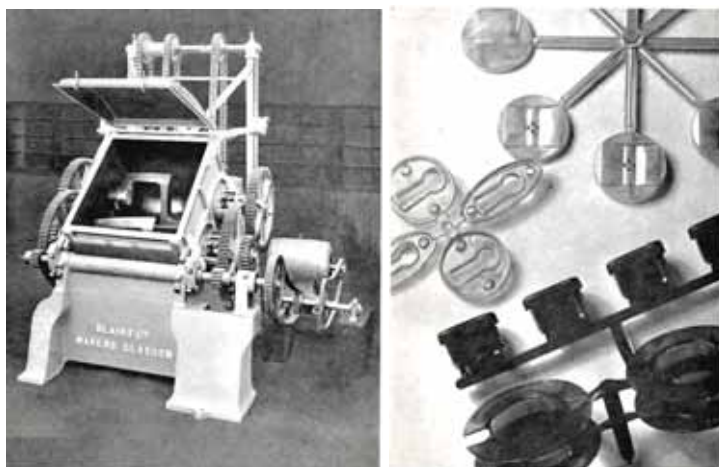


FIGURE 8-Left: An early “Dough mixer” (1930s) used for mixing cellulose acetate with additives and pigments [10].

FIGURE 9-Right: Early cellulose acetate mouldings (1930s) as they leaved the injection mould with gates still attached [10].

The properties of CA plastics as well as their characteristics and applications depend from the acetyl degree that normally is in the range of 1.5 to 2.76. The scheme of a modern process for the production of CA in the form of mouldable flakes is shown in figure 15 [14].

Cellulose triacetate, that according to the Federal Trade Commission definition is a CA where at least "92% of the hydroxyl groups have been acetylated, is significantly more heat resistant than normal cellulose diacetate. This polymer, mostly used for the manufacturing of fibers and film base, contrary to diacetate is not mouldable due to its very high soften temperature, then it can only be processed by casting or extrusion of its viscous solutions.

As solvent a mixture of methylene chloride and methanol is usually employed. By using those procedures triacetate may be conveniently transformed in films, sheets and fibres, which are characterized by the following interesting properties:

- Good gage uniformity;
- Grain less and good optical;
- Good dimensional stability;
- Resistance to water;
- Good folding endurance and burst strength;
- Low aging tendency;
- High resistance to the action of greases, oils, and against most of the common solvents as acetone;
- Good heat resistance and high dielectric constant;
- Good scratch resistance;
- Easy to be pressure formed, creased, punched and folded [5].



FIGURE 10-left: Television cabinet moulded from cellulose acetate [2].

FIGURE 11-right: Tubes, extruded from cellulose acetate, which were used as disposable syringes [11].

By using the method described in figure 16 it is possible the manufacturing, from narrow sheets, of variously coloured and comfortable-wearing eyeglasses frames in cellulose acetate [15].

Such eyeglasses frames as shown by the exemplary reproduced in figure 17 resulted to be:

< capable to fulfil the innovative and creative demands from the customers and suitable for matching an unique style of dressing of the wearers > [16].



FIGURE 12-Left: Old cellulose acetate handbag from University of Rhode Island Conservation Collection. Donated by J. Butterworth in 2002 [12].

FIGURE 13-Right: Egyptian handbag with cellulose acetate ornaments, purchased by tourists in the 1920's [12].



FIGURE 14: Elegant box and cover patterned with cherries in low relief manufactured in cellulose acetate. The artefact was introduced by René-Jules Lalique (French, 1860–1945) in 1925–26. This model was manufactured in a range of different colours [13].

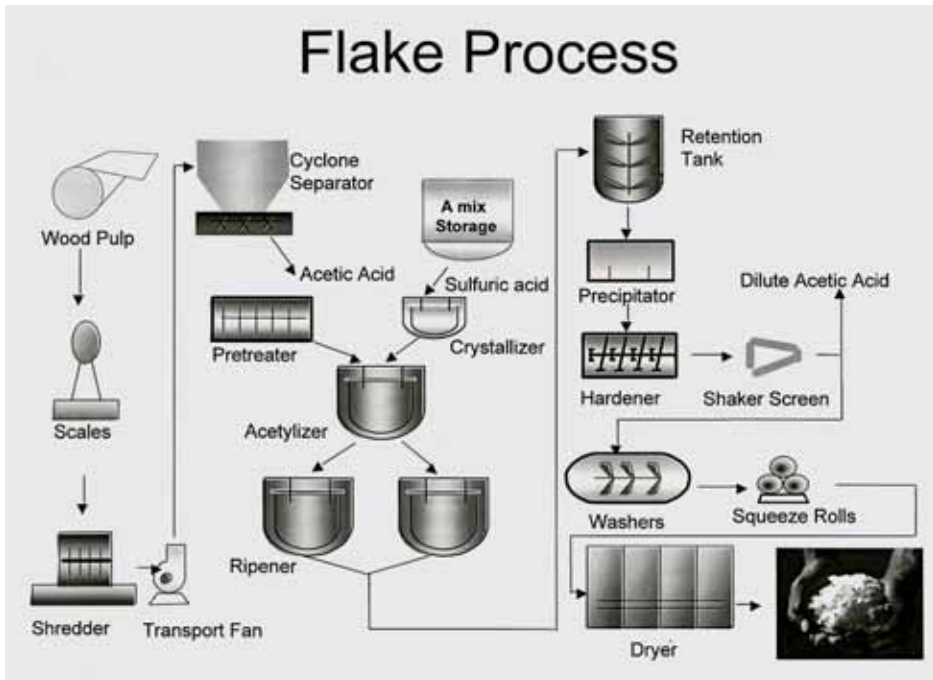


FIGURE 15: Modern process for the production of mouldable flakes of cellulose acetate. In figure the sequence of the various steps is schematically represented [14].

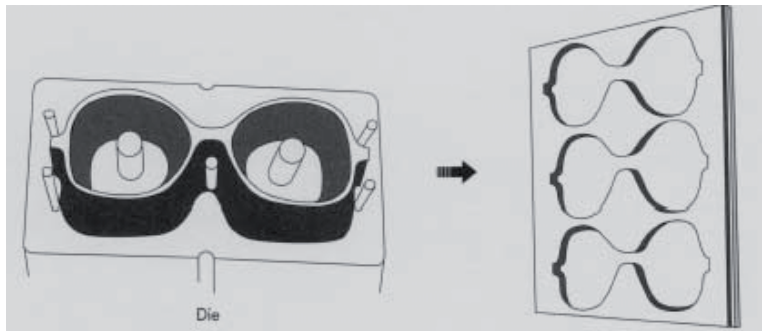


FIGURE 16: Blanks for plastic eyeglass frames are die cut from sheets of cellulose acetate [15].

Some of the most relevant physical properties of CA are listed in table 3 [17].

In 1938 (cellulose acetate butyrate, CAB) and in 1945 (cellulose acetate propionate, CAP), two new artificial polymers, derivative from cellulose chemical modification, were industrially developed and introduced in the market.

TABLE 3: Physical properties of a generic commercial sample of cellulose acetate [17].

Tenacity	
- Standard Conditions	1.2 - 1.4 g/d
- Wet, 70° F	0.8 - 1.0 g/d
Elongation at break	
- Standard Conditions	25 - 45%
- Wet, 70° F	35 - 50%
Specific gravity	1.32
Moisture regain	6.3%
Thermal properties	
Softening temperature	357 - 400° F 180 - 205° C
Melting temperature	500° F 260° C
Other	
Bondable	Thermal Ultrasonic Plasticizer
Hydrophilic	
Safe	USP Class 6 approved Food-contact (USCFR)



FIGURE 17: eyeglass frames in cellulose acetate with fine and elegant design [16].

Cellulose acetate butyrate (CAB) and cellulose acetate propionate (CAP) were synthesised by substituting part of acetic acid and its anhydride with propionic acid ($\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{OH}$) or butyric acid ($\text{CH}_3(\text{CH}_2)_2\text{C}(\text{O})\text{OH}$) and their corresponding anhydrides respectively.

Commercially samples of CAP generally contain 39 to 47% propionyl and 2 to 9% acetyl. While in CAB the content of butyryl and acetyl ranges between 26-39% and 12-15% respectively [5]. CAB and CAP are preferred to CA < for applications that require their advantage in weatherability, low temperature impact strength and dimensional stability. Faster injection moulding cycles and extrusion rates are possible due to good melt strength. Butyrate and propionate also have a lower density than acetate. Extruded butyrate and propionate sheeting have good gage uniformity, surface quality, brilliance and visual effects.... Can be very tough, and they have good colour stability >[5]

The success encountered by cellulose plastics (CA, CAP and CAB) has to be essentially ascribed to the wide range and versatility of their properties which include:

- Toughness;
- Surface gloss;
- Clarity;
- Capability to be manufactured by a large typology of processes;
- High dielectric constant, good dielectric strength and volume resistivity;
- Chemical resistance especially to aromatic hydrocarbons [5].

The structure of the three already mentioned cellulose organic ester, as shown in figure 18, consists of repeating anhydroglucose units where three hydroxyl groups are esterified. The degree of esterification is usually expressed as the weight % of acyl group or through the degree of substitution (DS). When DS=3 all the three -OH have been esterified; while DS=1 means that only one of the -OH has been substituted [18,19].

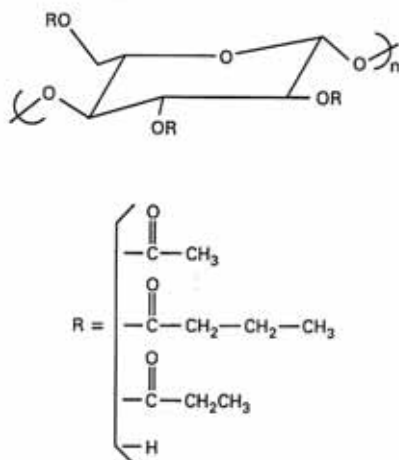


FIGURE 18: Molecular structure of different cellulose organic ester (CA, CAP, CAB) [18].

As can be seen from the data reported in tables 4, 5 and 6 most of the chemical/ physical properties (solubility, viscosity, glass transition temperature, melting point, density, etc.) of cellulose esters [CA, CAP and CAB] depend upon their chemical constitution (i.e. chemical nature of the substitute content; acetyl, butyryl or propionyl; number of -OH group per four anhydroglucose units) and of course by molecular mass [18].

In table 5 each sample is labelled according to the nomenclature used by Eastman that is based upon the following criteria [19]:

< --- for CA samples, the three digits following the letter prefix (CA) indicate the acetyl content by weight, omitting the decimal point between the second and third digits.

--- for CAB and CAP, the first two digits indicate the butyryl or propionyl content respectively, at the triester stage; the third digit gives the number oh hydroxyl per four anhydroglucose units.

--- for all three esters the suffix of the name indicates the viscosity in a designed solvent, which is related to degree of polymerisation or molecular weight > [19].

TABLE 4: Typical properties of cellulose esters commercialised by the Eastman Company [18].

Eastman™ cellulose ester	Viscosity ^b		OH %	Melting range °C	T _g °C	Wt/Vol		MW _n ^c
	S	Poise				lb/gal	kg/L	
Cellulose acetate butyrate								
CAB-551-0.01	0.01	0.038	1.5	127-142	85	9.67	1.16	16,000
CAB-551-0.2	0.20	0.76	1.8	130-140	101	9.67	1.16	30,000
CAB-553-0.4	0.30	1.14	4.8	150-160	136	10.00	1.20	20,000
CAB-531-1	1.90	7.22	1.7	135-150	115	9.75	1.17	40,000
CAB-500-5	5.00	19.00	1.0	165-175	96	9.83	1.18	57,000
CAB-381-0.1	0.10	0.38	1.3	155-165	123	10.00	1.20	20,000
CAB-381-0.5	0.50	1.90	1.3	155-165	130	10.00	1.20	30,000
CAB-381-2	2.00	7.60	1.3	171-184	133	10.00	1.20	40,000
CAB-381-2 BP	2.20	8.36	1.8	175-185	130	10.00	1.20	40,000
CAB-381-20	20.00	76.00	1.8	195-205	141	10.00	1.20	70,000
CAB-381-20 BP	16.00	60.80	0.8	185-195	128	10.00	1.20	70,000
CAB-321-0.1	0.10	0.38	1.3	165-175	127	10.00	1.20	12,000
CAB-171-15	15.00	57.00	1.1	230-240	161	10.50	1.26	65,000
Cellulose acetate propionate								
CAP-504-0.2	0.20	0.76	5.0	188-210	159	10.53	1.26	15,000
CAP-482-0.5	0.40	1.52	2.6	188-210	142	10.20	1.22	25,000
CAP-482-20	20.00	76.00	1.8	188-210	147	10.20	1.22	75,000
Cellulose acetate								
CA-398-3	3.00	11.40	3.5	230-250	180	10.90	1.31	30,000
CA-398-6	6.00	22.80	3.5	230-250	182	10.90	1.31	35,000
CA-398-10	10.00	38.00	3.5	230-250	185	10.90	1.31	40,000
CA-398-30	30.00	114.00	3.5	230-250	189	10.90	1.31	50,000

Notes to the table: a) properties are typical of average lots. b) viscosity is measured according to the ASTM D817 (formula A) and D1343 test. c) number average molecular weight MW_n are polystyrene-equivalent molecular weights determined by size excluded chromatography.

TABLE 5: Solubility of some Eastman samples of cellulose esters in common solvents (at 10% NV).

S = soluble; I = insoluble; PS = partially soluble, SH = soluble with slight haze [18].

Solvents	Eastman™ CA-398-3	Eastman™ CAB-171-15	Eastman™ CAP-504-0.2
Ketones			
Acetone	S	S	S
MEK (Methyl ethyl ketone)	S	S	S
Eastman™ MPK (Methyl n-propyl ketone)	I	S	PS
Eastman™ MIBK (Methyl isobutyl ketone)	I	I	I
Eastman™ MIAK (Methyl isoamyl ketone)	I	I	I
Eastman™ MAK (Methyl n-amyl ketone)	I	I	I
Cyclohexanone	S	S	S
Eastman™ DIBK (Diisobutyl ketone)	I	I	I
DAA (Diacetone alcohol)	S	S	S
Eastman™ C-11 Ketone	I	I	I
Esters			
Ethyl acetate (99%)	PS	S	S
Eastman™ Isopropyl acetate	I	I	I
Eastman™ n-Propyl acetate	I	S	S
Eastman™ Isobutyl acetate	I	I	I
Eastman™ n-Butyl acetate	I	I	I
Eastman™ IBIB (Isobutyl isobutyrate)	I	I	I
Eastman™ n-Butyl propionate	I	I	I
Eastman™ EEP solvent	I	I	PS
Eastman™ 2-Ethylhexyl acetate	I	I	I
DBE (Dibasic esters)	PS	S	S
Eastman Texanol™ ester-alcohol	I	I	I
Glycol ethers			
Eastman™ PM solvent	I	I	S
EE (Ethylene glycol monoethyl ether)	I	I	S
PTB (Propylene glycol monotertiary butyl ether)	I	I	I
Eastman™ EP solvent	I	I	S
PP (Propylene glycol monopropyl ether)	I	I	PS
PB (Propylene glycol monobutyl ether)	I	I	S
Eastman™ EB solvent	I	I	S
Eastman™ DM solvent	PS	PS	S
DPM (Dipropylene glycol monomethyl ether)	I	I	S
Eastman™ DE solvent	I	I	S
Eastman™ DP solvent	I	I	S
Eastman™ DB solvent	I	I	S
Eastman™ EEH solvent 85/15 ethylene glycol/ diethylene glycol 2-ethylhexyl ether	I	I	I
Glycol ether esters			
Ethylene glycol monoethyl ether acetate	I	I	S
Eastman™ EB acetate	I	I	I
EGDA (Ethylene glycol diacetate)	S	PS	S
Eastman™ DE acetate	PS	PS	S
Eastman™ DB acetate	I	PS	S
Eastman™ PM acetate	I	PS	S
Alcohols			
Ethyl alcohol (anhydrous)	I	I	I
Ethyl alcohol (95%)	I	I	S
Isopropyl alcohol (99%)	I	I	I

Many important physical properties of CA, CAP and CAB (for example: glass transition temperature (T_g), mechanical strength and elongation, and water vapour transmission rate (WVTR)) may be significantly modified by adding plasticisers. Usually it is observed that in case of film with increasing the content of a given plasticiser T_g decreases, while strength and flexibility increase.

As far as the WVTR is concerned it is found that if the plasticiser is water soluble its value increases with plasticiser content; the contrary occurs when the plasticiser used is water insoluble [19].

Such behaviour is exemplified by the diagrams in figure 19 where the effect of two different plasticisers, polyethylene glycol (PEG400) , water soluble, and triethyl citrate (TEC) , water insoluble, on the values of WVTR is shown [19].

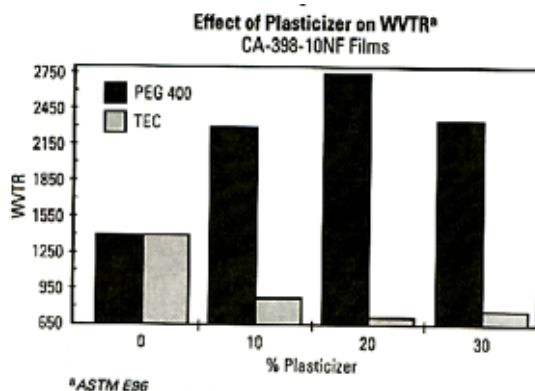


FIGURA 19: The effect of two different plasticisers, polyethylene glycol (PEG400) , water soluble, and triethyl citrate (TEC) , water insoluble, on the values of water vapour transmission rate (WVTR) of a CA film produced by the Eastman Company, is shown [19].

TABLE 6: Dependence of some mechanical properties (break to stress and elongation to break), T_g and of water vapour transmission rate (WVTR) on the constitution of cellulose esters (see text) [19].

	Break Stress, Elongation to			WVTR.
	MPa	Break, %	T_g °C	g-mil/m ² /day
CA-320S	50.9	4.1	203	1,201
CA-398-10NF	61.3	5.6	187	1,404
CA-435-75S	93.3	8.5	177	837
CAB-171-15PG	44.6	6.3	166	1,091

--- Identification of Cellulose Acetate in Plastic Artefacts by Instrumental Analysis

As in the case of celluloid also CA artefacts following degradation give off breakdown products dangerous to other objects kept in their proximity. Thus for any collecting house it is of extreme importance the preliminary assessment of the presence in their collections of items made in CA, and in this even to adopt specific conservation measures.

At the moment traditional instrumental analytical techniques such as FTIR, FTIR/microscopy and Raman spectroscopy, Differential Scanning Calorimetry (DSC) and X-ray diffraction are commonly used for the identification of CA plastics. All these methodologies however have the disadvantage of being inherently destructive.

As previously described in the case of celluloid identification, non-destructive and *in-situ* instrumental techniques have been developed by making profit of suitable fibre optic probes.

Hereafter some relevant applications of analytical instrumental procedures to the identification of CA are briefly illustrated.

--- Fourier Transform Infra Red Spectroscopy (FTIR)

FTIR spectroscopy, by producing a "*fingerprint*" spectrum, represents perhaps the most effective analysis for the identification of CA in plastic artefacts being capable to put in clear evidence the specific structural features of cellulose esters as well as of their most common additives employed.

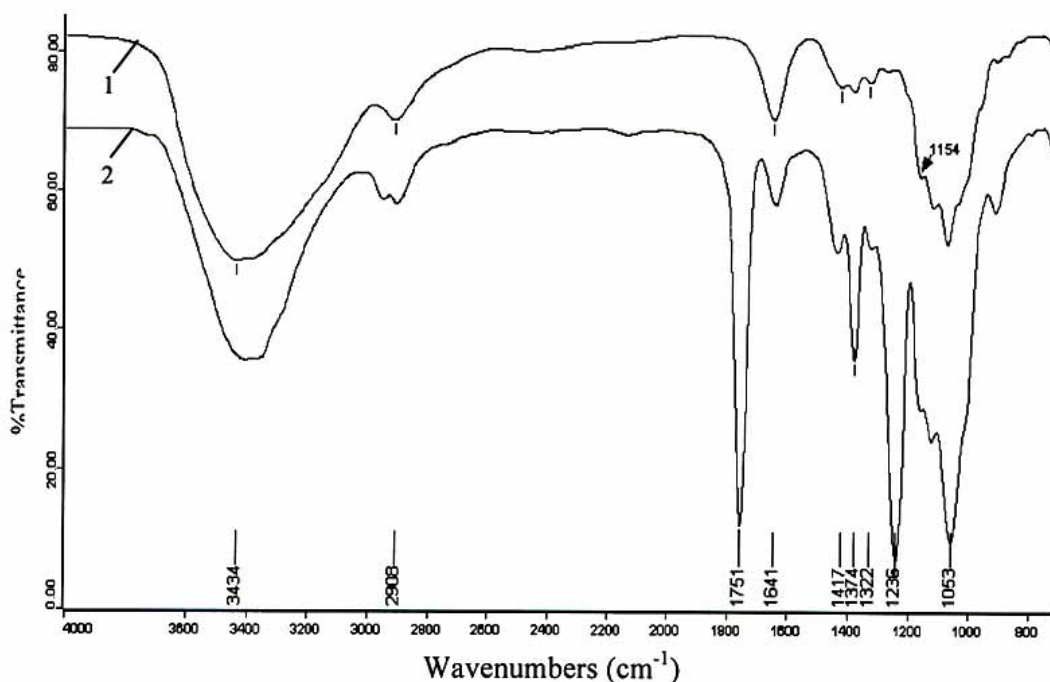


FIGURE 20: FTIR spectra of unmodified cellulose (spectrum 1), and acetylated cellulose, DS= 1.8, (spectrum 2) [20].

The main characteristics of the CA spectrum, with reference to figure 20 where the FTIR spectra of cellulose and CA (DS = 1.8) are compared, are hereafter summarized [20].

--- The presence of the three bands centred at 1751, 1374 and 1236 cm^{-1} to be attributed to carbonyl C=O stretching of the ester, C-H stretching in $-\text{O}(\text{C}=\text{O})-\text{CH}_3$, and C-O stretching of acetyl group, respectively.

--- The decreasing absorption intensity of the peak at 3434 cm^{-1} assigned to the stretching vibrations of the O-H when compared to native cellulose due to the fact that part of $-\text{OH}$ group are esterified .

Moreover it interesting to note that if the sample of CA contains free un-reacted acetic anhydride or acetic acid by-products, with carboxylic groups, then in the spectrum-2 in figure 20 peaks in the region of 1840-1760 cm^{-1} and at 1700 cm^{-1} should be observed [20].

Quite recently *Edwards' Analytical* in cooperation with *Buchi Analytical Ltd* developed a non-destructive and *in-situ* testing methodology by fitting the Buchi FT-NIR spectrometer with a proper fibre optic reflectance probe [21]. The set up of such technique allowed the activation of an identification service.

< Since there is no existing database of historical plastics in the NIR, to set up the identification service a data base was constructed in two parts:

--- Polymers were purchased from the Aldrich Chemical Company and their NIR spectra recorded.

--- With the exclusive cooperation of Colin Williamson of Smile Plastics, historical plastic objects with known provenance and identification were analysed > [21].

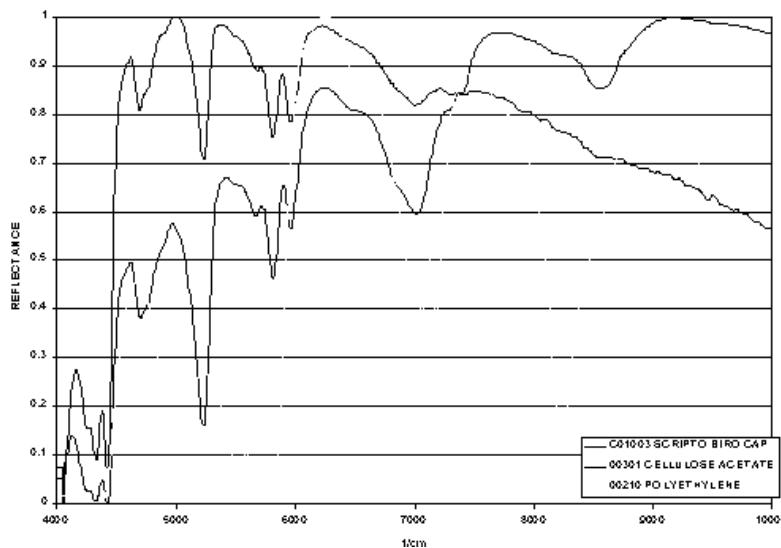


FIGURE 21: Comparison of the FT-NIR spectra of the *scripto biro cap* of unknown composition (top-diagram) with that of cellulose acetate in the database (bottom diagram).

On the ordinate is reported the reflectance, on the abscissa, the wavelength expressed in $1/\text{cm}$ [21].

The utility of the so built database was assessed on a certain number of artefacts in plastics belonging to the Hammer Horror collection recently acquired by the National Museum of Photography, Film & Television, Bradford, dating from the late 1950's – 1970's.

As exemplified by the spectra in figure 22, Infrared spectroscopy may be very effective in the identification of the chemical nature of additives present in a sample of CA. In particular the spectra refer to samples of cellulose triacetate (CTA) containing different amount of several kind of plasticisers [22].

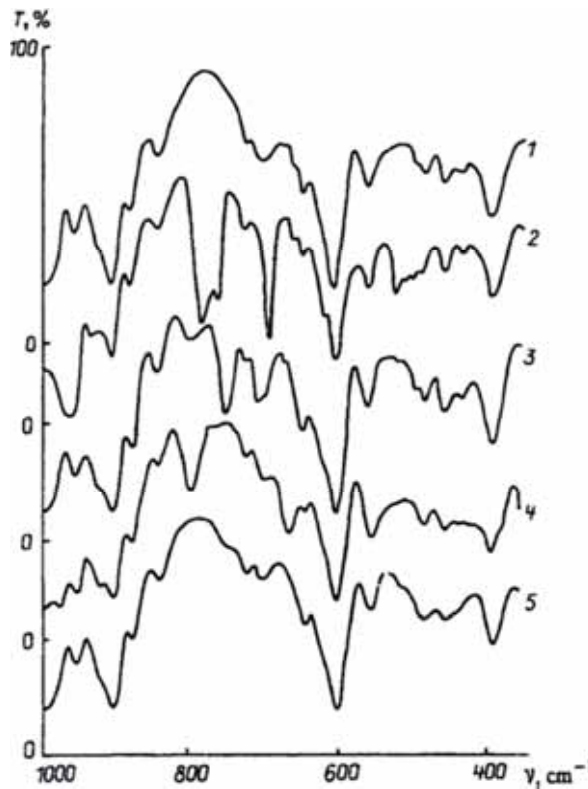


FIGURE 22: IR spectra of cellulose triacetate (CTA) films (1) and of CTA plasticized by 10% TPP (2), 20% DBP (3), 15% TCEP (4), and 1% BS (5) [22].

--- Raman Spectroscopy

< Raman spectra are obtained by irradiating a sample with a high powerful laser source of visible or NIR monochromatic radiation. During irradiation, the spectrum of the scattered radiation is measured at some angle (often at 90 deg) with a suitable spectrometer.....the Raman scattering spectrum and infrared absorption spectrum for a given species often resemble one another quite closely. There are however, enough differences between the kinds of groups that are infrared active and Raman active to make the techniques complementary rather competitive. For some problems,

the infrared method is superior tool: for others, the Raman procedure offers more useful spectra > [23].

Raman spectra are very specific (see Raman spectrum of a sample of CA in figure 23), thus through such a spectroscopy it is possible to perform accurate qualitative and quantitative analysis leading to information very useful for the identification of the chemical constitution of a polymer as component of a plastic object.

Chemical identifications can be accomplished < *by using search algorithms in digital data bases. Analyses are non-destructive; little or no sample preparation is required. Fibre optic lines can be used for analyses 'outside of the box'* > [24].

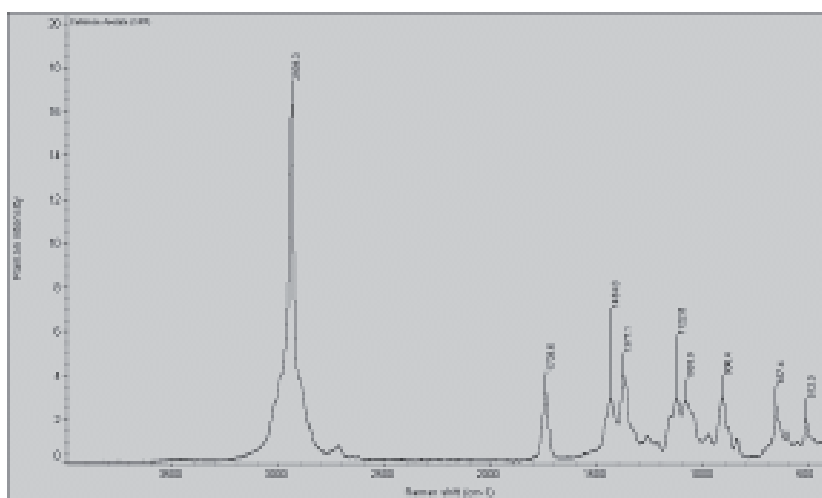


FIGURE 23: Raman spectrum of a cellulose acetate sample [24].

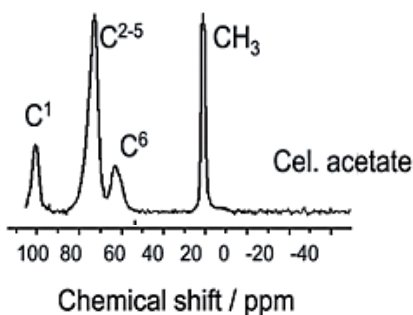
--- Nuclear Magnetic Resonance Spectroscopy (NMR)

< *NMR spectroscopy is based on the measurement of absorption of electromagnetic radiation in the radio frequency region of roughly 4 to 900MHz. In contrast to ultraviolet, visible, and infrared absorption, nuclei of atoms rather than outer electrons are involved in the absorption process* > [23].

NMR represents a powerful technique suitable to elucidate the structure of chemical species present also in multi component compounds as in the case of plastics.

Such a technique may be used to assess the presence of CA as constituent of plastic artefacts.

As matter of fact as shown by figure 24-a), C^{13} NMR spectra of CA samples exhibit a typical diagram with specific values of the chemical shifts [25].



Materials	δ / ppm	Assignments
Cellulose acetate ^b	102, 67	C ¹ , C ⁶
	73	C ²⁻⁵
	21	CH ₃

FIGURE 24-a: The C^{13} NMR spectrum of cellulose acetate exhibits a typical diagram with a specific peaked structure (top). The values of the chemical shifts and related assignments are reported on the bottom side [25-a].

The 1H -NMR spectrum of representative samples of cellulose triacetate from the N,N-dimethylacetamide (DMA)-formaldehyde system is shown in figure 24-b . The peaks observed at 2.09, 1.99, and 1.94 ppm have been assigned to O-acetyl substitutes at OH-6, OH-2, and OH-3, respectively [25-b].

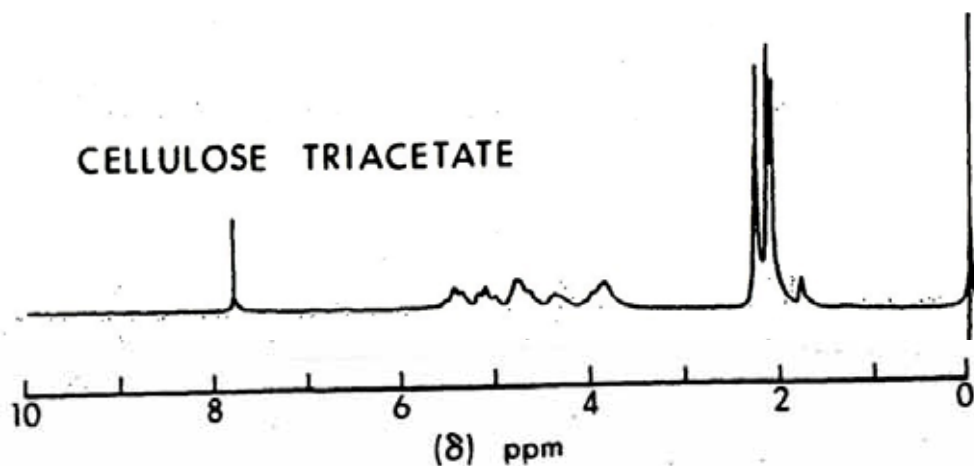


FIGURE 24-b: The 1H -NMR spectrum of a representative sample of cellulose triacetate from the N,N-dimethylacetamide DMA-formaldehyde system [25-b].

--- Differential Thermal Analysis and Thermogravimetry Analysis

Interesting information suitable to the identification of CA in artefacts can be derived from Differential Thermal Analysis (DTA) and Thermogravimetry Analysis (TGA), both being destructive methodologies.

The DTA and TGA traces corresponding to non-acetylated and acetylated samples of cellulose are reported in figure 25 and 26 respectively [20]. The experiments were performed from room temperature to 600°C at a heating rate of 10°C/min under nitrogen flow.

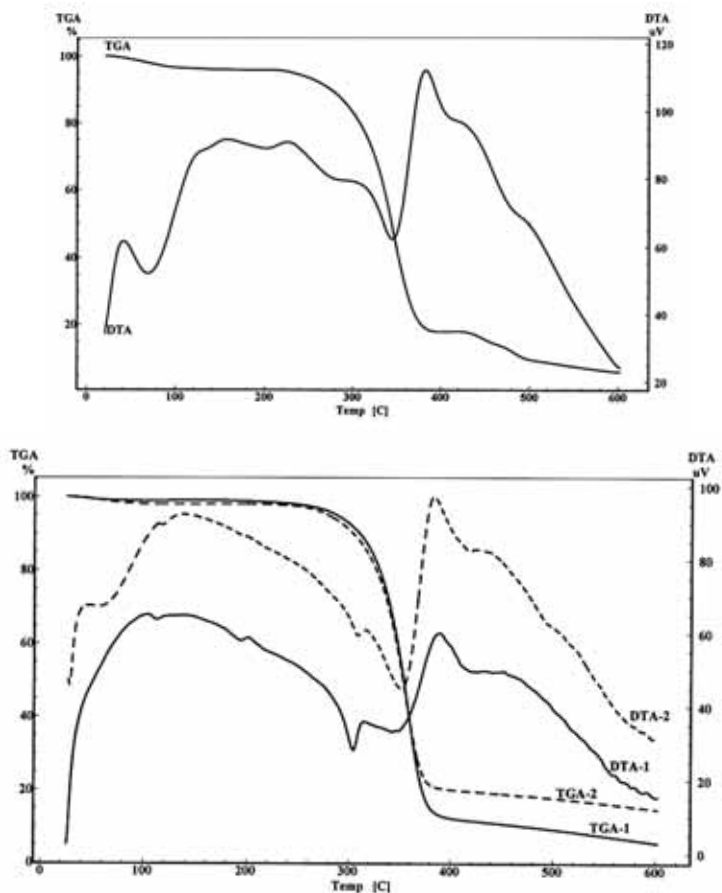


FIGURE 25, top: Differential thermal analysis and thermogravimetry analysis of cellulose [20].

FIGURE 26, bottom: Differential thermal analysis and thermogravimetry analysis of acetylated cellulose samples differing in the value of the degree of substitution (DS) (trace, 1, DS = 2.0, trace, 2, DS = 0.78) [20].

By comparing the thermograms the following observations were drawn:

< From room temperature to 120°C the TGA thermogram of un-acetylated cellulose displayed a minor weight loss which is attributed to water desorption, which can also be explained by the endothermic event observed between 40-120°C in DTA curve.

This minor loss of weight is not obvious for the acetylated samples,... the acetylated samples are more hydrophobic than native cellulose > [20].

Moreover it can be observed that the onset thermal degradation temperatures start at 296°C for un-acetylated cellulose (see figure 25), and at 329-322°C for the two acetylated samples (figure 26). This indicates that the thermal stability of acetylated samples is higher than that of cellulose.

The thermograms of cellulose and CA show endothermic peaks between 300-400°C, due to the melt process of crystals and peaks near 400°C related to decomposition effects [20].

--- Wide angle X-ray Diffraction Analysis (WAXS)

The diffractograms are characterised by two sharp discrete peaks, at 16.5 and 22.5 of 2θ , deriving from the scattering of the crystal regions, and assigned to the cellulose I-phase.

The presence of a halo with a maximum around 22.5 of 2θ is to be ascribed to the continuous diffusion scattering from amorphous regions. It is interesting to point out that the degree of crystallinity seems to decrease with the increase of the content of acetyl groups along the backbone chains of cellulose (the intensity of crystal peaks diminishes while that of the amorphous scattering increases) [20]. The WAXS technique results to be suitable for detecting the presence of any type of cellulose ester in a given artefact.

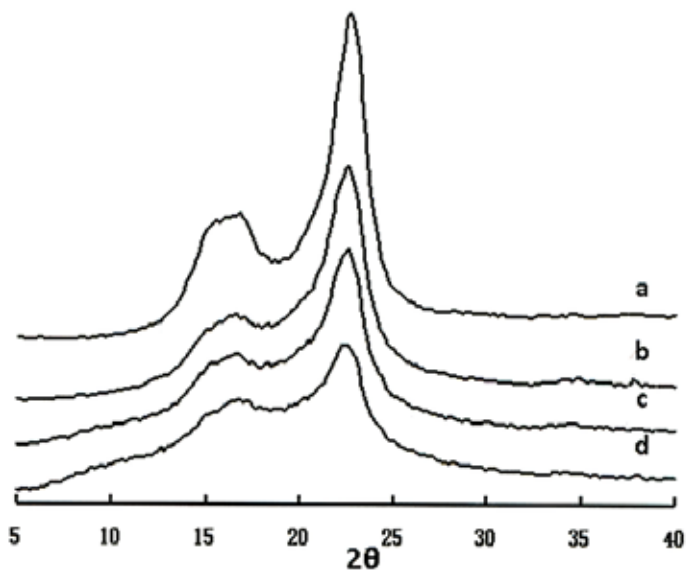


FIGURE 27: Wide angle X-ray diffraction curves of native cellulose (spectrum-a) and acetylated cellulose samples with different degree of acetyl content (spectrum-b, CD = 0.78; spectrum-c, CD = 1.4; spectrum-d, CD = 2.0) [20].

--- Energy dispersive X-ray fluorescence spectrometry (EDXRF)

In the EDXRF technique a sample is irradiated with a beam of X-rays from an X-rays tube. < Under these circumstances, the elements in the sample are excited by absorption of the primary beam and emit their own characteristics fluorescence X-rays > [23].

EDXRF spectrometry is a very effective analytical method for the qualitative or quantitative identification of elements with atomic numbers greater than that of oxygen (>8). Thus it results to be useful in case of polymers compounds to verify the presence of some inorganic additives, pigments and or degradation by products [26].

A particular advantage of this procedure of elemental analysis relies on its non-destructive character.

Quite recently M.L.Carvalho and others [26-a] developed a portable EDXRF spectrometer for elemental characterization of valuable samples *in situ*. The apparatus is reproduced in figure 28 [26-a)], while in figure 29 is reported a typical EDXRF spectrum obtained on a sample of ancient cellulose paper artefact [26-a)]. It can be seen as the various elements present in the sample may be easily recognized by the frequency of the light emitted following X-rays absorption.

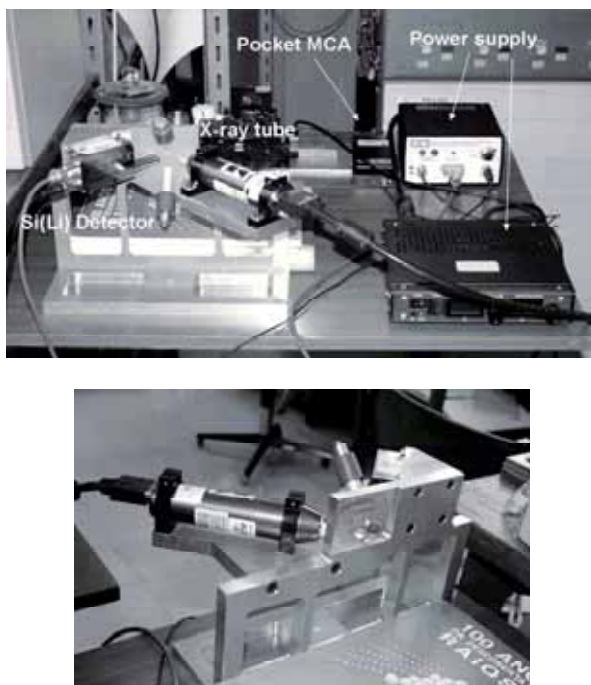


FIGURE 28: The portable EDXRF spectrometer, suitable for *in situ* non destructive elemental characterization of samples, developed by M.L.Carvalho and others in the framework of EU-Papertech project [26-a)].

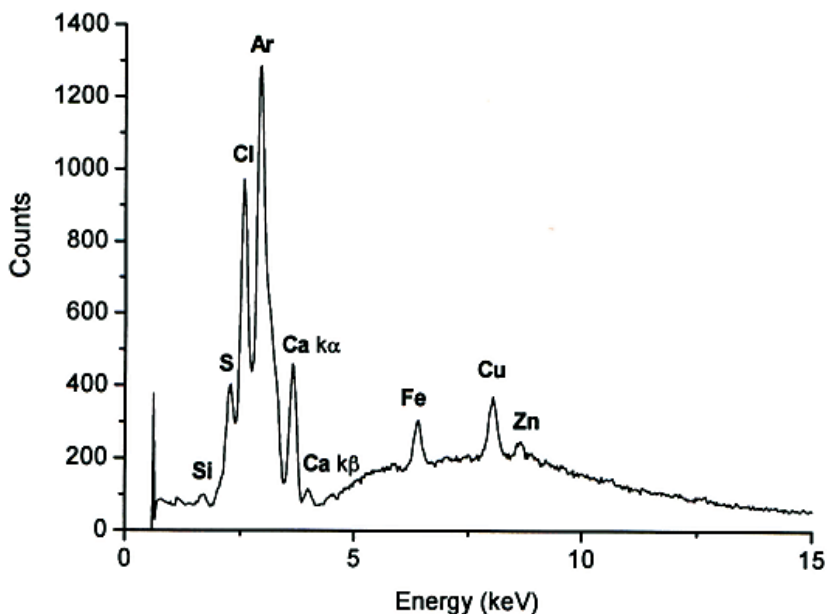


FIGURE 29: A typical spectrum obtained with the portable EDXRF spectrometer. The sample examined is a paper based artefact [26].

--- Solid state cross-polarization magic angle spinning carbon-13 nuclear magnetic resonance (CP/MAS¹³C-NMR)

Solid state ¹³C NMR, that received a great impulse only after the introduction of cross polarization and magic angle spinning (CP/MAS), is an useful tool for studying the effects of process history and physical aging on physical properties of plastics [27-30].

CP/MAS¹³C-NMR techniques < have also been used to study the motional dynamics of low-molecular weight molecules in high-molecular weight polymer matrices. For example, NMR studies of plasticizer motions in poly(vinylbutyral)-plasticizer blends have revealed that a portion of the plasticizer has the mobility of a neat liquid, whereas another portion has the relative rigidity of the surrounding polymer matrix > [27].

Moreover CP/MAS¹³C-NMR procedure found interesting applications < to establish important links between 1) molecular-level variables (i.e., hydrolysis and motional dynamics); 2) macroscopic-level variables (i.e., thermal history and environmental process history); and 3) macroscopic-level properties (i.e., adhesion)..... Solid state NMR experiments are capable of providing information about the motional heterogeneity in polymer systems. This type of information can in turn be used to elucidate information about morphology in semi-crystalline and bi-amorphous systems > [27].

From above it can be concluded that CP/MAS¹³C-NMR techniques represent at the moment a quite powerful tool for the characterization of structure and dynamics in solid plastics. By using such a methodology it is possible to probe in molecular solids the electronic environments of specific nuclei in the condensed state over a large timescale. Thus this non-destructive technique, that can be also applied *in situ*, may be considered in many respects as complementary to X-ray diffractometry and solution-state NMR spectroscopy [31].

Solid state CP/MAS¹³C-NMR spectra performed on native cellulose (spectrum-a) and various samples of cellulose acetate with different degree of acetyl content (spectrum-b, CD = 0.78; spectrum-c, CD = 2.0) are shown in figure 30 [20]. The specificities of such spectra are evidenced in reference [20] as follows:

--- < The signals between 50 to 110 ppm are attributed to the different carbons of cellulose. The resonance line at 106.0 ppm is assigned to the C-1.

--- The peaks at 89.8 and 85.2 are related to the C-4 of crystalline cellulose and disordered cellulose respectively. A similar trend can be seen in the signal to C-6, namely, the signal at 65.8 ppm is attributed to the crystalline cellulose and the peak at 63.1 ppm is assigned to disordered or crystal surface of cellulose.....

--- In addition, the two representative peaks at 171.8 and 21.5 ppm in spectra b and c, which belong to the CO and CH₃ in acetyl group, indicated the occurrence of acetylation reaction.

--- On the other hand, the intensity of the signal at 89.7 ppm for crystalline C-4 and 65.9 ppm for crystalline C-6 decreased sharply in spectra b and c, which reveal that the crystalline structure of cellulose was disrupted and the acetylation reaction occurs in the system.

--- Finally, the increase of the intensity of the peaks at 171.8 ppm (CO) and 21.5 ppm (CH₃) and the decrease of the strenght for peaks at 73.5, 75.6 ppm (C-2-C-5) and 65.8 (C-6) in spectra b and c indicated that the extend of acetylation for sample c is higher than sample b, which is consistent with the value of DS > [20].

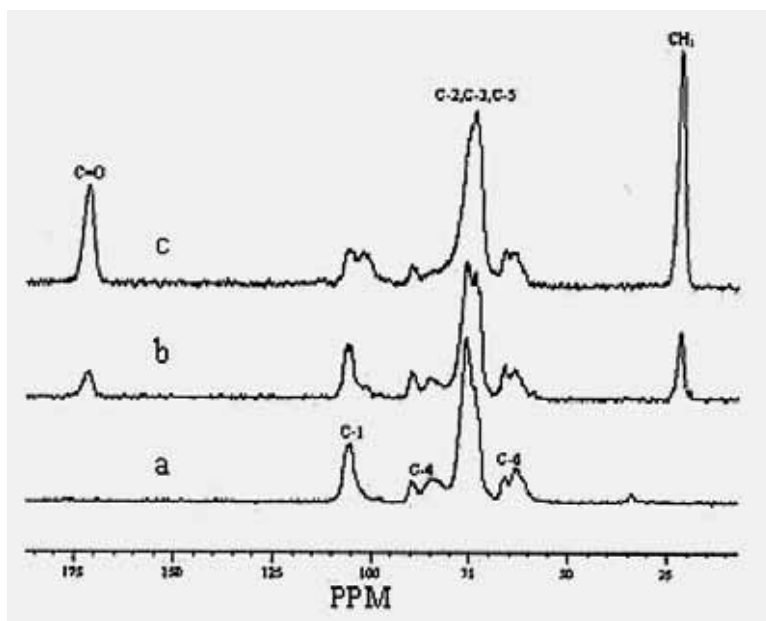


FIGURE 30: Solid state CP/MAS¹³C-NMR spectra performed on native cellulose (spectrum-a) and various samples of cellulose acetate with different degree of acetyl content (spectrum-b, CD = 0.78; spectrum-c, CD = 2.0) [20].

--- Identification of Cellulose Acetate in Plastics by using micro-test

Some of the most common destructive micro-tests used for the identification of CA in plastic artefacts are hereafter briefly described [32].

--- Hydroxylamine Hydrochloride Test

This test is effective to identify esters and acetate ions, and in the identifying artefacts manufactured in cellulose acetate as well as adhesives-based on polyvinyl acetate.

The hydroxylamine hydrochloride test is carried out in a test tube and requires 4 different reagents each in the form of solution:

Solution 1— 1 N potassium hydroxide in methanol.

Solution 2— Saturated hydroxylamine hydrochloride solution in methanol (1 g/19 ml of methanol).

Solution 3— 1% (w/v) ferric chloride in water.

Solution 4— 20% (v/v) hydrochloric acid in water, hydroxylamine hydrochloride, methanol, ferric chloride.



FIGURE 31: The hydroxylamine hydrochloride test used to identify cellulose acetate in artefacts.

If the test is positive, the solution turns violet-red. A yellow colour does not indicate a positive test (see text) [32].

The procedure is described as follows:

< Place the sample in a test tube. Add 1 ml of solution 1 and two drops of solution 2. Shake, wait three minutes, then add two drops of solution 3. Shake and add solution 4 a drop at a time, shaking after each drop. Up to ten drops may be required. If the test is positive, the solution turns violet-red. A yellow colour does not indicate a positive test >, (see figure 31) [32].

The disadvantage of the test, that is destructive in nature, rely on the fact that it requires a relatively large sample.

--- Molisch's Test

This test has been already previously described as it can be applied also for recognizing cellulose nitrate. As reported cellulose acetate and cellulose nitrate, react to the test giving rise to products with different colours (for details see previous chapter dedicated on cellulose nitrate).

--- Tests based on the determination of the pH of vapours and of combustion products and on density values

One of the tests requires the determination of the values of the pH of the vapours released from materials when slowly heated in a pyrolysis tube. In the case of cellulose triacetate the value of the pH is ≈ 2.5 .

Another test is based on the colouration imparted by combustion vapours to litmus paper (white, un-sized paper saturated by litmus, a water soluble powder from various lichens that in water turns red in solutions at pH 4.5, and blue at pH 8.3), used as a acid-base pH indicator.

Samples of CA are characterized by vapours of combustion capable to give a reddish colouration to the litmus paper (pH in the range 0.5–4.0).

Determination of density may help in the identification of CA by taken into account that the density of CA is between 1.25-1.35 g/cm³.

---- The polarisation test

Films in cellulose nitrate, cellulose tri acetate; and poly (ethylene terephthalate) have been commonly used as base material for motion picture film, microfilm, microfiche and photographic negatives. The cellulose acetate family includes also the mixed esters of cellulose acetate butyrate and cellulose acetate propionate as well as cellulose diacetate.

The polarization test is a clear-cut and non-destructive through which it is possible to distinguish polyester-based films from cellulose acetate and cellulose nitrate.

The test is based on the observation that *< when viewed between cross-polarised filters, polyester film exhibits red and green interference colours while cellulose nitrates and the cellulose acetates do not.....Polarisation tests for polyester-based film may be conducted by placing a sheet of Polaroid or other polarising material on both sides of the film; when these are rotated the film should exhibit interference colours >* (see figure 32) [33].

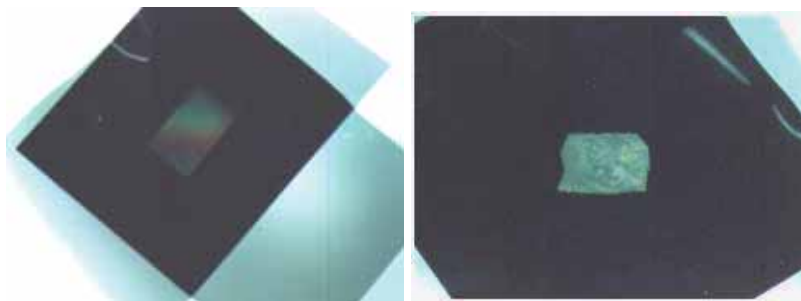


FIGURE 32: The polarization test to distinguish polyester-based films from cellulose acetate and cellulose nitrate. Left) Polyester based film; (Right) Cellulose acetate based film (see text for explanation) [33].

As happened for celluloid nitrate many artefacts in cellulose acetate due to their technological, historical, artistic and cultural value are nowadays part of important private and public collections. Thus the knowledge of the main mechanisms of deterioration of such artefacts should deserve great attention to adopt proper conservation and protection procedures against inherent and external factors of degradation.

REFERENCES

- 1) -a) M. Kaufman, < *The first century of plastics* >, the Plastics Institute , London (1963).
-b) www.dreyfus.org/about/history.shtml, (2009).
- 2) J. Gordon Cook, < *Your guide to Plastics* >, Merrow Publishing Co LTD, England (1964)
- 3) www.celaneseacetate.com/index/why-acetate/his..., (2009).
- 4) www.azom.com/details.asp?ArticleID=2424, date added: Mar 25, (2004)
- 5) < *Encyclopedia Handbook, Modern Plastics* >, Edited by Modern Plastics Magazine, McGraw-Hill, Inc. USA (1994).
- 6) T. Alfrey, E. F. Gurnee, < *Organic polymers* >, Prentice-Hall series in material science, New Jersey (1967).
- 7) H. Saechtling, < *Manuale delle materie plastiche* >, Tecniche Nuove, Milano, (1983).
- 8) L. Mascia, < *Thermoplastics, Materials Engineering* >, Elsevier Applied Science, London (1989).
- 9) T. Vitale, < *History, Science and Storage of Cellulose Acetate Film base* >, http://videopreservation.conservation-us.org/library/history_science_storage_of_acetate_base_film_16b.pdf, v16, Updated, 6/5 (2009).
- 10) H. W. Rowell, < *The Technology of Plastics* >, Plastics Press Ltd., London (1937).
- 11) J. H. DuBois, F. W. John, < *Plastics* >, Van Nostrand Reinhold Company, London, (1981).
- 12) R. Walker, < *Conserving Plastics in Nineteenth and Twentieth-Century Costume Collections* >, Department of Textiles, Fashion Merchandising and Design, University of Rhode Island Power Point presentation (2009).
- 13) René-Jules Lalique: Box (24.145.3ab)". In < *Heilbrunn Timeline of Art History* >. New York: The Metropolitan Museum of Art, 2000–.
http://www.metmuseum.org/toah/hd/mome/ho_24.145.3ab.htm, October (2006).
- 14) http://www.celanese.com/index/productsmarkets_index/products_markets_acetate/acetate_whyacetate/acetate_whyacetate_physical.htm, (2009).
- 15) www.madehow.com/Volume-5/Eyeglass-Frame.html, (2009).
- 16) www.hktcdc.com/sourcing/company_product_detail..., (2009).
- 17) www.celanese.com/index/productsmarkets_index/... Celanese Corporation, (2009).
- 18) < *Eastman Cellulose-based Specialty Polymers* >, Eastman Chemical Company (2009).
(www.eastman.com) .
- 19) < *Eastman Cellulose Esters for Pharmaceutical Drug Delivery* >, Publication PCI-105C, October (2005).
- 20) Jing Li, Li-Ping Zhang, Feng Peng, Jing Bian, Tong-Qi Yuan, Feng Xu, Run-Cang Sun, *Molecules*, **14**, 3551 (2009).
- 21) J. Edwards, < *Artifact Analysis using FT-NIR techniques* >, Edwards Analytical, January (2003).
www.pcn.org/Technical%20Notes%20-%20Artifact%...
- 22) I. V. Skorniyakov, V. P. Komar, *Journal of Applied Spectroscopy*, **Vol. 65, No. 6**, (1998).
- 23) D. A. Skoog, F. J. Holler, T. A. Nieman, < *Principles of Instrumental Analysis* >, Books/Cole, USA (1998).
- 24) < *MCI Instrumentation: Supporting Smithsonian Science* >, www.si.edu/.../about_mci/facilities/index.html, (2009).
- 25) -a) G. Splendore, E. V. Benvenuti, Y. V. Kholin, Y. Gushikem, *J. Braz. Chem. Soc.*, **Vol.16, No.2**, Mar./Apr. (2005).
-b) T. J. Baker, L. R. Schroeder, D. C. Johnson, < *Formation of Methylol Cellulose and its Dissolution in Polar Aprotic Solvents* >, The Institute of Paper Chemistry, Appleton, Wisconsin Ipc Technical Paper Series, Number 96, MAY (1980).

- 26) a)- M.L.Carvalho, M. Manso, S. Pessanha, A. Guilherme, A. Cavaco, G. Picado, < *Non-destructive Elemental characterization in Art and Cultural Heritage Research* >, in “Innovative Materials and Technologies for the Conservation of Paper of Historical, Artistic and Archaeological Value”, Chapter-B.6. Editors, D. Acierno, E. Martuscelli, E. Pedemonte, E. Princi, CAMPEC, Napoli (2007).
- b)- S. Bruni, S. Caglio, V. Guglielmi, G. Poldi, *Appl. Phys. Materials Science & Processing Applied Physics A*, DOI: 10.1007/s00339-008-4454-x, (2008).
- c)- A. Galli, G. Poldi, M. Martini, C. Montanari, E. Sibilìa, *Appl. Phys. A*, **83**, 675 (2006).
- 27) A. A. Parker, < *Solid State NMR of Polymers: A Review of Molecular Motions and Morphology* >, Consulting & Product Development , Web Address: <http://aaparkerconsulting.home.att.net> , (2004).
- 28) C. S. Yannoni, *Acc. Chem. Res.*, **15**, 201 (1982).
- 29) J.Schaefer, E. O. Stejskal, R. Buchdahl, *Macromolecules*, **8**, 291 (1975).
- 30) Schaefer, J., Stejskal, E. O., Buchdahl, R., *Macromolecules*, , **10**, 384 (1977)
- 31) S. M. Reutzel-Edens, J. K. Bush, < *Solid-State NMR Spectroscopy of Small Molecules: From NMR Crystallography to the Characterization of Solid Oral Dosage Forms* >, Lilly Research Laboratories, Eli Lilly and Company, americanpharmaceuticalreview.com/ViewArticle,.© Russell Publishing (2008).
- 32) F. Rémillard, < *Identification of Plastics and Elastomers Miniaturized Tests* >, Centre De Conservation Du Québec, pdf, (2007).
- 33) < *Assessment Guidelines* >, Australian network for information on cellulose acetate ANICA, National Library of Australia, also available as Word version, www.nla.gov.au/anica/Guide_pg11.ht, May (2001).

SECTION-2

SEVENTH-CHAPTER

PLASTICS BASED ON NATURAL PRE-FORMED POLYMERS: PLASTICS FROM CHEMICAL TRANSFORMATION OF CELLULOSE

CELLULOSE ACETATE: INHERENT AND EXTERNAL FACTORS OF DEGRADATION AND RELATED CHEMICAL MECHANISMS

As any other plastic material the degradation of cellulose acetate (CA) may originate from the combination of several inherent or external factors which include:

- Constitution (molecular mass and degree of acetylation);
- Composition (impurities from cellulose raw material, free acetic/sulphuric acid residues, type of additives and their content);
- Glass transition temperature, degree of crystallinity and melting or decomposition temperatures;
- Modality of processing;
- Storage conditions and contact with chemical agents in use;
- Exposition to light, heat, oxygen, moisture, ozone, or other atmospheric contaminants and biological attack;
- Plasticisers loss [1,2,3,4,5].

Some of the most common symptoms of degradation of cellulose nitrate and cellulose acetate are compared in table 1 [1].

Hydrolysis and oxidation are the two prominent chemical processes involved in the degradation of cellulose acetate.

The reaction of acetylation of CA, according to the scheme depicted in figure 1, is reversible. As already reported, it is accomplished by treating cellulose with a mixture of acetic acid and acetic anhydride in presence of sulphuric acid acting as a catalyst and as a dehydrating agent.

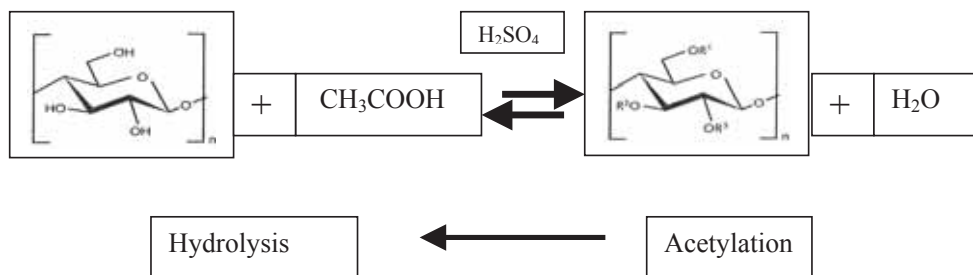


FIGURE 1: The reaction of acetylation of cellulose is a reversible process (see text).
R is for CH₃CO- group.

TABLE 1: A comparison between the deterioration characteristics of cellulose nitrate and cellulose acetate [1].

Symptom	Nitrate	Acetate
Yellow/amber base	Common	Rare
Brittle base	Yes	Yes
Base shrinkage	Yes	Yes
Warping	Yes	Yes
Vinegar smell		Yes
Rancid butter smell		Yes
Sickly sweet smell	Yes	
Choking, chemical smell	Yes	
Blue or pink colours	Rare	Common
Soft, sticky emulsion	Common	Rare
Syrupy emulsion	Yes	
Buckled emulsion or backing layer		Yes
Crystals under gelatine		Yes
Bubbles	Yes	Yes - liquid filled
White circular plugs of crystals		Yes
Image relief	Yes	
Mirroring with purple, green, blue or bronze interference colours	Yes	

In the course of the process the water is removed from the mixture due to its strong affinity with concentrated H_2SO_4 , consequently the equilibrium is shifted towards the right hand.

It is well known that to avoid shrinkage a certain amount of water ($\approx 6\%$) is usually contained in CA plastics, and this creates favourable conditions for hydrolysis. This means that in the above described scheme the reaction is reversed and the equilibrium slowly shifted to left (*hydrolysis process*). The rate of the hydrolysis increases especially when the CA samples are exposed to elevated values of relative humidity and temperature as well as to the presence of acids.

The molecules of acetic acid released have the capability of catalysing further the de-acetylation: *the reaction becomes autocatalytic* [1].

The scheme of the partial hydrolysis of cellulose triacetate, with a value of the degree of substitution (DS), the number of acetyl groups per glucose unit, between 2.9-3.0, to cellulose diacetate ($DS \approx 2.4$) is shown in figure 2.

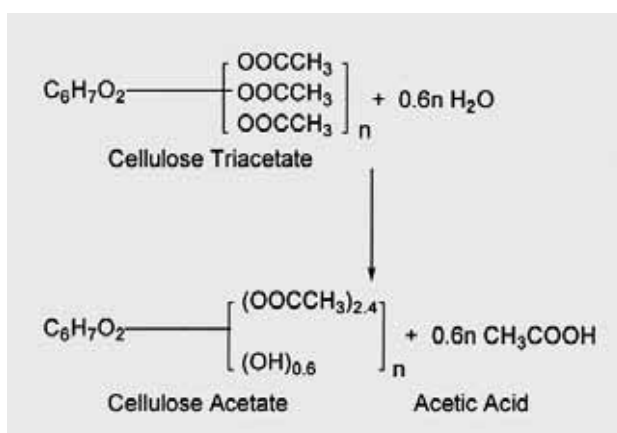


FIGURE 2: The reaction of partial hydrolysis of cellulose triacetate to diacetate [5].

As represented in figure 2, following hydrolysis, side groups are removed from the cellulose polymer backbone and free acetic acid molecules are produced (de-acetylation reaction). The molecules of acetic acids, released inside the plastic, gradually diffuse towards the surface, and then escape to the environment giving rise to characteristic vinegary smell (*vinegar syndrome*).

From figure 3, where it is schematically represented the variation of the acidity level versus time in CA samples undergoing hydrolysis, it can be observed that the curve shows first a slow rate trend (induction period) followed by an abrupt increasing change in the rate of the reaction at ≈ 0.5 free acidity value (auto catalytic phase).

It is generally assumed that during the first slow phase the reaction is governed essentially by temperature and relative humidity, while after the auto catalytic point the hydrolysis is almost independent by heat and humidity. According to literature data the CA samples presenting a clear vinegar syndrome should be considered to be already in a state of advanced degradation [1].

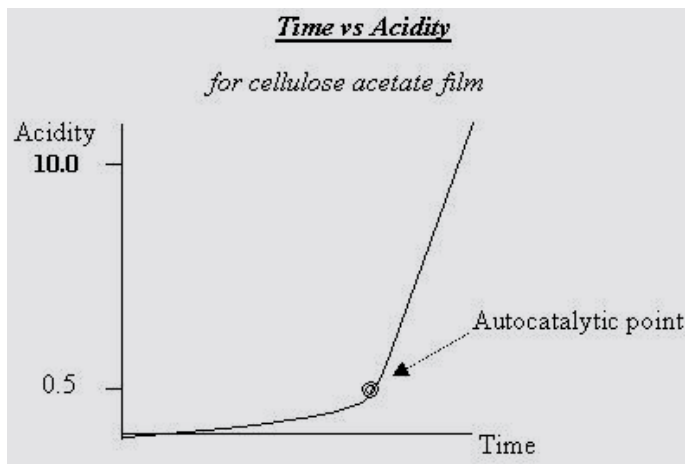


FIGURE 3: Acidity versus time in a sample of cellulose acetate undergoing hydrolysis (see text for explanation) [1].

The reaction of hydrolysis favours hydrolytic or oxidative scission of the glycoside linkages present along the backbone of cellulose macromolecules. Because of such processes plasticisers are forced to migrate towards the surface of CA samples. The loss of plasticisers gives rise to shrinkage effects, consequently the material results to be less resistant to external mechanical stresses.

Concerning this last point it must be furthermore pointed out that CA plastics contain \approx 20-40% (w/w) of plasticizers (triphenyl or tributylphosphate, dimethylglycol or dibutylphthalate, etc.) added to increase flexibility. Some of them act also as flame-retardants. As the CA ages, the plasticizers may migrate to the surface, and such a process may result in oily or sticky surfaces.

Moreover it has been observed that

< uneven loss of plasticiser from cellulose acetate plastic is responsible for distortion and is quite common with objects made from this material. It is often, however, a sign that the cellulose acetate is also chemically deteriorating; the plasticiser becomes less compatible with the degrading polymer and migrates to the surface > (see figure 4) [4].

It must be pointed out that some plasticisers may themselves undergo hydrolysis. For example the triphenylphosphate esters are catalytically decomposed by acetic acid giving rise to the formation of non-volatile acids that remain in the plastic mass of CA.

The migration of plasticisers towards the surface is clearly documented by figure 5 where

< needle shaped crystals of triphenylphosphate (see enlargement lower left) are growing between the gelatine and the cellulose acetate base of this microfilm roll. The air in the metal can smelled strongly of acetic acid. The phosphate ester plasticiser is so poorly compatible with the regenerating cellulose that it diffuses to the surface and crystallises just below the gelatine layer > [6].



FIGURE 4: Object in cellulose acetate with evidence of distortion due to uneven migration of plasticisers [4].

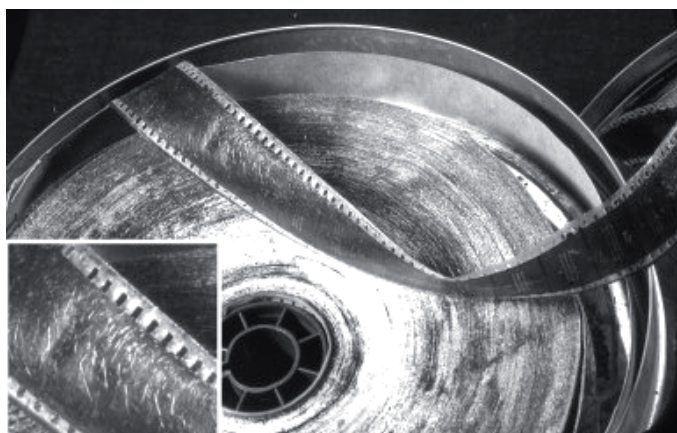


FIGURE 5: Needle shaped crystals of triphenylphosphate (see enlargement lower left) formed after migration on the surface caused by the degradation of the base film made in cellulose acetate (see text) [6].

A clear evidence of shrinkage effect in a cellulose acetate bangle, due to loss of plasticiser, is documented in figure 6 [7].

Derham, and others by using NMR techniques were able to demonstrate that the hydrolysis of CA does not occur randomly but it seems to start preferentially on the C-2 carbon atom in the glucose ring and then follows the de-acetylation on C-6 and finally on C-3 (see figure 7) [8,2].



FIGURE 6: shrinkage effects (see whitened regions) observed in a cellulose acetate bangle due to plasticiser loss [7].

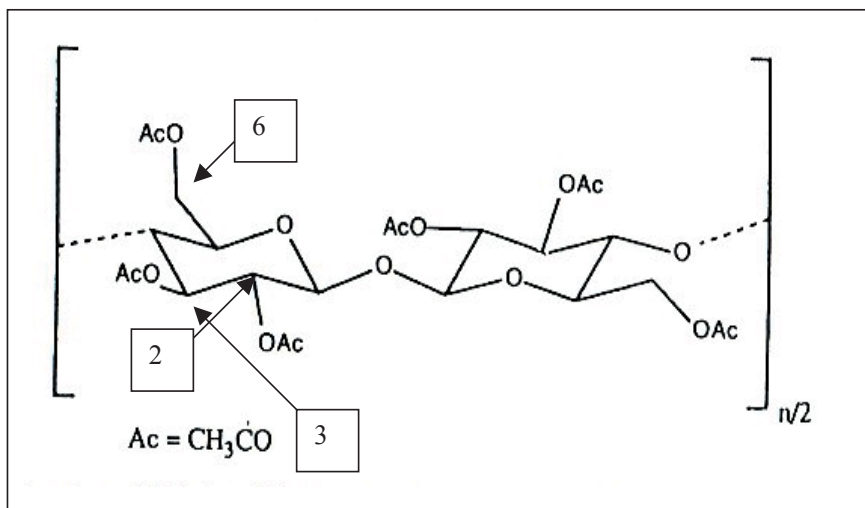


FIGURE 7: Structure of cellulose triacetate showing arrangement of cellulose sub-units. The arrow indicates the C-2 atoms in the glucose ring where preferentially the hydrolysis starts (see text) [2,8].

Cellulose acetate samples may also suffer degradation due to oxidation induced by chemical oxidizing agents (O₂, Cl₂, etc.,). The reactions of oxidation determine essentially scission of CA macromolecules, thus producing reduction both in molecular weight as well as in mechanical strength of the CA plastic based material.

To assess the state of conservation of a CA-made artefact it is quite often necessary to have information about the entity of the hydrolysis as well as of oxidation of polymer base.

< Hydrolysis can be detected by determining the degree of polymer acetylation, whereas oxidation can be detected by changes in polymer molecular weight as measured directly, for example by the intrinsic viscosity measurement, and/or indirectly by determining polymer tensile strength > [9].

Hereafter some of the most common procedures followed for assessing hydrolysis or oxidation are briefly described.

--- Hydrolysis degree through determination of the degree of acetylation

The entity of hydrolysis is usually detected by determining the degree of cellulose acetylation.

In reference [9] the below method (destructive in nature) was suggested.

< A known amount of ...sample (0.7 g) was first added to 70 ml of acetone in an Erlenmeyer flask and was continuously stirred using a magnetic stirrer for 1 hour, followed by adding 5 ml of methanol. After 30 minutes of additional stirring, 1N NaOH was added in excess (15 ml), to the highly swollen (not completely soluble)... sample solution and stirred for another hour. After adding hot (60°C) distilled water for washing down the sides of the flask and continuous stirring for another 10 minutes, the unreacted excess amount of NaOH was titrated against standard sulphuric acid (0.5 N) using phenolphthalein indicator.

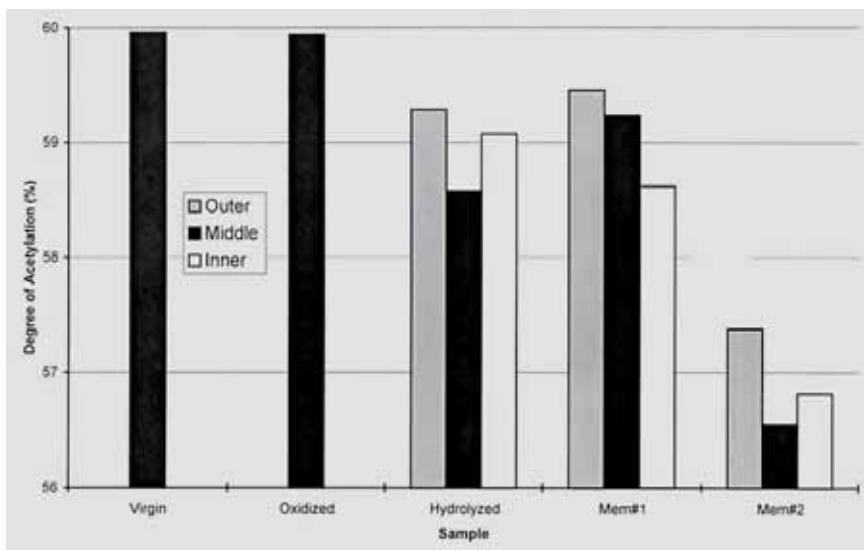


FIGURE 8: Degree of acetylation of various cellulose acetate samples drawn from different types of membranes (see text) [9].

When the pink color disappeared completely, an excess (0.2 - 0.3ml) of sulphuric acid was added and re-titrated with 0.1 N NaOH. For each sample, a duplicate was also carried out as well as two blank analyses. The acetylation degree was then calculated as the percentage weight of combined acetic acid formed to the total weight of ...polymer during hydrolysis by the excess NaOH >[9].

The efficiency of the test above described emerges from the type of results summarized through the histograms in figure 8 where the degree of acetylation was quantified in samples of CA having different history and origin [9]. In particular the tested samples were drawn from CA membranes. Some of them, before analysis underwent oxidation, others hydrolysis, and the remaining refer to samples taken from different commercial membrane which were in use, under different conditions, for ≈ 5 years (Mem #1) and for ≈ 2 years (Mem #2).

From the diagrams shown in figure 8 it comes out how the hydrolysed samples are characterized by a lower degree of acetyl content than that of the virgin or the oxidized membranes, where no hydrolysis is believed to occur. The sample referring to the Mem #2 commercial membrane exhibits a significant loss in degree of acetylation [9].

--- Oxidation assessment through tensile mechanical tests

Measurements of tensile strength (TS) and of the percentage elongation at break (EB%) are suitable to have information about the degree of oxidation being such quantities very sensitive to molecular weight of the mass polymers.

From the results shown in figure 9 and 10 the following interesting information are obtained:

-- A maximum and comparable value of TS and EB% are observed in the case of virgin, and the only hydrolysed samples.

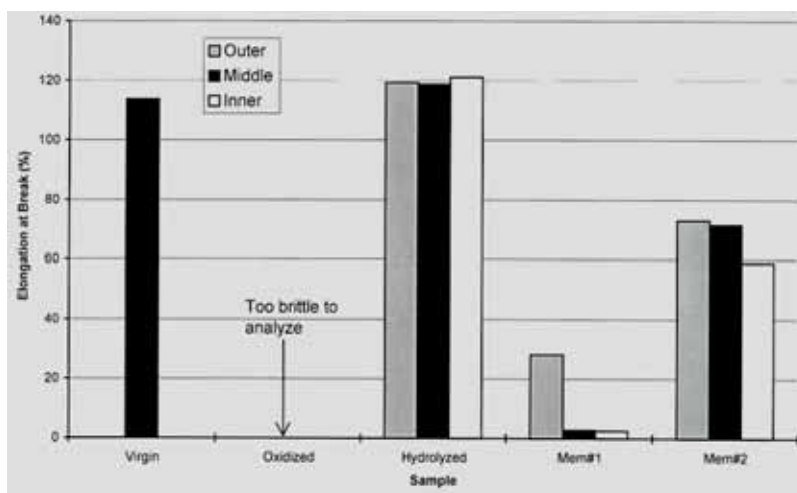


FIGURE 9: Percentage elongation at break for various CA samples (see text) [9].

-- The case of the artificial oxidized samples, due to their brittleness, TS and EB% could not be measured.

-- Mem #1 and Mem #2 exhibit lower values of TS and EB% in comparison to those of virgin and hydrolysed samples. This indicates that both samples have undergone oxidation during their usage [9].

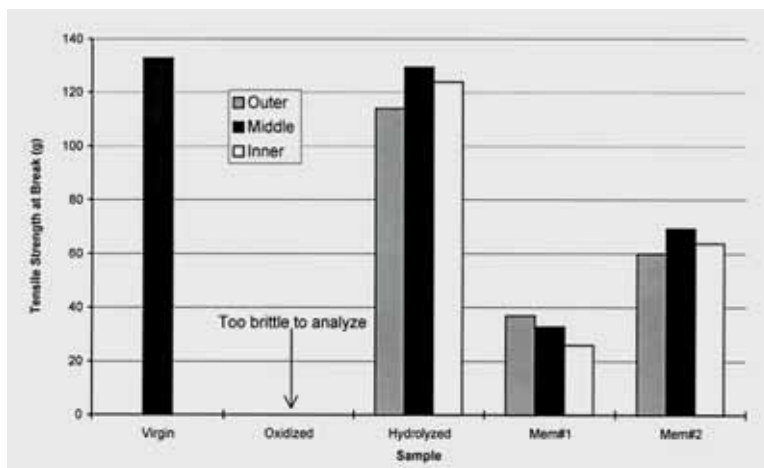


FIGURE 10: Tensile strength at break of different cellulose acetate samples (see text) [9]

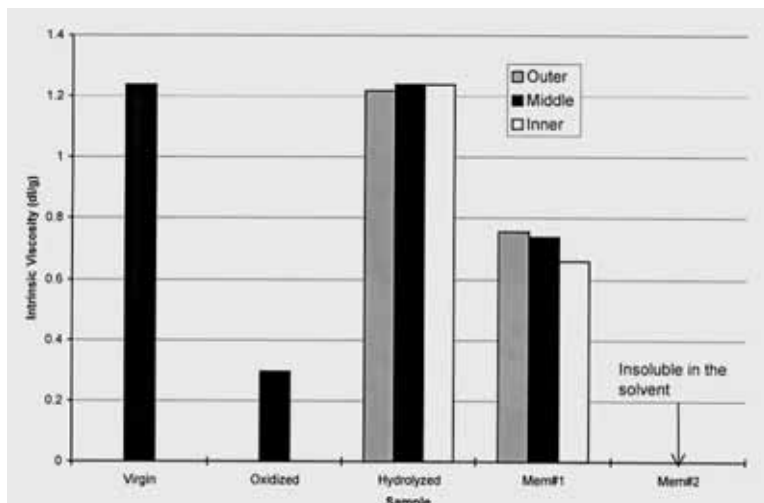


FIGURE 11: Intrinsic viscosity of various samples of cellulose acetate (see text) [9].

--- Oxidation assessment through Intrinsic viscosity measurements

As can be seen from the data reported in figure 11 artificial oxidized samples had the lowest value (0.30 dl/g) of intrinsic viscosity. On the contrary virgin and hydrolysed samples result to have the maximum value of intrinsic viscosity (≈ 1.24 dl/g). This behaviour is indicative of the fact that in such materials almost no oxidation occurs. The Mem #1 sample presents a significant reduction in intrinsic viscosity (0.72 dl/g) attributable to polymer chain scission caused by oxidation processes. Thus it can be affirmed that intrinsic viscosity measurements supports the result obtained by tensile tests [9].

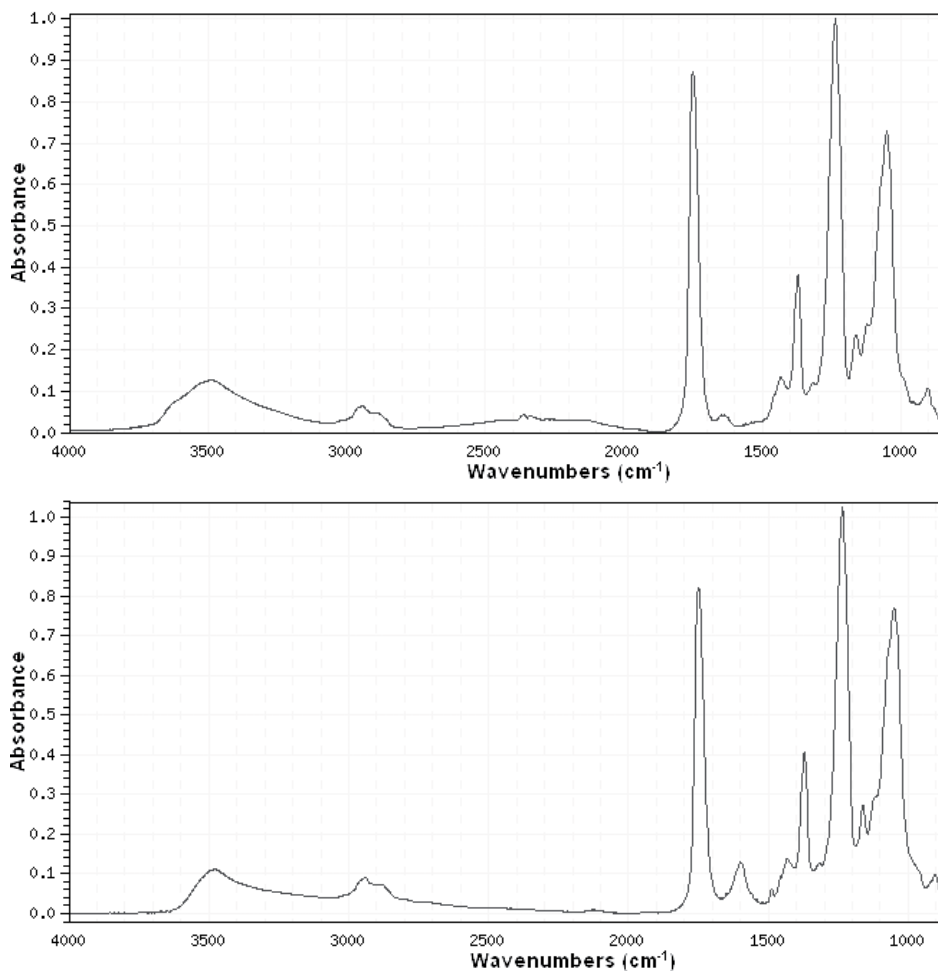


FIGURE 12: Top, FTIR spectrum of virgin cellulose acetate (39.8% acetate).
Bottom, FTIR spectrum of cellulose acetate (39.8% acetate) natural aged for 63.5 years [10].

From the cited study it comes out how measurements of the degree of acetylation, tensile properties and intrinsic viscosity can be very effective in establishing the type of degradation processes (hydrolysis or oxidation) active in CA samples.

Oxidation processes occurring in CA samples may be also evidenced by comparing their FTIR spectra with those of un-aged samples (see figure 12) [10]. As matter of fact absorbance bands typical of products of oxidation are clearly present on the FTIR spectrum of aged materials especially in the region of wave number between 1200-1800 cm^{-1} [10].

Biodeterioration of cellulose acetate

In general, according to H. J. Hueck, < *biodeterioration has been defined as "any undesirable change in the properties of a material caused by the vital activities of organisms"* > [11].

It is well known that natural cellulose materials (vegetable fibres as cotton, flax, jute, hemp, etc.) are prone to be degraded by cellulolytic fungi which have the capability to produce cellulose-digesting enzymes named as cellulases.

As exemplified in figure 13, the spores of specific microfungi present in the environment under favourable conditions of temperature and humidity may settle and grow on cellulose substrates. Some of those organisms by producing pigments may cause discolouration and staining of the substrate [11].

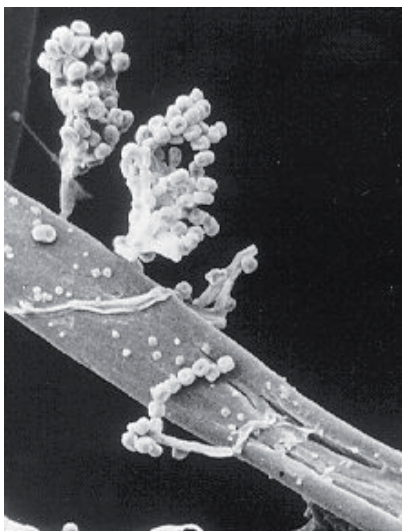


FIGURE 13: Electron micrograph showing the settling and growth of the spores of specific microfungi present in the environment on cellulose substrates [11].

The cellulases enzymes, in presence of water molecules give rise to a reaction that leads to the cleavage of the "glycosidic" bonds present along the backbone of the cellulose chains (see scheme of the reaction in figure 14) [11]. In the case of pure cellulose material *< the insoluble polymer is converted into soluble sugars which can then be metabolized inside the bacterial or fungal cells >*. [11].

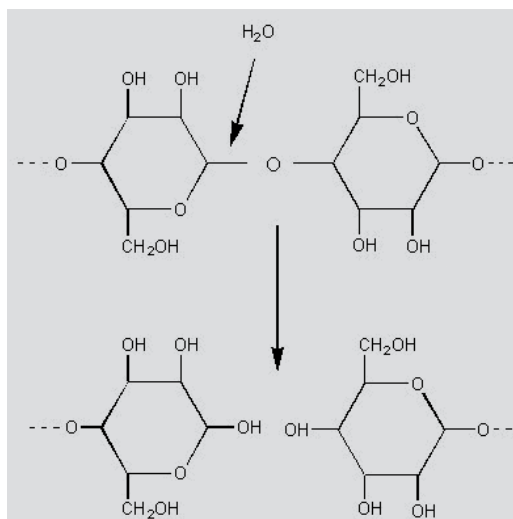


FIGURE 14: Scheme showing how cellulases enzymes, in presence of water give rise to the cleavage of the "glycosidic" bonds present along the backbone of the cellulose chains [11].

From literature data it comes out that the biodegradability of CA strongly depends on the value of acetylation degree DS. As matter of fact it was found that the rate of biodegradation decreases with increasing DS, the rate-determining step being the de-acetylation reaction and the presence of acids acting as catalysts [12].

The biodegradability of CA results to be dependent upon the type and content of acid additives. It was demonstrated by Yamashita Yoichiro and Endo Takeshi that *< the biodegradation rate of the CA films containing polyphosphoric acid, phosphoric acid, and p-toluenesulfonic acid increased compared to that of the no additive CA film. CA films containing mandelic acid and maleic acid showed a small tendency to increase. Conversely, CA films containing adipic acid did not affect the biodegradability of CA >* [13]. Moreover it was found that *< The acid-containing CA film, which showed an accelerated biodegradation rate, was chemically deacetylated by contact with water in the environment and was consequently converted to a lower degree of acetyl group substitution matter that had higher biodegradability >* [13].

Bacteria capable of assimilating cellulose acetate, as *Rhizobium meliloti* and *Alcaligenes xylosoxydans* were isolated from soil on a medium containing cellulose acetate as a carbon source [14].

Samples of CA melt compounded with two compatible different plasticizers, belonging to the family of citric acid esters: triethyl citrate and acetyl triethyl citrate, besides the reduction of the tensile modulus and the increase of the elongation showed a dramatically increase of the biodegradation rate with plasticizer content [15].

The effects of UV, light, moisture and pollutants (including solvents) on cellulose plastics (see an another example of application in figure 15), are summarized in table 2 [16].

TABLE 2: The effects of UV, light, moisture and pollutants (including solvents) on cellulose acetate plastics [16].

Plastic	UV radiation and excess light: photolysis, photo oxidation	Moisture (high relative humidity) and moisture fluctuations: hydrolysis, swell/shrink	Pollutants: solvents dissolution, environmental stress cracking	Danger to neighbors: stains, corrosion, stickiness, gases
cellulose acetate	yellowed brittle	hydrolysis produces acetic acid, oily plasticizer liquids	dissolved, swelled	acetic acid gas, oily plasticizer and degradation products on surface



FIGURE 15: Plastic cards made in cellulose acetate.
< They have been long known as the best plastic cards available and used around the world in casinos > [17].

REFERENCES

- 1) Australian network for information on Cellulose Acetate (ANICA), National Library of Australia, Appendix 4: Deterioration Pathway of Cellulose Acetate, and Guide lines. Degradation of Cellulose Acetate, website: www.nla.gov.au/anica/Guide_pg11.html, (2009).
- 2) Y. Shashoua, < *Conservation of Plastics* >, Elsevier, London (2008).
- 3) cameo.mfa.org/browse/fullrecord.asp?name=Cell, (2009).
- 4) www.plastiquarian.com/deterio.htm, (2009).
- 5) PERP-Program-New Report Alert, Nexant Cem. Systems, Acetic anhydride /cellulose acetate (03/04S1), June (2004).
- 6) T. Padfield < *The Preservation Index and the Time Weighted Preservation Index* >, Image Permanence Institute, www.conservationphysics.org/twpi/twpi_01.php, September (2004).
- 7) :C. Rogerson, < *Caring for Plastics in Collections: a brief overview* >, British library, file:///C:/Documents%20and%20Settings/Smed/Impostazioni%20locali/Temporary%20Internet%20Files/Content.IE5/S36T276B/plastics-rogerson%5B1%5D.ppt#256,1, (2009).
- 8) M. Derham, and Others, post print of < *Polymers in Conservation Conference* >, pp. 125-137, Royal Society of Chemistry, Manchester,17-19, July (1991).
- 9) A. Mohammed Farooque, Ahamed Al-Amoudi, K. Numata, < *Desalination* >, **123**, 165, (1999)
- 10) IRUG-DATA-BASE, Infrared and Raman Users group, Web-site, (2009).
- 11) P. F Hamlyn, < *Textiles* >, **19**, 46 (1990) and < *Talking rot...and mildew* >, NWFG Newsletter issue of December (1998). <http://fungus.org.uk/nwfg/rot.htm>, (2009).
- 12) Yamashita Yoichiro, Endo Takeshi, < *Nippon Kagakkai Koen Yokoshu* >, **81**, 361 (2002)
- 13) Yamashita Yoichiro, Endo Takeshi, *Journal of applied polymer science*, **98**, n^o1, 466 (2005).
- 14) Sakai Kiyofumi, Inoue Koichi, Sugawara, Kunio, Oe Tatsuiko, Tominaga Yoshio, *Science and Industry*, **73**, 131 (1999).
- 15) Vatsal P. Ghiya, Vipul Dave Richard, A. Gross, Stephen P. Mccarthy, *Journal of Macromolecular Science, Part A*, **33**, 627, Issue, May (1996).
- 16) R. Scott Williams, Waac- Newsletter, **24**, Number 1, January (2002).
- 17) cgi.ebay.com/KEM-Arrow-Plastic-Playing-Cards-. (2009).

SECTION-2

EIGHT-CHAPTER

PLASTICS BASED ON NATURAL PRE-FORMED POLYMERS: PLASTICS FROM CHEMICAL TRANSFORMATION OF CELLULOSE

CELLULOSE ACETATE: GUIDELINES FOR CONSERVATION, PRESERVATION AND STORAGE OF RELATED ARTEFACTS

Cellulose acetate (CA) artefacts are generally obtained from the processing of two commercial grades with different degrees of substitution. Cellulose triacetate (CTA) is most used for making sheets like photographic film base and fibers, while tri-dimensional shaped objects and thicker sheets are usually manufactured by utilizing cellulose diacetate (CDA).

It is widely recognized that cellulose acetate (CA) plastics, including cellulose triacetate (CTA) films, suffer deep degradation processes due to the impact of either intrinsic factors (e. g., composition, plasticisers, additives and molecular characteristics of base polymer) or external factors (e. g., climate and storage conditions). Thus great attention should be given to the problem of the conservation and safer storage of collections of artefacts in CA, and this for the benefit of the preservation of relevant witnesses of our history.

To extend the life time of artefacts in CA extrinsic factors should be kept under control. This can be fulfilled following two basic preservation strategies.

The first consists in reducing the rate of chemical degradation by controlling temperature and relative humidity. The second forecasts the removal from the storage place of the by products of the CA intrinsic decay (i. e. acetic acid). Of course the latter becomes relevant once the vinegar syndrome is detected [1,2,3].

When some artefacts, manufactured in CA, part of a collection, present a vinegar syndrome then specific actions should be taken to minimize/avoid the risk of contamination of the non-degraded objects due to the by products arising from decaying materials.

To reduce the concentration of acidic vapours in the storage environment two procedures may be followed. The first is based on the removal of the degradation by-products from the storage space. This can be fulfilled by:

- using activated charcoal and molecular sieves filters;
- Installing filtration systems;
- Using alkaline compounds [1].

The second procedure forecasts the segregation of the decaying artefacts in individual sealed enclosures (with adsorbents (e.g. molecular sieves) and scavenging systems able to reduce the moisture content as well as acidic degradation by-products) where a number of degrading objects may be accommodated [1]. The degrading effect of moisture on CTA samples presenting already vinegar syndrome is documented through the diagram shown in figure 1 [3].

Mass spectrometry (MS) is one of the most powerful analytical methods used for the structural identification of organic substances produced by degradation processes. Quite recently innovative

and more efficient MS based procedures have been developed at the Library of Congress, using Direct Analysis in Real Time (DART) mass spectrometry (figure 2) [2-a)]. The method is described as follows in reference [2-a]):

< an open-air ionisation method called direct analysis in real time (DART) can provide alternative methods of mass spectrometric analysis that can either eliminate or significantly reduce the need for destructive sampling. Ionisation in MS has traditionally been done within the vacuum system of the MS. However, in "open-air ionisation" using DART, the sample is placed in a stream of helium that contains ionised atmospheric gases (such as water vapour and oxygen), and the analytes in the

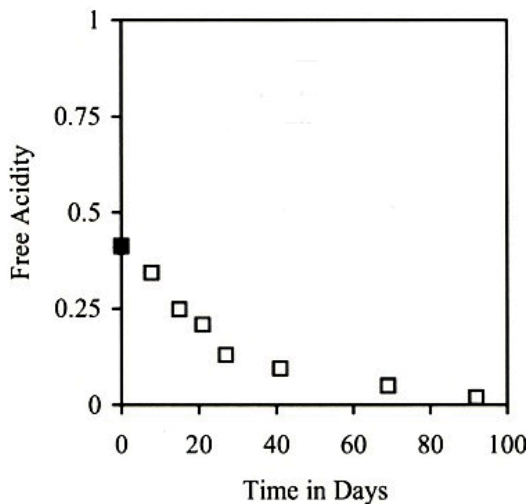


FIGURE 1: Free acidity of degraded film in cellulose triacetate versus exposure time at 21°C and 50% relative humidity [3].

sample are ionised in the open air of the laboratory environment. This means that organic compounds in the sample can be directly, and in real time, determined without time-consuming analytical protocols and thus with high sample throughput > [2-a)].

The possibility of determine, through DART method, the emission of volatile acetic acid from the decomposition of a cellulose acetate artefacts is documented by the spectrum shown in figure 3 [2-a)].

Dart procedure seems to be useful in the early recognising of CA samples with the symptoms of the vinegar syndrome, thus helping the curators in selecting those of the artefacts, part of a collections, that need to be separated from the non contaminated articles.

Following a cooperation between the “School of Conservation” (Copenhagen) and the “National Museum of Denmark”, a methodology based on “ direct measurements of acetic acid by SPME-Gc/Ms, and calculation of emission rates from emission chamber tests” was developed [2-b)].

The procedure, suitable to measure the emission of acetic acid from CA samples is described as follows in reference [2-b]):

< --- Sampling is performed using Solid Phase Micro Extraction (SPME) (Supelco). SPME consists of a fused silica fibre coated with a highly adsorbent polymer which is fitted in a syringe-like holder.....Sampling is performed by exposing the fiber to the air leaving the chamber.

--- Analysis of collected components was performed by gas chromatography/mass spectroscopy (GC/MS) using the injector to desorb the components collected > [2-a)].

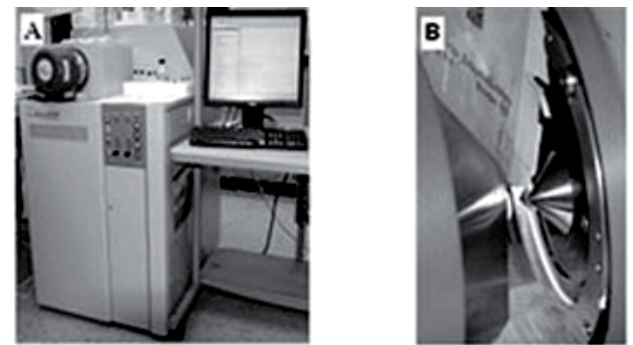


FIGURE 2: The open-air ionisation method (direct analysis in real time (DART) represents an alternative methods of mass spectrometric analysis that can either eliminate or significantly reduce the need for destructive sampling (see text) [2]. < The images are of (left) the JEOL JMS-AccuTOF mass spectrometer with the (blue) DART ion source installed;(right) a leaf from a book being non-destructively sampled and analysed in real time for volatile organic acids >[2-a)].

A cellulose acetate negative from the late 1950's, showing signs of degradation (the vinegar syndrome) was used to test the method.

First of all the emission of acetic acid vapours from the negative was determined. It resulted = $924 \mu\text{g}/\text{m}^3 \times 0.096 \text{ m}^3/\text{h} = 89 \mu\text{g}/\text{h}$. Then taking the surface area into account the area specific emission rate (ER) was quantified ($\text{ER} = 924 \mu\text{g}/\text{m}^3 \times 0.096 \text{ m}^3/\text{h} / 0.0190 \text{ m}^2 = 4685 \mu\text{g}/\text{m}^2\text{h}$).

The Mass spectrum of the acetic acid peak from an emission test performed on the above cited negative film in cellulose acetate is shown in figure 3-b). Together with the retention time from the GC chromatogram, the mass spectrum gives a high confidence in identification of chemical compounds [2-b)].

Moreover in order to point out the effectiveness of the method the chromatogram of acetic acid emission from a wooden drawer is shown in figure 3-c) [2-b)].

< The acetic acid emission was measured quantitatively but a formic acid peak is also visible > [2-b)].

The impact of enclosures designs and micro-environmental conditions in minimizing the deterioration of acetate base films was investigated by J. L. Bigourdan and others [3].

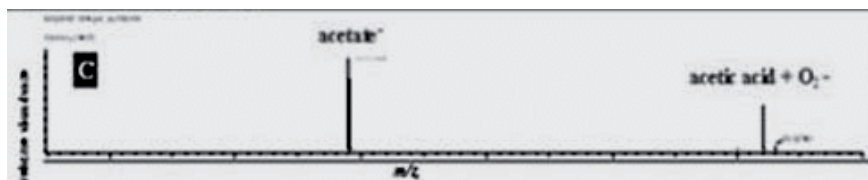


FIGURE 3-a): < The DART mass spectrum of acetic acid vapours in the housing microenvironment of a historic cellulose acetate motion picture film > [2-a)].

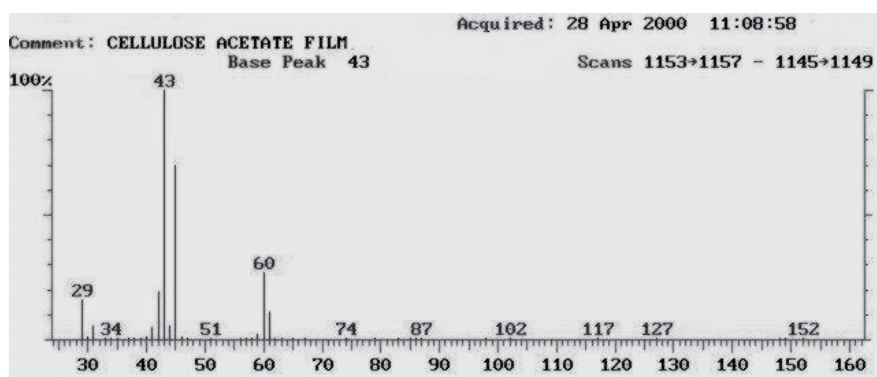


FIGURE 3-b): Mass spectrum of the acetic acid peak from an emission test performed on a negative film in cellulose acetate. Together with the retention time from the GC chromatogram, this mass spectrum gives a high confidence in identification of compounds [2-b)].

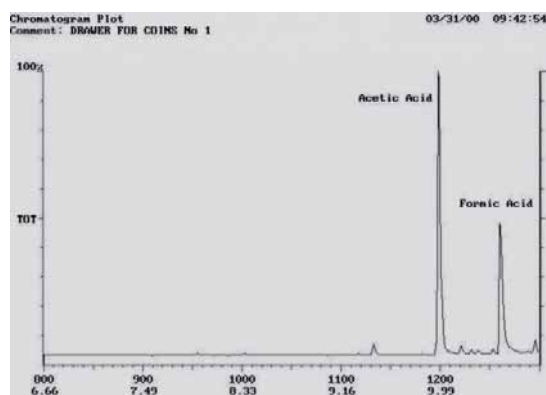


FIGURE 3-c): < Chromatogram of emission from the wooden drawer. The acetic acid emission was measured quantitatively but a formic acid peak is also visible > [2-b)] (see text).

The study was aimed at assessing effectiveness of various storage conditions in inhibiting the further decay of already artificially degraded CA films. <The film was brought to the onset of vinegar syndrome prior to the experimentation > [3].

The efficacy of enclosure types was investigated by using five different container systems, namely:

- I) Buffered cardboard box;
- ii) Untaped metal can;
- iii) Metal can without lid;
- iv) Untaped plastic box;
- v) Drilled plastic box [3].

To study the influence of the of micro-environments the samples were kept in sealed metal cans under the following different conditions:

- a) Moisture control by means of a dessicant (silica gel with colour indicator) or by moisture pre-conditioning.
- b) Acid removal by using a suitable acid-scavenger system (molecular sieves, based on zeolites able to absorb both moisture and acetic acid vapours);
- c) Acid neutralization by means of a cardboard buffered with CaCO_3 [3].

The chemical degradation of the CA samples was followed by measuring the film acidity assuming that the free acidity is one of the most sensitive indicator of decay [3].

Some of the results of the study performed by J. L. Bigourdan and others are hereafter summarized [3].

--- Effect of enclosure design

As shown by figure 4 the pre-degraded CTA films after 8 months incubation at 40°C and at 50% RH stored in buffered cardbox showed the lowest acidity level in comparison with the other type of configuration. Such a behaviour was attributed to the porosity of the cardboard that allows the escaping of vapours of acetic acid [3].

--- Effect of different micro-environments

From the diagrams shown in figure 5 it emerges that films stored in presence of molecular sieves (5%) and silica gel or conditioned to values of RH = 20% show an improved stability in comparison to the behaviour presented by film conditioned at 50% RH. It was remarked as molecular sieves are capable to absorb both acetic acid vapours and moisture.

The effect of the presence of two different prepared cardboard disks (Disk (A): cardboard with CaCO_3 and zeolites. Disk (B): cardboard with 5% alkaline reserve) on the stability of pre-degraded CTA film rolls, first conditioned at 21°C, 50% RH and then incubated at 40°C for 8 months in sealed metal cans was also investigated. From the diagrams reported in figure 6 it can be seen that the best performances are obtained by using molecular sieves (zeolites), while the presence of both types of cardboard determines a significant loss in stability (increase of film acidity, see data in figure 6). This result was accounted for by assuming that cardboard disks are capable to introduce extra moisture inside the sealed metal cans [3].

In the above study was also investigated the effect of different dessicants as well as their content on the free acidity level of pre-degraded CTA films, first conditioned at 21°C, 50% RH and then incubated at 35°C for 18 month. It was found that under the experimental conditions used the best results was obtained by using molecular sieves at 5% (see results in figure 7) [3].

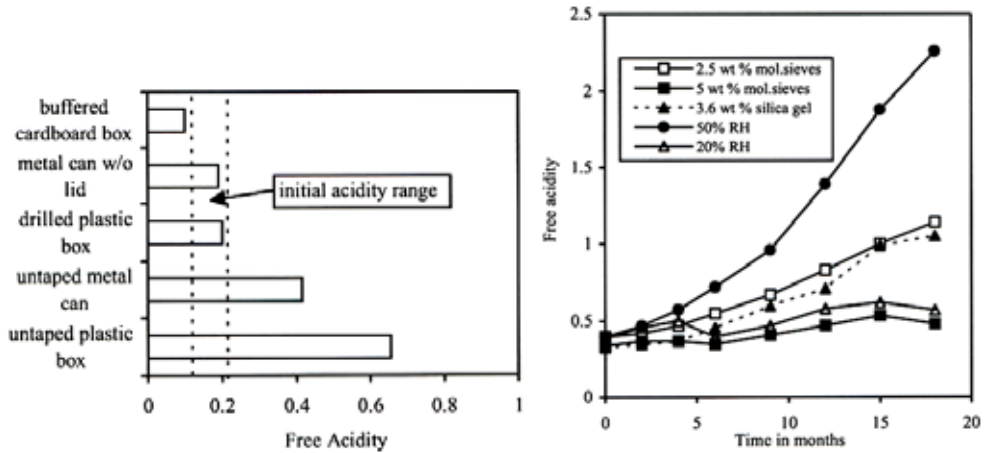


FIGURE 4- right: Effect of enclosure designs on the acidity of degraded CTA films after 8 months incubation at 40°C and at 50% RH [3].

FIGURE 5- left: Acidity of CTA films incubated at 35°C in various micro-environmental conditions [3].

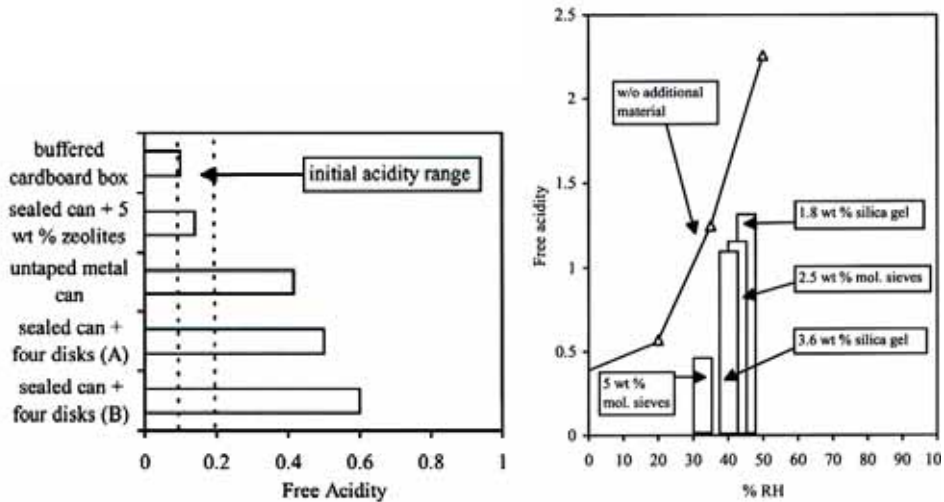


FIGURE 6, left: Effect of cardboard disks in sealed cans on the acidity of degraded CTA film after 8 months incubation at 40°C, 50% RH. Disk (A): cardboard with CaCO₃ and zeolites. Disk (B): cardboard with 5% alkaline reserve [3].

FIGURE 7, right: Acidity of CTA film rolls after 18 month incubation at 35°C in sealed cans with various desiccants [3].

From experiments performed on CTA films, pre conditioned at 35°C, 50% RH, stored in sealed cans at 21°C in various micro-environments for a period of 20 months, as shown by the data reported in table 1, it was observed that the samples stored under the micro-environmental conditions characterized by:

- Pre-conditioning at 21°C and 20% RH, without additional material,
 - The presence of 5% molecular sieves,
 - The presence of 3.6% of silica gel,
- exhibit the lowest and comparable increase in the values of the acidity level (0.02 - 0.03, 0.01 – 0.03 and 0.03 respectively, see table 1) [3].

J. L. Bigourdan and others, from their investigation, were able to draw the following concluding remarks:

- Micro-environments leading to reduce the moisture content in sealed containers (pre-conditioning the film to 21°C at 20% RH or adding dessicants as molecular sieves or silica gel) determine a certain degree of stability in the CTA films by retarding further degradation.
- The improvement observed in the case of molecular sieves or silica gel were ascribed to their capability in absorbing both moisture and acetic acid vapours.
- The acid-adsorption capability of 5% molecular sieves contributes in minimizing further deterioration of CTA films at 35°C. At 21°C, after 20 months of storage in sealed cans this benefit was comparable with that obtained lowering the value of RH to 20%.
- Molecular sieves have a minimal impact on lowering the acid content of CTA films showed already symptoms of degradation [3].

TABLE 1: Free acidity change (in ml NaOH 0.1M/g of film) of CTA roll films stored in sealed cans at 21°C in various micro-environments; acidity values were assessed in duplicate on three location in the roll [3].

micro-environmental alternatives	20 months
2.5 wt % molecular sieves	+ 0.09
	-
	+ 0.10
5 wt % molecular sieves	+ 0.01
	-
	+ 0.03
1.8 wt % silica gel	+ 0.12
	-
	+ 0.15
3.6 wt % silica gel	+ 0.03
	-
	+ 0.03
pre-conditioning to 21°C 50% RH	+ 0.29
	-
	+ 0.37
pre-conditioning to 21°C 35% RH	+ 0.16
	-
	+ 0.16
pre-conditioning to 21°C 20% RH	+ 0.02
	-
	+ 0.03

According to R. Scott Williams [4], to preserve from further degradation, artefacts in CA should be displayed and stored under ventilated conditions to remove harmful gaseous degradation by-products and to prevent damage to objects in the vicinity. In case of unventilated enclosures acetic acid scavengers should be used. Moreover CA objects should be never kept in enclosures with, or in proximity to acetic acid sensitive materials (i.e. metals, textiles, and paper; see example of damages induced in figure 8) [5,6]).

The best conservation procedure consists in adopting environmental conditions characterized by a low values of both RH and temperature. Low temperature is effective, in decreasing the rate of degradation reactions as well as in reducing the rate of plasticizer loss . CA artefacts badly deteriorated should be removed and separated from other objects of the rest of the collection [4, 7].

From above it emerges that the lifetime of CA artefacts may be prolonged essentially by adopting a suitable storage/display environment. Such an objective may be, to a great extent, fulfilled by suitably adjusting values of RH and of temperature. As matter of fact such a measure is the only effective in reducing the influence of the external factors that affects the stability of objects made in CA.

According to literature data the lowering of the storage temperature determines the reduction in the rate of any chemical reactions that may occur inside the film. In case of CA films it ha been demonstrated that a decrease in the storage temperature from 10 °C to -12 °C increases the life expectancy of the film by a factor of 100. It must be noted, however, that maintaining a cold store at low temperatures could be very expensive. For such a reason it is suggested to use, as compromise, storage temperatures, for a collections of CA artefacts between 2 °C to 16 °C [8].

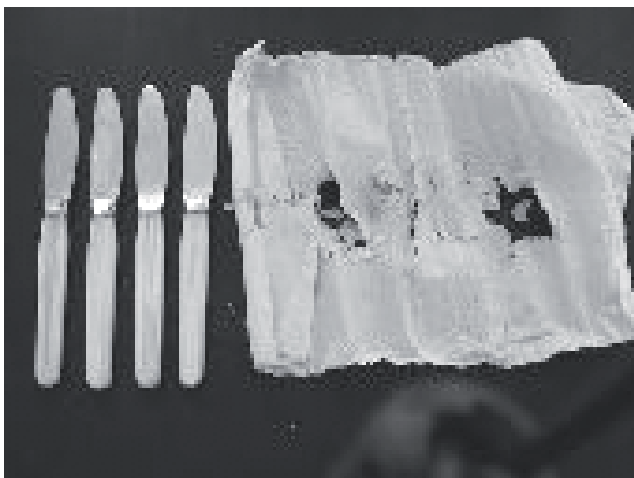
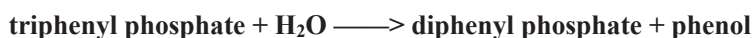


FIGURE 8, left: Acetic acid produced by the degrading cellulose acetate handles of the knives has deeply damaged the wrapping tissue (see text) [5,6].

The control of RH is also of great relevance in preserving CA artefacts. The reasons for this are:

--- The presence of water favours the deacetylation reaction of CA;

--- Water, as shown by the scheme below depicted, is capable to react with some of degradation products of plasticisers (i.e. diphenyl phosphate) giving rise to the formation of strong acids.



Moreover it must be also pointed out that *< as the polymer degrades, its affinity for water increases and degradation accelerates >* [8].

Concerning enclosures, where CA objects showing already symptoms of degradation (vinegar syndrome) may be suitably and safer stored, the following recommendations are reported in reference [8]:

--- Open or permeable enclosures may show positive effects only when the climatic parameters of macro-environment are under control.

< This is because they permit evaporation and diffusion of acetic acid, thereby slowing deterioration > [8].

--- The use of enclosures is especially encouraged when the macroclimatic humidity control is not available. In such a situation it is suggested to use enclosure systems, containing also adsorbents (silica gel or zeolites), suitably designed to create a beneficial microclimates *< to buffer and protect materials from fluctuations in temperature and relative humidity, and from condensation during warm-up, and/or to segregate deteriorated material >*[8] (see example in figure 9).

--- The materials which are the components of enclosures must be as much as possible chemically inert thus unable to release chemicals reacting with the constituents of the CA objects.



FIGURE 9: Systems of enclosures used to preserve collection of objects from further degradation while are displayed.

Two procedures (*FICA* and *CMI*) capable to preserve CA objects from the attack of moisture by sealing them in a vapour-proof enclosures are described in reference [8].

< The FICA system uses enclosures that have a very low permeability to moisture vapour, consisting of fused layers of polyethylene, aluminium, plastic, and sometimes paper. The enclosures are heat-sealed, and a moisture preconditioning procedure is generally recommended >. The main disadvantages of the system consist on the difficulty *< to monitor the condition of the material because the packaging is opaque, and preconditioning the material increases time out of storage >* [8].

The *CMI* system, an improvement of *FICA*, *< uses two 'zip-lock' low-density polyethylene (LDPE) bags, one inside the other, with a moisture buffer between the two (eliminating the need for preconditioning). A cobaltous chloride humidity indicator, which is visible though the outer PE bag, indicates when humidity levels are getting high >* [8]

The beneficial effects of adsorbents (essentially molecular sieves (i.e. Zeolites) and Silica gel) may be accounted for by considering the already discussed mechanism of internal induced de-acetylation [8].

Active ventilation in certain conditions seems to be effective in reducing the amount of acid available for the catalytic reaction [8].

It must to be pointed out however that removal of the acetic acid may produce shrinkage in the sample [8]).

It can be concluded that by suitably controlling the microclimate, that is the environment immediately surrounding a CA artefact, in a sealed showcase, storage cabinet or archive room it is possible to reduce the rate of further degradation processes thus prolonging the life span of the objects. To fulfill such an objective microclimate environmental systems should be designed and adopted capable to provide safe and accurate control of humidity, temperature and chemicals in museum display cases and storage rooms [9,10,11,12].

Creating and maintaining a microclimate in a showcase or storage cabinet where CA objects are kept for preservation may result to be *< easier, more accurate, and far more cost-effective than modifying the environment in an entire building, gallery, or room >* [9].

It is worthwhile to remind that cellulose acetate has been labelled as “*malignant*” due to the fact that following inherent deterioration processes reactive vapours of acetic acid, harmful for metals, papers, textiles or other plastics stored in their vicinity, are produced. Moreover, this damaging off gassing can’t be prevented or completely inhibited. For such a reason it is strongly suggested to isolate degrading CA artefacts (see example in figure 10) from other objects in museum collections [13].

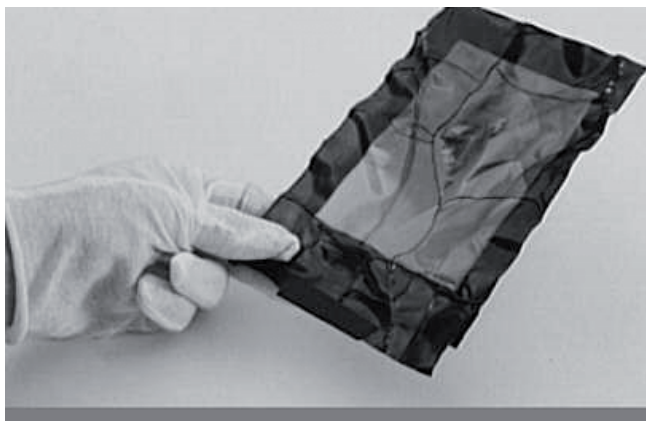


FIGURE 10: Safety film in cellulose acetate, following ageing, becomes embrittled and gives off vapours of acetic acid. Other signs of deterioration include shrinkage and warping. Plasticisers may also crystallize on the surface [14].

REFERENCES

- 1) Jean-Louis Bigourdan, *Vinegar Syndrome: An Action Plan*, Image Permanence Institute, Rochester Institute of Technology, http://www.imagepermanenceinstitute.org/shtml_sub/actionplan.pdf, (2009).
- 2) –a) < *Direct Analysis in Real Time (DART) Mass Spectrometry* >, *Chemical & Engineering News*, October 8, Cover, **Vol. 85**, Issue 41, pp 13-18, (2007).
<http://pubs.acs.org/cen/coverstory/85/8541aboutcover.html>
The Library of Congress >> Librarians, Archivists >> Preservation, October 7 (2009).
- .- b) Morten R. Svendsen, J. Glastrup,
< *Direct Measurements of Acetic Acid by Spme-Gc/Ms, and Calculation of Emission Rates from Emission Chamber Tests* >, IAQ 2000, Presentation 14, iaq.dk/iap/iaq2000/2000_14.htm, (2000).
- 3) Jean-Louis Bigourdan and Others, *Journal of Imaging Science and Technology*, **42**, 59 (1998).
- 4) R. Scott Williams, < *Care of Plastics: Malignant plastics* >, *waac Newsletter*, 24 N. 1, January (2002).
- 5) Y. Shashoua, Chr. Christensen, www.natmus.dk/sw9042.asp, (2009).
- 6) Y. Shashoua, < *Conservation of Plastics* >, Elsevier, London (2008).
- 7) Photograph Preservation, Behind-the-Scenes of PhillyHistory.org
www.phillyhistory.org/PhotoArchive/StaticCont..., (2009).
- 8) < *Storage of Cellulose Acetate Collections: A Preliminary Survey of Issues and Options* >, National Library of Australia, February, (2002). www.nla.gov.au/anica/Guide_pg11.html
- 9) www.microclimate.biz/, (2009).
- 10) National Film Preservation Foundation. *The Film Preservation Guide: The Basics for Archives, Libraries, and Museums*. San Francisco: National Film Preservation Foundation, (2004).
- 11) A.T. Ram, “Archival Preservation of Photographic Films-A Perspective.” *Polymer Degradation and Stability*, **29** no. 1, 3, (1990).
- 12) James M. Reilly, “Basic Strategy for Acetate Film Preservation.” *Microform and Imaging Review*, **31** no. 4, 117, (2002).
- 13) < *Materials Science* >, Smithsonian Institute, cell.acet.3445_file/problem-plastics-in-museum-collections-have-conservators-on-alert.htm, Posted on 12 August (2009).
- 14) < *Genthe Collection: Deterioration and Preservation of Negatives* >, The Library of Congress, Prints & Photographs Division, Prints & Photographs Online Catalog, February 16, (2005).
memory.loc.gov/pp/agchtml/agcdetne.html
- 15) A. Leggio, H. Berthon, C. Webb, < *A National Cellulose Acetate Search?* >, Preservation Services, National Library of Australia - presented to the First National Symposium, Book and Paper Group, AICCM, Canberra, March (2000).
www.nla.gov.au/nla/staffpaper/2000/webb3.html

CONCLUDING REMARKS

In the present volume the properties, the processing procedures, as well as the composition and formulation of the most important plastics belonging to the so-called “*Pre-Synthetic Era*” (i. e. plastics directly deriving from fully natural macromolecules (i.e. *Natural Polymers*) or obtained by chemically modified natural polymers, (i.e. *Artificial Polymers*) have been described assuming that, together with the knowledge of use functions developed, and storage and maintaining conditions, it was possible to explain the chemical/physical mechanisms involved in the main degradation processes (due to internal or external factors) of related artefacts valuable to be part of collections kept in dedicated museums.

The whole set of information attained allowed the critical evaluation of the up to date conservation procedures from one side and from the other the suggestions of innovative preservation and protection methodologies capable to suitably prolong the life span of this plastic objects.

It is believed that the issues presented and discussed may help in the identification of strategies, more supported by scientific studies and experiences, finalized at improving conservation and maintenance of plastics objects in museum collections by establishing better practices for displaying, cleaning and restoring such a valuable objects which are considered to be a witness of about the last two centuries of our history.

In a short coming volume the same set of elements taken into consideration in the present volume, but concerning plastics having as main component *Man Made Polymers*, that is polymers belonging to the so called *Synthesis Era* will be presented and discussed aiming at identify also for those materials the best practices suitable for their conservation, protection and maintenance.

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