

POLYURETHANE TYPES

The different types of polyurethane are defined depending on the different raw materials used in their production, and therefore depending on the structure of the segments of the polyurethane chain. That is why, and before referring to polyurethane types, it is necessary to briefly describe the main raw materials used in polyurethane production: diisocyanates, long-chain diols and chain extenders.

RAW MATERIALS

1. DIISOCYANATES

Diisocyanates used in polyurethane production are divided into two types:

1.1 AROMATIC DIISOCYANATES

1.2 ALIPHATIC DIISOCYANATES

1.1 AROMATIC DIISOCYANATES

a) DIPHENYLMETHANE DIISOCYANATE (MDI)

It was developed in the early 1960s. It is a white solid at room temperature that melts at 38 ° C. It is obtained from the condensation of aniline with formaldehyde to produce methylene dianiline (MDA), which is in turn reacted with phosgene to form MDI. Commercial MDI consists of over 98% 4,4'-MDI with small amounts of 2,4'-isomer.

b) TOLUENE DIISOCYANATE (TDI)

It was developed prior to the Second World War. The commercial product, a distilled colorless liquid, is a mixture of the 2,4- and 2,6-isomers. The major TDI product has a composition of 80:20 of the two isomers, but 65:35, 95:5 and pure 2,4-isomer are also available. It is obtained by nitration of toluene; hydrogenation of dinitrotoluene is then obtained to produce toluendiamine (TDA), which is in turn reacted with phosgene to form TDI. The freezing point of the commercial product (80:20 isomer mixture) is 14° C.

c) P-PHENYLENE DIISOCYANATE (PPDI) AND NAPHTHALENE DIISOCYANATE (NDI)

These are less usual aromatic diisocyanates.

1.2 ALIPHATIC DIISOCYANATES

a) HEXAMETHYLENE DIISOCYANATE (HDI)

This is the classical aliphatic diisocyanate, developed prior to the Second World War. It is a liquid at room temperature, with a freezing point of -55°C . The starting chemical for HDI is Hexamethylene diamine, the monomer for nylon-6,6, which is reacted with phosgene to form HDI.

b) ISOPHORONE DIISOCYANATE (IPDI)

It is based on Isophorone chemistry. Isophorone is reacted with HCN and afterwards the cyanoketone obtained is reduced by amination to form isophorone diamine (IPDA), which in turn is reacted with phosgene to form IPDI. It is a liquid at room temperature. Commercial IPDI is a mixture of cis and trans isomers with a 75:25 composition.

c) DICYCLOHEXYLMETHANE -4,4'-DIISOCYANATE (H_{12}MDI)

This is hydrogenated MDI. Methylene dianiline (MDA) is hydrogenated and afterwards, the obtained product is reacted with phosgene to form H_{12}MDI . It is a liquid at room temperature with a melting range of $19\text{-}23^{\circ}\text{C}$. The commercial product is a mixture of different isomers (trans,trans ; cis,trans and cis,cis with a close relation of 20:50:30).

d) META-TETRAMETHYLYLYLENE DIISOCYANATE (TMXDI) AND TRANS-CYCLOHEXANE DIISOCYANATE (CHDI)

These are less usual aliphatic diisocyanates.

2. LONG-CHAIN DIOLS

There are four main types of long-chain diols used in the production of polyurethanes. These are:

2.1 POLYESTERS

2.2 POLYCAPROLACTONES

2.3 POLYETHERS

2.4 POLYCARBONATES

2.1 POLYESTERS

These are low molecular weight polyesters made by the condensation reaction between glycols and dicarboxylic acid (generally adipic acid). As the esterification proceeds the water produced is removed from the reaction and finally, the elimination of glycol under reduced pressure results in polyester with the desired molecular weight.

Polybutanediol adipate is the most usual polyester in the polyurethane production. It is very crystalline and solid at room temperature with a melting point of about 50°C .

Polyethylene adipate and copolyesters with a mixture of different glycols are also used.

2.2 POLYCAPROLACTONES

These are a peculiar type of polyesters produced by the ring-opening polymerization of ϵ -caprolactone. They have a lower viscosity than the polyadipates of the same molecular weight, due to their narrower molecular weight distribution. They are similar to polybutanediol adipate in both crystallinity and melting point (about 45-50 °C).

They have an excellent temperature resistance, being more water resistant than polybutanediol adipate.

2.3 POLYETHERS

The main polyethers used in polyurethane production are:

a) Polytetramethylene ether glycol (PTMEG)

This is a waxy, low crystalline solid that melts near room temperature. It is produced by polymerization of tetrahydrofuran. Compared to polycaprolactones and adipate-polyesters, it has lower crystallinity, a lower melting point and lower viscosity. This is the most used polyether in TPUs production.

b) Polyoxypropylene-glycols (PPG)

These are liquid, amorphous polyethers produced by the polymerization of propylene oxide. They are mainly used in the production of polyurethane prepolymers and polyurethane emulsions.

c) Polyoxyethylene glycols (PEG)

These are from oily liquids to waxy, low crystalline solids depending on their molecular weight. They are produced by polymerization of ethylene oxide. They are soluble in water and are used for producing polyurethanes that need this characteristic.

2.4 POLYCARBONATES

These are white, crystalline solids produced by polycondensation reaction of diethyl or dimethylcarbonate with a diol, generally 1,6-hexanediol. Their melting point is in the range of 35-50°C, depending on their molecular weight.

3. CHAIN EXTENDERS

Any short-chain diol could be used as a chain extender, but 1,4-butanediol is the most frequently used in polyurethane production due to the optimum size of hard segments that it produces. It is a liquid with a melting point of 16°C and a boiling point of 230°C.

POLYURETHANE TYPES

Depending on the diisocyanate used in the production of polyurethane, they could be aromatic or aliphatic.

1. AROMATIC AND ALIPHATIC POLYURETHANES

The most important difference between both types is their resistance to sunlight. Exposed to an ultraviolet radiation in the presence of oxygen, such as an incidental solar radiation, aromatic polyurethanes suffer an ultraviolet initiated auto oxidation degradation, with a deepening color of the exposed polyurethane which changes from colorless to yellow and to amber and, on extensive exposures, even to a brown color, with loss of mechanical properties. This is due to the fact that the aromatic ring, under such conditions, is auto oxidized to a chromophore such as a quinone-imine structure.

Aliphatic diisocyanates cannot undergo such quinoid formation, yielding polyurethanes that show a superior stability to ultraviolet radiation and thus superior color stability and good mechanical property retention.

On the contrary aromatic polyurethanes have better thermal resistance (in the absence of oxygen) than aliphatic polyurethanes. This is an important point, as the urethane group is the least thermal resistant group in the polyurethane structure.

Thermooxidation resistance is mainly influenced by the type of long-chain diol, more than by the difference between aliphatic or aromatic diisocyanate.

2. POLYESTER, POLYCAPROLACTONE AND POLYETHER POLYURETHANES

These are different classes of polyurethanes, depending on the type of long-chain diol used in polyurethane production.

We will focus on thermoplastic polyurethanes to explain the influence of long-chain diol on the properties of polyurethanes.

We will also refer to polybutanediol adipate and polytetramethylene glycol (PTMG) when polyester and polyether long-chain diols are mentioned. The different types of long-chain diols provide polyurethanes with different characteristics in the following parameters:

a) HYDROLYSIS RESISTANCE

It is well known that ether groups have much better hydrolysis resistance than ester groups. The hydrolysis reaction of an ester group follows the three-centre mechanism and is catalyzed by both acid and bases; since a

free acid is liberated as a result of the hydrolysis of ester bonds, this reaction becomes autocatalytic. Therefore polyethers TPUs have much better hydrolysis resistance than polyester and polycaprolactone TPUs.

It is also well known that polycaprolactone TPUs have better hydrolysis resistance than polyester TPUs. This is due to the fact that the stability of the ester bonds increases with the length of the hydrocarbon a polar chain that separates the ester bonds; moreover, the TPU becomes then more hydrophobic, absorbs less water, and is thus less prone to hydrolysis. (Polycaprolactone has five $-CH_2-$ groups between two ester bonds whereas polyester has only four).

To sum it up, the hydrolysis resistance would be:

Polyether TPU >>> Polycaprolactone TPU > Polyester TPU

b) MICROBIAL STABILITY

Polyether TPUs have much better microbial resistance than polyester and polycaprolactone TPUs. In other words:

Polyether TPU >>> Polycaprolactone TPU = Polyester TPU

c) THERMOOXIDATIVE STABILITY

Oxidation usually starts with attacking the hydrocarbon chains to produce radicals, which in turn, develop several reactions until chain scission (a typical oxidation mechanism). The more the hydrocarbon chain has labile hydrogen atoms, the less the polymer has thermooxidative stability.

In ethers the hydrogen bonded to the carbon adjacent to the oxygen is particularly sensitive to oxidation, readily forming peroxides. By contrast, the ester bonds are those TPUs moieties most resistant to oxidation.

To sum it up, thermooxidative stability:

Polycaprolactone TPU = Polyester TPU >>> Polyether TPU

d) POLYURETHANE STRUCTURE

Hard segments have a high polarity, therefore the less polarity the long-chain diol has, the more phase separated the polyurethane is. Using long-chain diols of the same molecular weight, polyether TPU is more phase separated than polycaprolactone TPU and this is more phase-separated than polyester TPU.

This fact is responsible for the lowest T_g and the better flexibility at low temperatures for polyether-TPUs, while polyester TPUs have the highest T_g and the poorest flexibility at low temperatures.

By contrast, the size of hard segments is higher in polyether TPUs, showing higher crystallinity and higher melting point. Polycaprolactone-TPUs also have higher crystallinity than polyester TPUs and therefore a higher speed of recrystallization, being very suitable for injection molding. For the same

reason polycaprolactone TPUs show more adhesion onto substrates than polyester TPUs.

Polyether TPUs have poor mechanical properties in comparison with polycaprolactone and polyester TPUs; on the contrary they are more resilient than polyester and polycaprolactone TPUs.

To sum it up, the phase-separation in the polyurethane is:

Polyether TPU >>> Polycaprolactone TPU > Polyester TPU

e) OIL , GREASE AND SOLVENT RESISTANCE

By contrast with hydrolysis resistance, polyester TPUs have the best oil and grease resistance due to their higher polarity and polyether TPUs has the worst resistance.

Polyester TPU > Polycaprolactone TPU >>> Polyether TPU

A schematic summary would be the following:

Parameter	Polyester based TPUs	Polycaprolactone based TPUs	Polyether based TPUs
Hydrolysis resistance	--	-	++
Microbial stability	--	--	+
Adhesion strength	+	++	-
Thermooxidative resistance	+	+	-
Low temperature flexibility	o	+	++
Mechanical properties	++	++	+
Oil and grease resistance	++	+	-
Injectability (cycle time)	+	++	o

(++ excellent; + good ; o acceptable; - poor ; -- very poor)

2.1 COPOLYMER BASED POLYURETHANES

A peculiar type of polyurethanes is formed by those in which the long-chain diol has not a pure structure but a mixture of two structures copolymerized with special systems. These polyurethanes have thus properties of both structures, often showing synergistic effects.

An example of these is polyether-polycaprolactone copolymer TPUs, which have unique low temperature flexibility and hydrolysis properties combined with excellent mechanical properties and heat resistance.

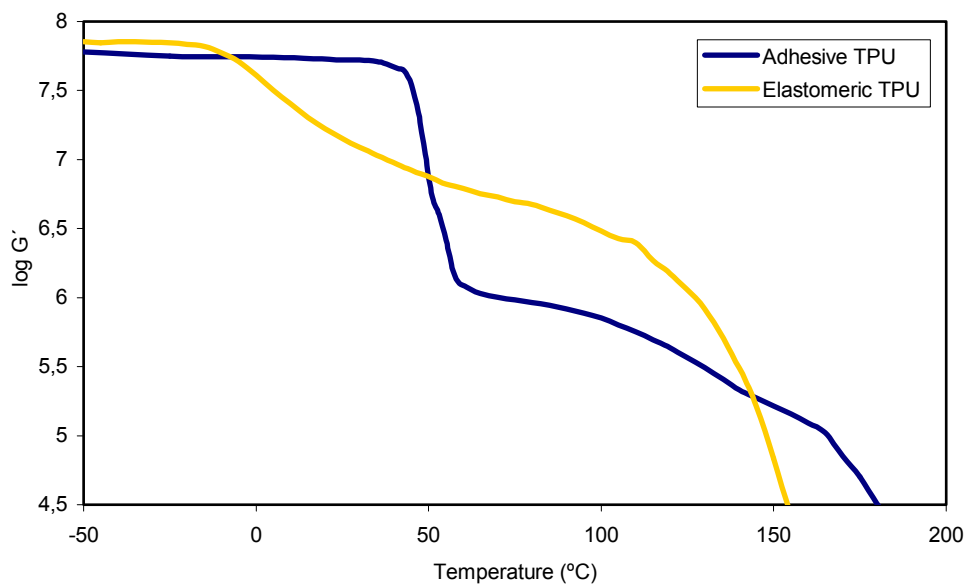
3. POLYURETHANES AND CRYSTALLINITY: CRYSTALLINE TPUS (AT ROOM TEMPERATURE)

In elastomeric polyurethanes (TPUs) the crystalline fraction of the polymer is formed by the hard segments. There is a peculiar type of polyurethanes in which the hard segment content is very low and the long-chain diol is very crystalline and therefore their crystalline fraction is formed by the soft segments instead of the hard segments.

These polyurethanes are white and crystalline at room temperature and when the soft segments melt, their modulus decreases dramatically, acquiring adhesive properties. Therefore they are used as high performance adhesives.

Only polycaprolactone and polyester are used in these crystalline polyurethanes because of the low crystallinity of polyethers.

A comparison between both types of polyurethanes can be seen in the following graph, which shows their typical dynamic mechanical properties:



MERQUINSA POLYURETHANES

In the plant of Montmeló (Barcelona), Merquinsa produces elastomeric polyurethanes (TPUs) and polyurethanes for adhesives that are crystalline at room temperature.

They are produced by continuous process in an extruder reactor designed specifically for an optimum polymerization of the components and they are then dried before packaging in order to guarantee a very low level of humidity.

Merquinsa produces also polyurethane prepolymers for the cork industry and polyurethane emulsions. The different grades of polyurethanes produced by Merquinsa have the following combination of raw materials:

Poliol \ Diisocyanate	Aromatic	Aliphatic
Polycaprolactone	Pearlstick® Pearlbond® Disperbond® Pearlthane®	
Polyester	Pearlstick® Pearlcoat® Pearlthane®	Quilastic®
Polyether	Pearlcoat® Pearlthane®	Pearlcoat®
Polyether - polycaprolactone copolymer	Pearlcoat® Pearlthane®	