3 Semi-Aromatic Polyamides (Polyphthalamides)

3.1 Introduction

Semi-aromatic polyamides (also known as polyphthalamides (PPA)) are combinations of aromatic and aliphatic functionalities. PPA are generally aimed at the performance gap between aliphatic nylons such as PA6,6 and PA6, and higher price polymers such as polyaryletherketone (PAEK). They are crystalline and offer high strength and stiffness at elevated temperatures. However, the aliphatic functionality limits the continuous-use temperature (CUT). There is a range of product forms: glass-filled, impact-modified, mineral-filled, high-flow, flame-retardant, high-reflectivity and electrical grades. They find uses in a wide range of applications, including under-bonnet automotive components, electronic devices and domestic appliances.

3.2 Chemistry and Manufacturing Processes

Semi-aromatic polyamides are generally combinations of aromatic and aliphatic functionalities. They invariably contain 1,4 and sometimes 1,3 phthalic acid, so they are also known as PPA. Fully aliphatic polyamides offer limited thermal performance. Polymers made from aromatic diacids and aromatic diamines (commonly known as 'aramids') have superb properties, and are the basis of high-performance fibre products such as Kevlar. However, they lack melt processability. This is improved by the use of aliphatic monomers and aromatic monomers. As we shall see, quite complex combinations of monomers are used to achieve the required performance combinations. There are several suppliers of PPA including Arkema, DuPont, EMS Grivory, Evonik, Mitsui, and Solvay (formerly Amoco).

Figure 3.1 shows the generic polymerisation reaction together with the structures of the most commonly used diacids (terephthalic acid (T), isophthalic acid (I), adipic acid) together with various diamines. In the standard nomenclature, 'T' and 'I' are combined with a number indicating the length of the aliphatic monomers. Therefore, nylon 6T might be assumed to be made from hexamethylene diamine and terephthalic acid. Based on structure–property considerations, 6T looks like an interesting high-temperature material. However, the melting point (T_m) is too high for melt processing without significant thermal degradation. Accordingly, comonomers are used to reduce the melting point.
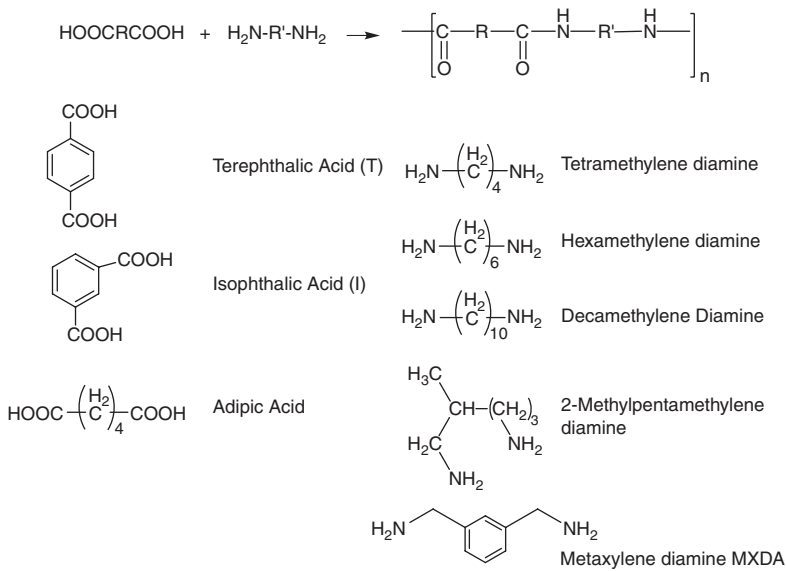
Figure 3.1 Synthesis of polyamides

The combination of aromatic diacids is sometimes represented in the product name. For example, PA 6T is produced from hexamethylene diamines and terephthalic acid, whereas PA 6T/6I would be a copolymer of hexamethylene diamines with both acids. Units designated '6.6' can be produced by the reaction of adipic acid and hexamethylenediamine. However, many copolymers are simply referred to as 6.T or 6.T/X, and this tells us little about the exact nature of the '6' unit or the presence of other monomers. There is a wide range of possible copolymer compositions, and these are used to 'tune' the exact thermal characteristics of particular products. Copolymers are often necessary to reduce the T_m to acceptable levels. For example, mixtures of terephthalic acid and isophthlaic acid can be copolymerised with hexamethylene diamine and 2-methylpentamethylenediamine to produce polymers with values of T_m in the range 280–330 °C [1]. DSM have found that combinations of 4T and 6T produce polymers with T_m which are very high but well below the thermal decomposition temperature [2]. A very recent DSM patent illustrates ongoing research into ever more complex copolymer compositions, in this case involving mixtures of short- and long-chain diamines [3].

Manufacturers do not routinely disclose comomoner compositions. However, the structures of common commercial grades can be found in the patent literature, often linked to actual product trade names. Information can also be available on the proportions of acid and amine end groups, the nature of endcapping, as well as molecular weight and mechanical properties as a function of composition [4–12]. **Table 3.1** shows how T_m and the glass transition temperature (T_g) can be affected

Table 3.1 Thermal properties as a function of molar composition of high-performance polyamides

Terephthalic acid mol %	Isophthalic acid mol %	Adipic acid mol%	Hexamethylene Diamine mol%	2-Methylpentamethylene diamine	Glass transition temperature (T_g)/°C	T_m/°C	Trade name reported to be related to this type of structure
65	25	10	100	0	126	311	Amodel 1000
65	0	35	100	0	100	325	Amodel 4000
55	5	40	100	0	94	303	-
50	5	45	100	0	88	296	
60	0	40	100	0	95	317	
50	0	50	100	0	84	305	
55	0	45	100	0	88	312	Amodel 6000
100	0	0	50	50	125	305	Zytel HTN 501

by composition, and relates these to the compositions of Amodel 1000, 4000 and 6000 and Zytel HTN. Other commercial products with structures disclosed in the literature include Mitsui Arlene CH230 (6.6/6.T), EMS-Grivory HT1 (6.T/6.I) and EMS-Grivory HT2 (6.6/6.T).

Polymers can also be produced using longer-chain diamines such as 10T/X made by Evonik or the similar HT3 (10.T/6.T) made by EMS-Grivory. The decam-ethylenediamine used in these products can be derived from castor oil, and the product is marketed for its performance and environmental credentials. The use of 6T units to control the T_m in 10T polymers is described in detail in a patent by EMS-Grivory [12]. A 65:35 10T:6T composition has a T_m and T_g of ~280 °C and 121 °C, respectively.

Polyamide polymerisation can be achieved by gradually removing water from an aqueous mixture of the monomers. The process takes place under pressure at high temperatures [8]. Solid-phase post condensation can be used to increase molecular weight [7]. The chemistry lends itself to continuous processing [13, 14]. A two-stage process might involve the formation of a low-viscosity, low-molecular-weight pre-polymer which is subsequently post-polymerised in the solid phase or in the melt (e.g., via melt extrusion). There are also three-stage processes involving precondensa-tion, solid-phase polymerisation, and polymerisation in the melt [15].

Polyamides can be compounded with a wide range of reinforcing fibres and other fillers. The presence of aliphatic groups means that thermal stabilisers and anti-oxidants are used [6]. Other important additives include fire-retardants [16] and toughening agents [17].

A slightly different class of semi-aromatic polyamide is made by condensing adipic acid and *m*-xylylenediamine (MXDA). This type of product is known as PMXD6, and is sold by Solvay under the trade name 'Ixef' [18].

3.3 Properties and Processing

Section 3.2 illustrates the exceptionally versatile chemistry of semi-aromatic polya-mides. However, certain structure–property principles limit the performance of polyamides, notably effects involving oxidative stability and moisture absorption.

The combination of crystallisable structures and hydrogen bonding between the amide groups mean that T_m are typically close to or >300 °C. Many grades are glass fibre-reinforced and the heat distortion temperature (HDT) routinely approaches the T_m. However, the presence of aliphatic C-H groups is a major weakness, and the relative thermal index (RTI) is commonly ~115–140 °C. This is not a prob-lem for all applications. The RTI is based on a 100,000-hour half-life and many

applications (e.g., automotive-engine components) require much shorter lifetimes. Care should be taken when comparing loosely defined CUT values: some will be quoted for as little as 500 hours! Much effort has been put into improvement of the CUT. Recently, DuPont introduced 'Shield Technology', which combines a special set of stabilising additives with a new polymer backbone and polymer modifications. The resulting products have more than twice the lifetime and are targeted at conventional polyphenylenesulfide (PPS) applications in which they can also offer higher levels of toughness.

Moisture absorption is a problem for many polyamides. It causes dimensional instability and reduces the T_g and mechanical properties. Data tables often list properties as a function of humidity (e.g., dry 'as moulded' and at a standard relative humidity). In the case of semi-aromatic polyamides, the rate of moisture absorption may be very slow, and they may not have reached equilibrium at the time of testing (or an accelerated equilibration regimen may have been used). Knowing the conditions under which measurements were made and the sensitivity of key properties to moisture is important. In extreme cases, the T_g may drop below the service temperature, or components may seize or warp due to dimensional changes. However, the effect of moisture is less than that seen in aliphatic polyamides. The effect on mechanical properties at room temperature can be relatively small. This can be an advantage for PPA *versus* aliphatic polyamides.

Moisture absorption is an inevitable consequence of hydrogen bonding between water and amide groups. It is reversible and so can be less of a problem at service temperatures >100 °C where the environment effectively dries the polymer. The effect is reduced with fewer amide groups and more hydrophobic chains. Semi-aromatic nylons have lower moisture absorption than aliphatic ones. Similarly, 10T would be expected to have lower moisture absorption than 6T. The higher-temperature aliphatic nylons (e.g., PA4.6) tend to have large proportions of hydrogen-bonding groups and can absorb relatively large amounts of water.

Flammability properties are inherently limited by aliphatic content. Many materials are rated 'horizontal burn' (HB) in UL94. However, grades containing flame-retardants (many of which are non-halogen-based) are available, and V-0 ratings can be achieved.

Aromatic content generally improves chemical resistance compared with aliphatic polyamides. However, the amide group is susceptible to hydrolysis and can be attacked by sufficiently strong acids and alkalis. Glycols and alcohols as well as water attack these materials aggressively only at high temperatures. Product literature from Amodel states that it has excellent resistance to hydrocarbons, greases, oils, chlorofluorocarbons, chlorinated hydrocarbons, ketones, esters, higher alcohols, alkalis, and gamma radiation but performs less well in methanol, strong acids and

methylene chloride. As always, a lot depends on stress, concentration, time, and temperature. Performance in phenol is described as 'unacceptable'. Manufacturers will have specific performance data.

PMXD6 has relatively low thermal properties (T_g = 85 °C and limited long-term thermal oxidative stability) but some of its other properties are exceptional. It typically contains ≤60% glass reinforcement (tensile strength, 280 MPa; flexural modulus, 24 GPa) and yet it has excellent flow properties. It can be used to produce very high strength, very high stiffness thin-wall components with excellent scratch-resistant surface finishes.

Table 3.2 shows the properties of some semi-aromatic polyamides and also the aliphatic polyamide nylon 6,6. For comparison, PA 4,6 would have a T_m of 295 °C, a T_g of 75 °C. The data are taken from Evonik datasheets, which allow comparison of 6T/X and 10T/X in unfilled and glass-reinforced forms. These numbers can be used as a baseline for comparisons with other materials such as DSM 4T materials, 6T products from Solvay, DuPont and EMS Grivory. The 6T material chosen has a T_m and T_g similar to those of Amodel 1000. The lower-T_g resins (e.g., Amodel 4000 and Amodel 6000) can have a HDT comparable with that of Amodel 1000 when reinforced because of their high T_m. Up to 60% (or even 66%) glass-filled grades

Table 3.2 Properties of semi-aromatic polyamides					
Material	**Vestamid M1000 '6T/X'**	**Vestamid M1000 '6T/X'**	**Vestamid M3000 '10T/X'**	**Vestamid M3000 '10T/X'**	**PA 6,6***
	Unfilled	50% Glass	Unfilled	50% Glass	Unfilled
T_g/°C T_m/°C HDT/°C	125 315 126	125 315 293	125 285 128	125 285 276	60 260 80
Tensile strength at break/ MPaTensile elongation at break/%	90 3	230 1.6	73 5	215 2.2	73 40
Tensile modulus GPa	3.6	17	2.7	15.5	2.4
Flammability UL94 3.2 mm**	HB	HB	HB	HB	HB
Moisture absorption % (23 ºC, 50% humidity)	0.3	0.2	0.15	0.08	
Density, g/cm³	1.2	1.64	1.1	1.58	1.12
* For comparison, PA 4,6 would have a melting point of 295 ºC at a T_g of 75 ºC *** Halogen-free, flame-retardant grades can have V-0 ratings*					

are available for some polymers. Moduli of ~23 GPa are achievable. However very highly filled systems may have limited flow and be suitable only for thicker parts.

In comparison with PA66, 6T is said to offer better: heat resistance; dimensional stability; resistance to chemicals and hydrolysis; stiffness; and tensile strength; it also offers lower absorption of humidity. Impact strength and processability are slightly lower. In comparison with 6T, 10T is said to offer better: resistance against hydrolysis; moisture uptake; chemical resistance; processability; impact strength; and elongation at break. The HDT, tensile strength and stiffness are lower. Such comparisons are dependent upon the precise composition of the polymer and compound.

The advantages of PPA compared with other polymers have been described, as listed below:

- *Versus* liquid crystalline polyesters (LCP), PPA can offer better weld line strength and dynamic stress performance

- *Versus* polyethersulfone (PES)/polyphenylsulfone (PPSU), PPA can offer better resistance to chemicals and environmental stress cracking (PES/PPSU are amorphous)

- *Versus* PPS, PPA can offer better toughness and elongation up to break, and can be better for dynamic stress

- *Versus* PA46, PPA can offer lower water absorption, better dimensional stability and mechanical properties that are less susceptible to moisture

Semi-aromatic nylons can be processed using standard thermoplastic techniques. However, they must be dried according to manufacturer recommendations. Failure to do so can result in poor part appearance, drooling at machine nozzles, and brittleness due to reduction in molecular weight. The drying temperature and drying time need to be limited to avoid resin discolouration; desiccant dryers are recommended. High mould temperatures are required to develop full crystallinity. For Amodel, mould temperatures >135 °C are required to produce parts with the best chemical resistance, dimensional stability and HDT. Excessive melt temperatures and residence times can give rise to degradation.

3.4 Applications

PPA are generally aimed at the performance gap between aliphatic nylons such as PA6,6 or PA6 and high-price polymers such as PAEK. There is a wide range of

product forms, including glass-filled, impact-modified, mineral-filled, high-flow, flame-retardant, high-reflectivity and electrical grades.

PPA are found in a wide range of under-bonnet automotive applications. Benefits include adequate heat aging resistance for automotive lifetimes, easy processing with good surface appearance, high stiffness and strengths at elevated temperatures, hydrolysis resistance, dimensional stability, surface appearance, paint adhesion and weldability. Examples include tank flaps, electrical water pump and thermostat housings, engine mount orifice bodies, digital water valves, capless fuel filler systems, fuel filter housings, exhaust-gas recirculation components, air-intake manifolds, oil coolers, heater core end caps, snap-fit electrical terminals, moulded-in-place gaskets, control system enclosures, noise encapsulation devices, and engine covers.

Complex electronic components can be produced from high flow grades. Benefits can include resistance to hot and humid environments and compatibility with lead-free soldering technologies. Applications include light-emitting diode (LED), surface mount technology components, connectors, motor parts, and controller housings. PPA are used in connectors and sockets for serial advanced technology attachment connectors, notebook memory backplanes and memory cards. Flow is inferior to LCP but toughness and weld-line strength are better. Halogen-free flame-retardant grades reduce the relative advantages offered by inherently fire-retardant LCP. Laptop base frames can be made from flame retardant grades. LED require durable, highly reflective sockets. PPA can offer a light natural colour and high-reflectivity whites combined with good ultraviolet and dimensional stability as well as excellent adhesion to metal and silicone. This allows the creation of longer-lasting, more robust and more efficient LED. Thermally conductive grades can improve heat management.

Many small domestic appliances such as power tools and gardening equipment contain PPA components. The conventional connectors currently used in many domestic appliances (e.g., washing machines, clothes dryers) are being converted to surface mount technology, thereby creating further opportunities for PPA.

Conventional rubber components are fastened and fixed using composite structures that contain a metal component. PPA can remain stable at vulcanisation temperatures to provide a lightweight, corrosion-resistant alternative. Complex parts can be manufactured inexpensively by injection moulding. The composite components are used in a wide variety of applications, including shock-absorbing bearings and buffers or reinforced seals.

PMXD6 resins offer very high strength and stiffness in thin-wall components with an excellent, scratch-resistant surface finish. They can look and feel like metal, and are used in aesthetic components such as mobile-phone housings, shaver heads, electric iron parts, sewing-machine components, automotive door handles, mirror housing and headlamp surrounds.

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