ENGINEERING THERMOPLASTICS

1. Introduction

The development of plastic materials is one of the most successful stories of the twentieth century. In the 1960s, plastics represented a small fraction of the total annual consumption of materials, but 20 years later they surpassed metallic materials (mostly, iron based) in terms of consumed volume. At the end of the century, plastics reached the astonishing sum of 150 million metric tons produced per year. Of this amount 70% is comprised of the so-called commodity plastics [high-density polyethylene (HDPE), lower-density polyethylene (LDPE), polyproplene (PP), poly(vinyl chloride) (PVC), and polystyrene (PS)], 11% by thermoset resins, 7% by elastomers, and 12% by engineering thermoplastics.

The definition of engineering plastics is rather arbitrary. In the last edition of this Encyclopedia they were defined as *thermoplastic resins, neat or filled, which maintain dimensional stability and most mechanical properties above 100*°C and below 0°C. In such a definition, engineering plastics are obviously intended as engineering thermoplastics and the terms are used interchangeably. They encompass plastics that can be formed into parts suitable for bearing loads and able to withstand abuse in thermal environments traditionally tolerated by metals, ceramics, glass, and wood. A more general definition defines engineering plastics as those *high performance materials that provide a combination of high ratings for mechanical, thermal, electrical, and chemical properties*. This article adopts this latter definition, with the following three restrictions: (*1*) thermoplastics generally are considered to be produced on an industrial scale; (*2*) with some exceptions, their predominant application is as solid parts or films, not fibers or cellular materials; (*3*) sophisticated derivations of commodities, (reinforced polypropylene, ultra high molecular weight polyethylene, etc), widely used in engineering applications are excluded. Following these guidelines, Table 1 was compiled; occasionally copolymers, blends, and reinforced polymers are included. The materials have been arbitrarily grouped by considering the most representative heteroatom present in their chemical structure.

The selection of polymer families treated here is somewhat arbitrary. For example, fluoropolymers are more functional materials than engineering materials, and acrylic resins suffer enough thermal instability to be considered by some authors as outside the border of engineering plastics. However, PTFE (together with some copolymers) and PMMA have been considered because of their notoriety and some specific engineering applications.

Table 1 categorizes polymeric materials as *engineering polymers* (lower performance) or *high performance polymers*; the borderline between the two groups is rather vague. Relatively good indicators for such a classification are the selling price and/or the amount produced per year. Polymers can be either *amorphous* or partially *crystalline*, depending on their molecular structure and conditions of formation of the solid phase (polymerization and/or thermal history). The amorphous or semicrystalline nature of each material is reported in Table 1 as the form predominantly used in applications. A polymer is considered semicrystalline when it develops a detectable crystalline phase upon nonaccelerating cooling of the melt. However, in particular conditions a polymer normally crystalline appears amorphous. For example, PET, is crystalline by slow cooling of the melt, but by rapid quenching it is amorphous. Crystalline and amorphous polymers are distinguished by several different properties, and the most evident of them is light transmission: crystalline polymers are opaque, whereas amorphous polymers are transparent. Finally, Table 1 collects the acronyms that are assigned to the various polymers through the text, as well as the Chemical Abstract Service Registry Number (CASRN). In the case of polymers, the assignment of more than one CASRN to the same material is frequent.

In Table 2, the qualitative dependence of some properties of polymeric materials as a function of their morphological state is reported. Such properties are determined directly or indirectly by the different response of chains to solicitations (chemical, thermal, and so on) when they are in an ordered arrangement or in a random one. Totally crystalline (100%) polymers are impossible to obtain, due to the unavoidable presence of chain folds; further, the crystallinity degree can change under the effect of thermal, mechanical, or chemical operations.

2. History of Thermoplastics Development

The development of engineering thermoplastics began in the 1930s and is still continuing. The first patent on polyamide (nylon) was obtained by Carothers

Table 1. **Engineering Thermoplastics**

Material	Class[a]	Morphology[b]	Acronym[c]	CAS Registry number
C-containing polymers				
cyclic olefin copolymers	E	A	COP, COC	[26007-43-2]
ethylene/tetracyclododecene				
ethylene/norbornene				
syndiotactic polystyrene	E	C	sPS	[28325-75-9]
O-containing polymers				
acetal resins (polyoxymethylene)	E	C	POM	[25231-38-3]
polyester resins	E	C		
poly(ethylene terephthalate)			PET	[25038-59-9]
poly(butylene terephthalate)			PBT	[24968-12-5]
poly(ethylene naphthalate)			PEN	[25230-87-9]
polyarylates	E	A	PAR	[39281-59-9]
liquid crystal polymers	HP	C	LCP	[144114-03-4]
poly(phenylene ether)	E	A	PPE	[24983-67-8]
polycarbonate	E	A/C	PC	[25037-45-0]
aliphatic polyketones	E	C	PK	[88995-51-1]
poly(ether ketones)	HP	C	PEEK	[31694-16-3]
			PEK	[27380-27-4]
			PEKK	[54991-67-2]
			PEKEKK	[60015-05-6]
acrylic resins	E	A	PMMA	[9011-14-7]
S-containing polymers				
poly(phenylene sulfide)	HP	C	PPS	25212-74-2
polysulfone	E	A	PSU	[25135-51-7]
poly(ether sulfone)	HP	A	PES	[25667-42-9]
poly(aryl sulfone)	HP	A	PAS	[25839-81-0]
N-containing polymers				
styrene copolymers	E	A	ABS	9003-56-9
			SAN	[9003-54-7]
			SMA	[9011-13-6]
polyamide resins (aliphatic)	E	C/A	PA6,6	[32131-17-2]
			PA6,10	[9008-66-6]
			PA6,12	[24936-74-1]
			PA4,6	[50327-22-5]
			PA6	[25038-54-4]
			PA11	[25035-04-5]
			PA12	[24937-16-4]
polyamide resins (aromatic)	HP		ArPA	[24938-64-5][d] [24938-60-1][e]
polyimide resins	HP	A/C	PI	[25036-53-7]
polyamideimide	HP	A	PAI	[61970-49-8]
polyphthalamides	HP	C	PPA	[25750-23-6]
polyetherimide	HP	A	PEI	[61128-46-9]
F-containing polymers				
fluoropolymers		C		
poly(tetrafluoroethylene)			PTFE	[9002-84-0]
ethylene–tetrafluoroethylene copolymer			ETFE	[25038-71-5]

Table 1 (*Continued*)

Material	Class[a]	Morphology[b]	Acronym[c]	CAS Registry number
fluorinated ethylene–propylene copolymer			FEP	[25067-11-2]
perfluorovinylether-tetrafluoroethylene copolymer			PFA	[26655-00-5]

[a] E = engineering plastics (medium performance); HP = high performance plastics.

[b] C = crystalline; A = amorphous.

[c] Acronyms used through the text are reported.

[d] Referred to poly(*p*-phenylene terephthalamide).

[e] Referred to poly(*m*-phenylene isophthalamide).

in 1931. Before the second World War acrylic and polyester resins were discovered, as well as styrene-based copolymers (ABS) and PTFE. The latter was brought to full production in 1950 as Teflon by Du Pont. In the same years, polycarbonates were introduced by General Electric and acetal resins by Celanese. In the period 1960–1980, most of the actual high performance polymers were developed. Among them were polyimides, PES, PPS, PEEK and PEI, as well as other engineering resins such as PPO and PBT. At that time, the potential of development of novel engineering plastics was overestimated, and when it was realized that the volume growth was not so fast, the introduction of new families slowed down. Several factors contributed to this change of attitude, from the growing of costs necessary for the introduction of a new materials, to a lower demand of materials studied for structural applications, and finally to the competition of tailored grades of existing polymers (also commodity plastics, like PP), new blends, and reinforced materials. Furthermore, the time from the invention of a new polymer structure to the achievement of the industrial stage remained quite high (10–12 years), in spite of the experience accumulated in such processes. Thus, from an originally forecasted 25% of the whole plastics market, engineering plastics cover only 10% roughly. It remains true that the growth rate is higher than that of commodities, but this expands their total fraction only

Table 2. **Relationships Between Polymer Properties and Morphology**

Property	Crystalline	Amorphous
light transmission	high	none to low
solvent resistance	high	low
lubricity	high	low
dimensional stability	high	low
mold shrinkage	high	low
resistance to dynamic fatigue	high	low
facility to form high strength fibers	high	none
thermal expansion coefficient	high	low
melting temperature	sharp	absent
dependence of properties on temperature	high	low

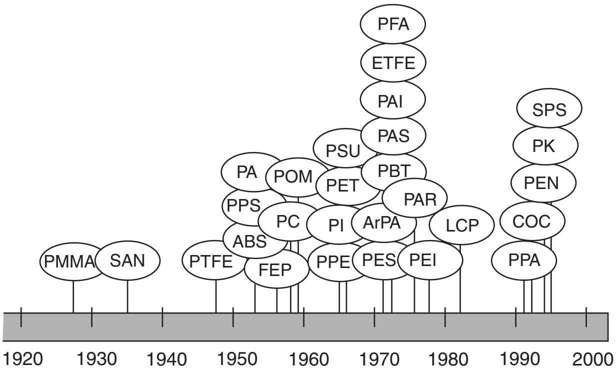


Fig. 1. The historical development of synthetic thermoplastic resins. The reported years indicate the presumed entry into the market. See Table 1 for an explanation of acronyms.

very slowly. In Figure 1, the chronological development of commercial thermoplastic polymers is sketched, taking into account commodities near the engineering polymers in properties (1,2). This figure shows that most of the engineering thermoplastics were introduced industrially in the 1950–1980 period. The new flourishing in the 1990s is partly enhanced by some particular events, like the development of metallocene catalysts, which rendered convenient the fabrication of new materials like sPS and COCs, and the availability of the monomer for PEN.

Table 3 reports the most important producers and corresponding trade names, with the aim of helping the reader to identify materials. Some books are dedicated to this task (3,4), which is complicated by ongoing mergers and selling of operations, resulting in changed connections between producers and trade names.

Research advances concerning specific materials are considered only if they have already reached the commercial level. Recent books and reviews (5,6) provide more information. After a discussion of the general properties of engineering thermoplastics and the processing technologies used for manufacturing, single polymer families cited in Table 1 are treated individually. Then there are comparative considerations concerning the most important properties of engineering thermoplastics, in order to introduce the complex world of interpolymer and intermaterial competition.

3. Properties of Thermoplastics

Some material properties are intrinsic to the chemical substance under investigation, others depend on the processing operation that confers a shape and orientation to the material. Because some processing is often necessary to prepare testing specimens, intrinsic properties can be difficult to measure. Some properties acquire relevance only when the final article is manufactured and strictly depend on the specific use of the article. Properties have been distinguished as performance, maintenance, or aesthetic properties (1); however, this classifica-

Table 3. **Producers and Trade Names of Engineering Thermoplastics**

Material	Trade name	Manufacturer
COC	Topas	Ticona
	Apel	Mitsui Petrochemical
	Zeonex[a], Zeonor[b]	Nippon Zeon
	Arton	JSR
sPS	Questra	Dow
	Xarec	Idemitsu
POM	Delrin	Du Pont
	Hostaform, Celcon	Ticona
	Ultraform	BASF
	Tenac	Asahi
	Iupital	Mitsubishi
PET, PBT	see Table 8	see Table 8
PAR	U-Polymer	Unitika[c]
	Durel	Ticona
LCP	Vectra	Ticona
	Xydar	BP Amoco
	Zenite	Du Pont
	Summika	Sumitomo
	Siveras	Toray
PPE	PPO, Noryl[d]	GE Plastics
	Luranyl	BASF
	Vestoran	Degussa Hüls
PC	Makrolon	Bayer
	Lexan	GE Plastics
	Calibre	Dow
	Iupilon	Mitsubishi
PK	Carilon	Shell
	Ketonex	BP Amoco
PEEK	Victrex	ICI
	Ketron	DSM
PEK	Stilan	Raytheon
	Hostatec	Ticona
	Kadel	BP Amoco
PEKK	Declar	Du Pont
PEKEKK	Ultrapek	BASF
PMMA	Perspex, Diakon	ICI
	Plexiglas, Plexidur, Altuglas, Vedril	Ato Haas
	Acrifix	Rohm
	Vestiform	Hüls
	Paraglas, Degalan	Degussa
	Lucryl	BASF
	Sumipex	Sumitomo
PPS	Fortron	Ticona
	Ryton	Phillips
	Supec	GE Plastics
	Tedur	Bayer
	Craston	Cyba-Geigy
	Techtron	DSM
PSU	Udel	BP Amoco
	Ultrason S	BASF
PES	Radel A	BP Amoco
	Ultrason E	BASF
	Victrex PES	ICI
	Astrel	Carborundum

Table 3 (*Continued*)

Material	Trade name	Manufacturer
PAS	Radel R	BP Amoco
ABS	see Table 20	see Table 20
SAN	Luran	Bayer
	Lustran	BASF
	Tyril	Dow
PA	see Table 23	see Table 23
ArPA	Nomex	Du Pont
	Conex	Teijin
	Kevlar	Du Pont
	Twaron	Akzo
PI	Kapton, Vespel, Avimid	Du Pont
	Upilex	UBE
	Kinel, Matrimid	Ciba Geigy
	Apical	Allied
	Aurum	Mitsui Toatsu
	Kerimid	Nyltech
	Duratron	DSM
PAI	Torlon	BP Amoco
PPA	Amodel	BP Amoco
PEI	Ultem	GE Plastics
Fluoropolymer	Teflon, Tefzel	Du Pont
	Fluon	ICI
	Hostaflon	Dyneon
	Algoflon, Hyflon	Ausimont
	Neoflon, Polyflon	Daikin
	Aflon	Asahi Glass

[a] Homopolymer.

[b] Copolymer.

[c] Commercialized by Amoco for several years under the trade name of Ardel.

[d] In blend with other polymers.

tion is extremely subjective. Herein mainly intrinsic and processing properties are considered, divided into four conventional groups: physical, electrical, thermal, and mechanical. Several of these properties change remarkably depending on the morphology (amorphous or semicrystalline materials) or for the presence of fillers and reinforcing fibers. Because it is impossible to report the properties of all the grades present on the market (it was estimated that >5300 grades of engineering plastics were offered by producers in 1997, Ref. 7), the more representative of them will be described in the paragraphs dedicated to specific polymers. In Table 4, the most representative properties are reported, together with the proper SI units and, if existing, the respective standard measurement method. Several books describe the methods in more detail (2,3,8).

3.1. Physical Properties. Physical properties include density, properties connected to their combustion tendency (flammability and oxygen *index*), optical properties (refractive index and yellow index), and the ability to absorb water. Density ρ, ie, the mass per unit volume, depends on the nature of atoms present in the chemical structure and the way molecules (chains) pack together. Polyolefins, composed of C and H only, have densities in the range

Table 4. **Properties, Units, and Standard Methods of Measurement**

Property	Units	ASTM Method	ISO Method
Physical properties			
density	g/mL	D792	1183
flammability		UL94[a]	
oxygen index (LOI)	%	D2863	4589
refractive index		D542	489
yellowness Index (YI)		D1925	
water absorption, 24 h, 23°C			
Electrical properties			
dielectric constant, 1 MHz		D150	
dielectric strength, 1 mm	kV/mm	D149	
dissipation factor, 1 kHz		D150	
volume resistivity, 23°C, dry	$\Omega\cdot$cm	D150	
Thermal properties			
glass-transition temp (T_g)	°C		
melting temp. (T_m)	°C		
heat deflection temp. (HDT) at 0.45 or 1.8 MPa	°C	D648	75
specific heat capacity J/(kg · K)			
thermal conductivity, 23°C	W/(m · K)	C177	
thermal expansion coeff.	K^{-1}	D696	
upper working temp	°C		
Mechanical properties			
elastic modulus	GPa	D638	527
tensile strength	MPa	D638	527
flexural modulus	GPa	D790	178
flexural strength	MPa	D790	178
compressive strength	MPa	D638	527
elongation at break	%	D638	527
notched Izod impact resistance, 3.2 mm	J/m	D256	180
hardness (Rockwell M or R)		D785	2039
friction coefficient		D1894	8295
Rheological properties			
intrinsic viscosity	Pa · s		
melt flow index	g/10 min	D1238	1133

[a] UL94 is an Underwriters Laboratories method.

0.85–1; organic polymers containing heteroatoms rarely have densities >2. Conformations and crystalline phases strongly *influence* density. Crystalline phases are generally more dense than the amorphous phases, an average ρ_c/ρ_a ratio of 1.13±0.08 has been determined (1).

The limited oxygen index (LOI) test determines the minimum oxygen fraction in an oxygen/nitrogen mixture able to support combustion of a candlelight sample under specific test conditions. The LOI test is necessary but not sufficient for determining the burning behavior of polymers in real conditions. For this task, specific flammability tests have been established on an empirical basis. The most widely used test is UL94, elaborated by Underwriters Laboratories, rating the ability of a material to extinguish a flame once ignited (9). In decreasing order, the UL94 degrees are V-0, V-1, V-2, and HB, based on a specific specimen thickness. Only a few high performance polymers like polyetherimides, have been classified as inherently nonflammable (ie, V-0); other polymers can reach a good classification after the addition of specific additives, ie, flame retardants, in the material formulation.

The refractive index n measures the deviation of light when passing through matter, and is expressed as $\sin(i)/\sin(r)$, where i and r are the angles of incident light and refracted light, respectively. It is closely linked to molecular structure of polymers, and contributes to their optical properties, like clarity, haze, birefringence, color, transmittance, and reflectance. Most of engineering plastics here considered are opaque and/or inherently colored, with the exceptions of PC, PMMA, and COC. For them, when used in optical applications, the yellow index (YI) is relevant. YI indicates the degree of departure of an object color from colorless or from a preferred white toward yellow and is determined from spectrophotometric data.

Water absorption indicates the increase in weight of a polymer after immersion in water under specified conditions of temperature and time. Generally, it is referred to 24 h at room temperature (23°C) and is expressed as a percentage with respect to the initial weight. If water is absorbed by a polymer, drying is required before processing operations, because water's presence at high temperature results in uncontrolled degradation of the material and consequently poor performance. This is the case of PET and other polyesters. Some polymers like polyamides absorb water from air humidity, and hold water molecules rather firmly by hydrogen bonding. Absorbed water causes a slow variation of properties like electrical characteristics, mechanical strength, and dimensions. For this reason, polymers or specific grades insensitive to water must be employed in moist environments.

3.2. Electrical Properties.

Electrical properties include dielectric constant, dielectric strength, dissipation factor, and volume resistivity. All of them depend on temperature and water absorption.

The (relative) dielectric constant is the ratio of the capacitance of a condenser formed by two metal electrodes separated by a suitable layer of the material considered and the same separated by dry air. The dielectric strength measures the dielectric breakdown resistance of a material under an applied voltage. The applied voltage value just before breakdown is divided by the specimen thickness. Thus, because the result depends on thickness, this value must be specified. The dissipation factor, also called loss tangent, measures the tangent of the difference angle between 90° (ideal angle for a perfect dielectric material) and the true angle at which an alternating current leads the voltage. It is equivalent to the ratio of current dissipated into heat and current actually transmitted. The volume resistivity is the electrical resistance of a unit cube of a given material when an electrical potential is applied to two opposite faces of the cube.

3.3. Thermal Properties.

Thermal properties include some transitions like melting temperature (T_m) and glass-transition temperature (T_g), the heat deflection temperature (HDT), specific heat capacity, thermal conductivity, coefficient of thermal expansion, and upper working temperature.

The T_m is the temperature at which a solid becomes a liquid (or, on cooling, at which a liquid solidifies). For polymeric materials, T_m is often a temperature range rather than a single value, however, its point value should represent the maximum temperature at which crystallites exist. Amorphous polymers do not exhibit a T_m. The T_g is the temperature at which a solid, rigid, and brittle polymer becomes rubbery, by remarkably loosening its rigidity. Mechanical properties are also reduced at T_g, and other properties like volume, thermal expansion coefficient, and specific heat capacity change noticeably. Being kinetic in nature, T_g occurs over a temperature range (depending, eg, on cooling rate) and is hardly visible in some polymers. HDT measures the temperature at which a specimen is deformed a specific amount (eg, 0.25 mm) under a given load (usually, 0.45 or 1.82 MPa), applied in a three point arrangement. HDT is also called DTUL (deflection temperature under load) and should not be interpreted as a safe temperature for continuous operation (which is usually somewhat lower). The specific heat capacity represents the amount of heat necessary to increase the temperature of a unit mass of a substance by 1°. Depending on its definition at constant pressure or at constant volume, it is indicated as c_p or c_v, respectively. Thermal conductivity λ represent the amount of heat conducted per unit of time through a unit area of a material of unit thickness having a difference of 1° between its faces. The thermal expansion coefficient a represents the change in volume (or length) accompanying a temperature unit variation and is of great importance in molding operations of plastics articles, having mold shrinkage as a practical effect. The upper working temperature is a purely empirical indication at which a given plastic can be expected to perform safely and satisfactorily. It is generally lower than HDT.

3.4. Mechanical Properties. Mechanical properties include tensile properties (modulus and strength), flexural properties (modulus and strength), compressive strength, elongation at break, impact resistance, hardness, and friction coefficient. Other relevant properties are creep and fatigue but it is difficult to find comparative data among materials.

The tensile modulus (also elastic, or Young's modulus) E is the stress/strain ratio within its proportional limit for a material under tensile loading (in practice, the initial slope of the stress/strain curve). The tensile strength represents the maximum tensile stress observed when the specimen is being pulled. It may or may not coincide with the ultimate strength, ie, the tensile stress at specimen failure. In tough materials it can be equal to the yield stress. The flexural modulus is the stress/strain ratio within its proportional limit for a material under bending load conditions. It measures the stiffness of a material. The flexural strength is the ability of a material to flex without permanent deformation or breaking. The elongation at break ϵ_{BR} is equal to tensile strength at failure multiplied by 100. It is expressed as a percent of the original length of the specimen. The impact strength (or impact resistance) represents the ability of a material to resist physical breakdown when subjected to a rapidly increasing force and is accepted as a comparison guide for toughness. It depends strongly on the type of test used. The most widely used in the field of plastics is Izod. The Charpy test is less common. The Izod test requires specimens of thickness from 3.18 to 12.7 mm, preferentially notched following the test method prescriptions. A weighted pendulum arm released from a fixed height strikes the specimen in a specified way. The Izod impact energy is measured by dividing the energy lost by the pendulum (presumably absorbed by the specimen) by the specimen thickness. Hardness, defined as the resistance of a material to local deformation, is connected in a complex way to mechanical properties, elasticity, and plasticity. Hardness cannot be defined unambiguously and depends strongly on the test adopted for its determination. It is usually characterized by the combination of three parameters, ie, scratch resistance, abrasion resistance, and identation under load. For the identation test, different Shore and Rockwell scales are in use, Rockwell M and Rockwell R being the most popular for engineering plastics (2). The scale depends on the combination of load and indentor dimensions. The friction coefficient represents the resistance of surfaces of solid bodies in contact with each other to sliding or rolling. It is represented as $k = F/w$, where F is the force necessary to move one surface with respect to the other one, and w in the load exerted on them.

3.5. Rheological Properties.

Rheological properties, describing the deformation of materials under stress, and concerning their flow properties, must be considered in all processing techniques for the fabrication of plastics articles. In order to give operators necessary rheological information, melt viscosity vs shear plots are commonly included in data sheets provided by plastics producers. Here only a few properties connected to rheology are considered, ie, intrinsic viscosity (IV) and melt flow index (MFI).

Intrinsic viscosity measures the capability of a polymer in solution to increase the viscosity of the solution itself. Because IV increases with molecular mass, it is an indication of this last property. The melt flow index (or simply melt index) measures the isothermal resistance to flow through an extrusion plastometer commonly referred to as melt indexer. Practically, the amount of matter forced by a given load to pass in 10 min through a standard die is determined. MFI can be considered as a single point test (ie, resistance to flow at a single shear rate). Every plastics processing technology operates at a defined MFI range as follows (2): 5–100 g/10 min for injection molding, 5–20 g/10 min for rotational molding, 0.5–6 g/10 min for film extrusion, 0.1–1 g/10 min for blow molding and profile extrusion.

3.6. Chemical Resistance.

Chemical resistance is less rigidly defined than the properties discussed previously. Measurement methods include immersion in selected vapors or liquids of a test specimen, then determining the variation of mechanical properties after and before treatment. Optical properties are also considered, particularly in the case of transparent materials. The test results are generally indicated as excellent, good, fair or poor, or other arbitrary scale units. Chemical agents are chosen in order to simulate possible real situations: strong and weak acids, alkalies, saline solutions, hydrocarbons (aliphatic or aromatics), oils and greases, alcohols, aldehydes, ketones, etc. Engineering plastics are generally difficult to dissolve in most solvents. In strict correlation to chemical resistance is weathering resistance, where a combination of a particular environment, temperature, time, and ultraviolet (uv) irradiation is considered, also with cyclic experiments.

4. Processing of Thermoplastics

Processing of thermoplastic materials can be classified in four main categories: extrusion, post-die processing, forming, and injection molding (10–12).

In an extruder, the polymer is melted and pumped into a shaping device called a die, through which the material is forced to assume a particular shape. The pumping action is done by a single-screw or by a twin-screw device, the configuration of which is essential for a suitable result. Extruders are very often used at the end of the polymerization reactor, in order to obtain polymer pellets by chopping an extruded strand. Extruders are also currently used to mix in the proper additives for the polymer, to obtain mixed-polymer blends intimately, to devolatilize the material from the monomers or solvent residues, and in some special cases as a chemical reactor (reactive extrusion). For example, polyetherimide is prepared at the industrial level by reactive extrusion. Depending on the extrusion die geometry, final articles can also be obtained, including sheets, films, pipes, rods, profiles of various geometries (T, double T, C, etc). Coating on wires can be done, as well as coextrusion of two or more layers.

Post-die processing includes a number of operations carried out at the exit of the extruder die in a free-surface way. Examples of such processes are fiber spinning, film blowing and sheet forming. The shape and dimensions of the extrudate material are determined by the rheological properties of the melt, the die dimensions, the cooling conditions and the take-up speed (relative to the extrusion rate).

Forming processes use a mold to confer the final form to the article. Blow molding is widely used in the manufacture of bottles or other containers for liquids, widely using engineering polymers like PET and PC. Essentially, an extruded cylindrical parison is inflated with a gas until it fills the mold cavity. A good equilibrium between the melt strength of the resin under low shear conditions (parison stability) and the flow properties under high shear conditions (blowing) are essential for obtaining a satisfactory result. In thermoforming, a polymer sheet is heated to a temperature above its T_g (or sometimes above T_m) and then pressed into the female part of the mold by means of a suitable plug or by vacuum pulling. Simple-shape articles such as trays can be obtained. In compression molding, an amount of polymer is heated at the proper temperature and then squeezed by means of the male part of the mold into the mold cavity.

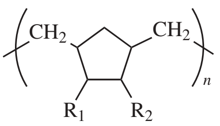
Injection molding is the most commonly used processing technique for engineering thermoplastics. Typically, the polymer pellets are melted and the melt pulled forward by mean of a screw as in extrusion, thus filling a mold under appropriate pressure. The shape of the mold, the number and relative location of the injection devices, and the mold cooling rate determine, together with the intrinsic properties of the material, the final quality of the molded articles. Very complex article shapes can be obtained by this technique. A viscosity of the resin $\sim$10,000 Pa · s and a shear rate of 100 s^{-1} are needed for a convenient operation.

The main problem in injection molding is shrinkage, caused by the volume changes during transition from the melt to the solid. The typical shrinkage of semicrystalline polymers during processing is $\sim$1–4%, compared to 0.2–0.8% for amorphous polymers (12). To reduce the problem, crystallinity could be maintained low, but this is to the detriment of mechanical properties. A compromise should be used. For polymers that crystallize slowly, like PET, it is preferable to allow the polymer to reach the maximum crystallization degree by the use of nucleating agents. If the shrinkage amount is different in different volume portions of the fabricated part, warpage of the part itself can be observed.

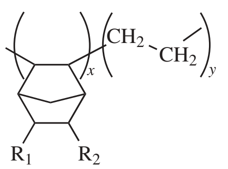
5. Hydrocarbon Materials

5.1. Cyclic Olefin Polymers. Cyclic olefin polymers (COP) and copolymers (COC) exhibit unique optical properties, accompanied by excellent moisture resistance, high T_g, and toughness.

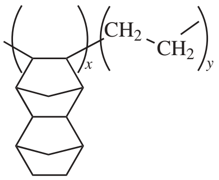
Until recent years, the only products on the market in limited amounts were Apel and Zeonex. Apel is a copolymer of ethylene and tetracyclododecene obtained by conventional Ziegler–Natta catalysis, produced and commercialized by Mitsui Petrochemical. Zeonex is the product of ring-opening metathesis polymerization of norbornadiene, followed by complete hydrogenation of double bonds (13). In 1997, they were joined by Topas, a copolymer of ethylene and norbornadiene jointly developed by Hoechst and Mitsui and based on metallocene catalysis. Topas is now produced by Ticona, the engineering polymer branch of Hoechst.



Zeonex



Topas



Apel

Standard and optical grades of Topas can be produced with a process analogous to those used for polyolefins (solution, bulk, or slurry), depending also on the catalyst (supported or unsupported). COCs are transparent copolymers having high clarity, low optical distortion, high moisture resistance and modulus, as well as good electrical properties.

Although initially targeted for the audio CD market, for their better optical properties with respect to PC, COCs lower thermal conductivity is problematic. Actual preferred applications include medical and food packaging, light management, business machines (as toner binder resin), electrical and electronics. Because the manufacturing process for Topas is based on the well-known and optimized homogeneous Ziegler–Natta technologies, the production cost of Topas is favorable with respect to Zeonex and Apel.

The Topas T_g depends linearly on the norbornadiene or tetracyclododecene content (60–226°C, for 35–79 mol% of NB, respectively) (14). Generally, no T_m is observed, due to the amorphous nature of the material. Available properties of some grades of Topas, Apel, and Zeonex are reported in Table 5.

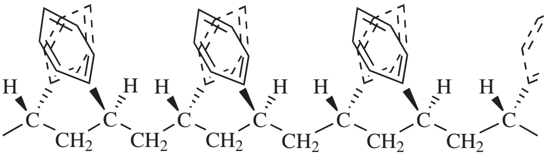
The 1999 production reached ~10,000 t, covered by four producers, Ticona, Mitsui Petrochemicals, Nippon Zeon, and JSR. In 2000, Ticona will start up a dedicated plant with a capacity of 30,000 t.

5.2. Syndiotactic Polystyrene. Polystyrene may exist in three different stereostructures: atactic polystyrene, known since 1839, is industrially obtained through radical or anionic polymerization and is one of the most important commodity plastics; isotactic polystyrene, discovered in 1955, has no practical interest; syndiotactic polystyrene was first synthetized by Ishihara (15) and was industrially developed by Idemitsu and Dow Chemical Co. during the 1990s.

Table 5. **Properties of COC Polymers**

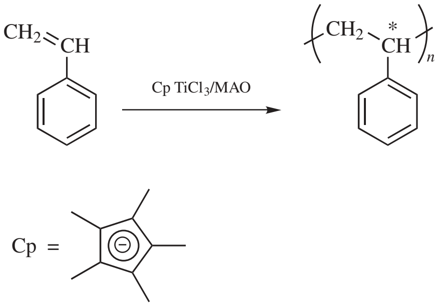
Property	Topas	Apel	Zeonex
density, g/mL	1.02	1.04	1.01
flammability		HB	
refractive index			1.53
water absorption, 24 h, 23°C, %	0.01	<0.01	
dielectric constant, 10 kHz	2.35		
volume resistivity, 23°C, dry, $\Omega \cdot$ cm	$<10^{13}$		
glass transition (T_g), °C	140	140	140
HDT at 0.45 MPa, °C	130	125	123
thermal expansion coefficient, K^{-1}	0.6×10^{-4}	0.7×10^{-4}	
elastic modulus, GPa[a]	3.2	3.2	2.4
tensile strength, MPa[b]		95	64
elongation at break, %	4.5		
notched Izod, 3.2 mm, J/m[c]		2.5	
melt flow index, 260°C, 2.16 kg, g/10 min	13	10	

[a] To convert GPa to psi, multiply by 145,000.
[b] To convert MPa to psi, multiply by 145.
[c] To convert J/m to lbf · ft/in., divide by 53.38.



Syndiotactic polystyrene

Syndiotactic polystyrene (sPS) is prepared through metal coordinated polymerization by using titanium complexes (in particular emititanocenes) activated with methyl aluminoxane (MAO) or fluorinated boranes (16) (see reaction below). MAO itself or aluminum alkyls act also as impurities scavengers.



Polymerization is carried out at 80–100°C in bulk in self-wiping reactors, because the initially liquid reaction mixture forms a gel after a short time and becomes solid at relatively low conversion. The catalyst is killed with protic agents and the polymer powder is dried, compounded if required, and pelletized. Comonomers can be added during polymerization to improve the toughness of the material (17). The molecular weight of the polymer, ranging from 10^5 to 10^6, can be tailored by modifying the structure of the catalyst ligands or by using suitable chain-transfer agents.

The outstanding properties of syndiotactic polystyrene have allowed a fast penetration in the engineering polymers market (18). It is a semicrystalline polymer having a T_g similar to that of atactic polystyrene. However, whereas atactic polystyrene is amorphous, syndiotactic polystyrene has a T_m of ~270°C; the crystallization rate is comparable to that of PET. Due to crystallinity, sPS is highly resistant to acids, alkali, and most organic solvents, except chlorinated and aromatic hydrocarbons that cause swelling. The density of neat sPS (slightly >1 g/mL) is much lower than other engineering plastics; moreover, owing to the fact that density of crystalline and amorphous phase are nearly the same, dimensional stability is good and warpage is low. Other relevant properties, such as electrical and mechanical properties (elastic modulus and tensile strength) are comparable to atactic polystyrene. sPS is brittle, which is a major drawback, but typical of styrene polymers. Addition of inorganic fillers or impact modifiers are essential to offset this disadvantage. Properties of neat and 30% glass filled sPS are reported in Table 6.

Syndiotactic polystyrene has only recently reached the commercial stage (~1995); therefore some of its applications are only proposed and have not achieved full development. At present, it is produced at the industrial scale by Dow (40,000 t/yr, trade name Questra) in different grades: neat, glass-filled and glass-filled/impact modified. The industrial plant started before the end of 1999. A second commercial supplier, Idemitsu Petrochemical, is foreseen in 2002; the plant will produce ~5000 t/yr of resin (trade name Xarec).

The material is conveniently processed by using conventional transformation methods, including extrusion (also into films), injection molding, and thermoforming. The aptitude of sPS for being very easily injection molded, combined

Table 6. **Properties of sPS (Unfilled and Reinforced with Glass Fibers)**

Property	Neat	30% GF
density, g/mL	1.04	1.25
flammability		V0
water absorption, 24 h, 23°C, %		0.05
dielectric constant, 1 MHz	2.6	2.9
dissipation factor, 1 MHz		$<10^{-3}$
glass-transition temperature, T_g, °C	100	100
melting temperature T_m, °C	270	270
HDT at 0.45 MPa, °C		269
at 1.8 MPa, °C	96	251
tensile strength, MPa[a]		121
flexural modulus, GPa[a]	3.0	9.6
flexural strength, MPa[a]	75	170
elongation at break, %		2.5
notched Izod, 3.2 mm, kJ/m[b]	2.0	11

[a] To convert GPa to psi, multiply by 145,000.

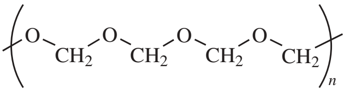
[b] To convert kJ/m to lbf·ft/in., divide by 0.05338.

with its material properties and the extremely low affinity to moisture, make sPS a serious competitor of polyamides and thermoplastic polyesters (PET, PBT) in automotive (under-the-hood) and electric applications (19). Typical applications are coolant circuit components, impellers for water pumps, lighting systems, electrical interconnects, printed circuit boards connectors, coil bobbins. sPS films may find application in capacitors. Medical equipment, eg, sterilization trays, surgical and dental devices, are other end-uses for which sPS is gaining increasing attention.

6. Oxygen-Containing Polymers

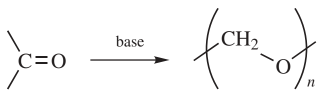
6.1. Acetal Resins.

Acetal resin is the common name for homopolymers of formaldehyde. This material is also referred to as polyoxymethylene, or copolymers of formaldehyde and oxiranes (20). Polymerization of formaldehyde to low molecular weight oligomers was observed for the first time $\sim$1860 by Butlerov; 60 years later, polyoxymethylene was obtained from the polymerization of trioxane (the cyclic trimer of formaldehyde). At the end of the 1950s, Du Pont began to commercialize polyoxymethylene (trade name Delrin) and some years later Celanese started to produce formaldehyde–ethylene oxide copolymers (trade name Celcon). A key point in the homopolymerization process was the prevention of depolymerization at high temperatures; this was accomplished through an end-capping with suitable compounds.

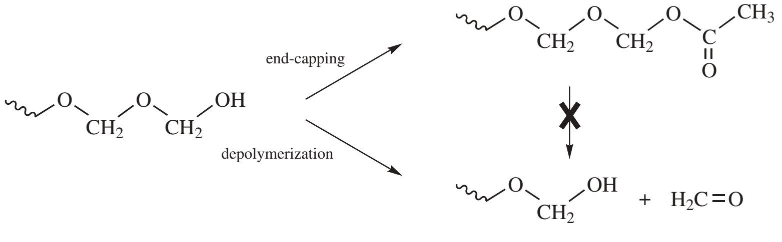


Polyoxymethylene

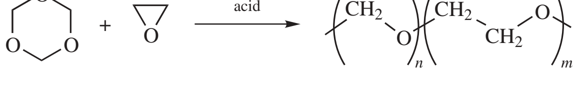
Both anionic and cationic mechanisms are effective in the polymerization of formaldehyde. The homopolymer is believed to be obtained by the anionic mechanism, amines are typical catalysts (eq. 1). End-capping of polymer chains is carried out through acetylation and avoids the decomposition of $-O-CH_2-OH$ hemiacetal terminal groups (eq. 2).



(1)



(2)



(3)

The copolymer is better obtained from trioxane and ethylene oxide (or 1,3-dioxolane) as starting monomer with BF_3-diethyl ether complex (eq. 3); $-O-CH_2CH_2-OH$ terminal groups are stable and do not need capping. However, possible hemiacetal chain ends must be removed from the polymer until an oxyethylenic moiety is generated.

Acetal resins are translucent, white, highly crystalline materials. The homopolymer and the copolymer have a melting temperature of 175 and 165°C, respectively. They are soluble in phenols and insoluble in hydrocarbons, alcohols, esters, and ketones. Acid and alkali solutions cause degradation. Acetal resins provide a high modulus of elasticity combined with high strength, stiffness, resistance to abrasion, and good wear properties; dimensional stability is also excellent because moisture absorption is very low. High surface gloss gives acetals a pleasant appearance. The copolymer exhibits slightly inferior mechanical properties compared to the homopolymer, but improved thermooxidative stability. High flammability, low uv light stability and low impact resistance are weak points of this material. Dielectric properties are comparable with those of other heteroatom-containing engineering plastics. Properties of the homopolymer and copolymer are reported in Table 7.

Most of the commercially available acetals are neat grades, but also reinforced (with inorganic or polymer fibers), impact modified, and uv stabilized grades are available. The Delrin AF family consists of PTFE filled polyoxymethylene. The most common transformation process of acetal resins is injection molding. The use of multicavity molds is possible because of good flow properties.

Table 7. **Properties of POM Materials**

Property	Homopolymer	Copolymer
density, g/mL	1.42	1.41
flammability	HB	HB
oxygen index (LOI), %	15	15
water absorption, 24 h, 23°C, %	0.25	0.25
dielectric constant, 1 MHz	3.7	3.7–4.4
dielectric strength, kV/mm	20	20
dissipation factor, 1 kHz	0.005	0.006–0.18
volume resistivity, 23°C, dry, $\Omega \cdot$ cm	10^{15}	10^{15}
melting temperature T_m, °C	175	165
HDT at 0.45 MPa, °C	170	160
specific heat, J/(kg · K)	1.5	1.5
thermal conductivity, 23°C, W/(m · K)	0.22–0.24	0.23–0.3
thermal expansion coefficient, K^{-1}	122×10^{-6}	$80–120\times10^{-6}$
upper working temperature, °C	80–120	80–120
elastic modulus, GPa[a]	2.9–3.1	2.3–2.8
tensile strength, MPa[b]	70	60–70
flexural modulus, GPa[a]	2.8	2.6
elongation at break, %	40–75	15–40
notched Izod, 3.2 mm, J/m[c]	75–130	70–80
hardness (Rockwell)	M94	M80

[a] To convert GPa to psi, multiply by 145,000.

[b] To convert MPa to psi, multiply by 145.

[c] To convert J/m to lbf.ft/in., divide by 53.38.

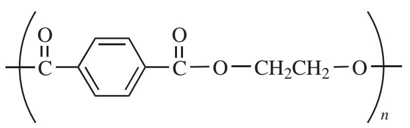
Applications range from gears, bearings and cranks in the automotive field, engineering components, appliance casings, cassette cartridges, container valves, to pump components. PTFE filled grades are used for moving parts, where low friction is important. World consumption in 1998 reached 550,000 t/yr, ~80% of the total world capacity (21). Du Pont remains by far the largest manufacturer of homopolymer, several companies produce copolymers (Table 3) (see Acetal resins).

6.2. Polyesters. Thermoplastic polyesters are polymers (or copolymers) obtained from aromatic diacids and aliphatic diols. Terephthalic acid is the most common aromatic diacid monomer; several different diols are used as comonomers. The most commercially important polyesters are PET, PEN, PBT, poly(1,3-propylene terephthalate) (PPT), and the copolymer of terephthalic acid, ethylene glycol and 1,4-cyclohexanedimethanol (PETG). Other important thermoplastic polyesters are poly(1,4-cyclohexylenedimethylene terephthalate) and poly(1,4-cyclohexylenedimethylene terephthalate-*co*-isophthalate) (20) (see Polyesters, Thermoplastic).

PET was the first polyester to be commercially developed, being discovered in the 1940s by Whinfield (22). For a long time, PET was used for fiber manufacture; subsequently, applications as packaging and engineering thermoplastic material were found. In packaging, partial substitution of ethylene glycol units with 1,4-cyclohexanedimethanol has led to improved materials. PBT was introduced, some years after PET, as an engineering plastic for its better processability and toughness. PEN was studied and commercialized starting in 1994 as a packaging material, for films and liquid containers, in applications where better performances than PET are required. PPT is the latest polyester of the family and is currently under development.

Polyesters are prepared by metal-catalyzed melt polycondensation of the dimethyl ester diacid in the presence of an excess of the glycol(s). Low molecular weight oligomers are formed in a first step as methanol is distilled from the reaction mixture. The molecular weight is brought to the final value by increasing the temperature and distilling the excess glycol under vacuum; the polyester is then extruded from the reactor and pellettized. For certain applications (especially for packaging materials) the molecular weight can be further increased through solid-state polymerization. Small amounts of some comonomers (eg, isophthalic acid diester), generally <3%, are sometimes added to obtain special grades with different characteristics. The increased availability of highly pure terephthalic diacid, has made the polymerization processes from acids more and more economically convenient as compared to the dimethyl ester route for PET; in this case the first step is a noncatalyzed esterification where water is removed as by-product.

Poly(ethylene Terephthalate). PET is manufactured by many producers worldwide and marketed under many different trade names (Table 8).



PET

Table 8. **Producers and Trademarks of Thermoplastic Polyesters**

Producer	PET	PBT	PEN
Eastman	Ektar, Eastapak, Kodapak, Tenite, Kodar	Ektar	
Allied Signal	Petra		
Du Pont	Rynite, Mylar	Crastin	
Dow	Lighter		
Ticona	Impet	Celanex	
Hoechst	Polyclear		
Bayer		Pocan	
BASF		Ultradur	
GE Plastics		Valox	
DSM	Arnite	Arnite	
Degussa/Hüls		Vestodur	
ICI	Melinar[a], Melinex[a]		Kaladex
Shell		Cleartuf[b]	Hipertuf[b]
Nyltech	Techster	Techster	
Mitsubishi		Novadur	
EMS Chemie		Grilpet	

[a] Business acquired by Du Pont.
[b] Business acquired by Mossi & Ghisolfi.

PET is a semicrystalline polyester with a T_g of 75°C and a T_m of 255°C. Both temperatures can be affected by the amount of diethylene glycol present in the chain, formed in low amounts (<1–2%) as a by-product through condensation of two ethylene glycol molecules. Crystallization rate is medium to fast, so that it is possible to control the crystallinity of the final product; nucleating agents can be used to reach higher crystallinity values in shorter times. Fiber grade PET is in the form of amorphous transparent pellets having an intrinsic viscosity, measured in phenol/tetrachloroethane 60:40 by weight, of $\sim$0.65 dL/g. For bottle manufacture, a higher viscosity (and thus higher molecular weights) resin is required ($\sim$0.74 dL/g), obtained after solid-state polymerization; bottle grade pellets are opaque and highly crystalline. PET is a stiff, hard, dimensionally stable material, with excellent wear resistance and a low friction coefficient. It absorbs low amounts of water and the resistance to solvents is good, except to alkali, especially at high temperatures. Barrier properties toward gases and vapors are remarkably good (see Barrier Polymers). PET can be easily biaxially oriented, and mechanical and barrier properties are improved after the treatment. Properties of PET, together with those of other polyesters, are reported in Table 9.

PET can be transformed with all the common processing techniques. Injection-stretch blow molding (mono or double stage) is the processing method adopted for bottle manufacture, whereas extrusion blow-molding requires special grades of high melt strength PET. Careful drying is required before processing to limit the thermo-hydrolytic scission of the ester bonds and degradation. The world production capacity in 1999 was estimated at $\sim$7 million tons, largely dedicated to the packaging market (23). A consumption of only 75,000 t was attributed to injection molding applications (24).

Table 9. **Properties of Unreinforced Polyester Resins**

Property	PET	PEN	PBT
density, g/mL	1.3–1.43	1.36	1.31
oxygen index (LOI), %	21		25
refractive index	1.58–1.64		
water absorption, 24 h, 23°C	0.1		0.1
dielectric constant, 1 MHz	3.0	3.2	3.2
dielectric strength, kV/mm	17		20
dissipation factor, 1 kHz	0.002	0.0048	0.002
volume resistivity, 23°C, dry, $\Omega \cdot$cm	$>10^{14}$	10^{15}	10^{15}
glass-transition temperature, T_g, °C	75	120	
melting temperature T_m, °C	256	265	
HDT at 0.45 MPa, °C	115		115
at 1.8 MPa, °C	80		60
thermal conductivity, 23°C, W/(m $\cdot$ K)	0.15–0.4		
thermal expansion coefficient, K^{-1}	$30–65\times10^{-6}$		
upper working temperature, °C	115–170		120
tensile strength, MPa[a]	50–55		40–55
flexural modulus, GPa[b]	1.0		2.3
flexural strength, MPa[a]	80		80
ultimate strength, MPa[a]	55		50–300
elongation at break, %	130		250
notched Izod, 3.2 mm, J/m[c]	13–35		60
hardness (Rockwell)	M94–101		M70

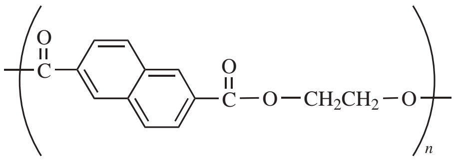
[a] To convert MPa to psi, multiply by 145.

[b] To convert GPa to psi, multiply by 145,000.

[c] To convert J/m to lbf.ft/in., divide by 53.38.

Applications of PET are primarily as fiber and packaging material (bottles and food films). Other end-uses include ovenable food trays, electrical components, fuel pump components, fuel system rotor and connectors, carousels, test equipment manifolds, industrial tire cords. PET and PET blends for technical applications are available in a wide range of grades (filled, flame retarded, nucleated, etc).

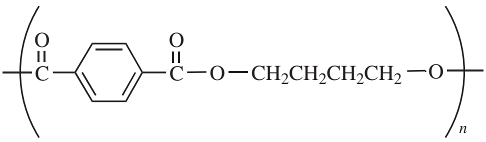
Poly(ethylene 2,6-naphthalenedicarboxylate). PEN is a rather new material that has been introduced on the market to overcome some limitations of PET. The synthesis of PEN on an industrial scale has become feasible after the discovery of convenient routes for the preparation of 2,6-dimethylnaphthalene as an intermediate for 2,6-dimethyl naphthalenedicarboxylate (DMNDC). The oxidation of 2,6-dimethylnaphthalene and the esterification of 2,6-naphthalenedicarboxylic are key steps in the attainment of pure, polymerization-grade DMNDC. In the PEN structure, a 2,6-oriented naphthalene ring is present in place of the PET 1,4-phenylene unit. As a result, PEN is much stiffer than PET, and transition temperatures are higher: the T_g is 120°C and the T_m is 265°C. Gas permeability is greatly reduced as compared to PET (almost one order of magnitude) and elastic modulus is improved, whereas tensile strength is similar. PEN is also a much more efficient uv barrier than PET. PEN is available in the form of pellets and films. Bioriented films begin to shrink at 190°, 45°C higher than similar films of PET.



PET 1,4-Phenylene unit

PEN films are used in electronic and electric fields. Liquid containers made of PEN can be used for oxygen-sensitive products, like beer. Refillable bottles can also be conveniently manufactured with PEN or PEN copolymers or blends. The market growth of PEN was limited at the beginning, and partially continues to be, by the availability and cost of the monomer (DMNDC). The 1999 annual production, that is carried out in PET plants, can be estimated at 30,000 t.

Poly(1,4-butylene terephthalate). PBT [24968-12-5] is a semicrystalline polyester having a T_g of 52°C and a T_m of 223°C. Due to the very high crystallization rate it is not generally possible to obtain PBT in the amorphous state. For the same reason, PBT can be injection molded without the need of nucleating agents.

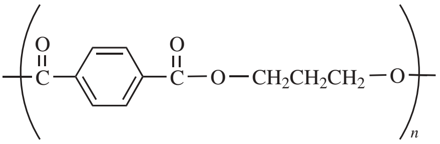


Poly (1,4-butylene terephthalate)

PBT has good impact resistance and toughness combined with good chemical resistance (toward water, steam, chlorine, and chemicals). Its coefficient of friction and wear are low. The strength and stiffness are slightly inferior to those of PET. The shrinkage is anisotropic, so manufacturing tolerances cannot be too tight.

Typical end uses are automotive parts—including underhood—(housings and connectors, distributor caps, air-blower deflectors), power tool casings, food and fuel pump components, valves and valve bodies, gears, and cams. Blends with PET (Valox, Enduran, GE Plastics) and PC (Xenoy, GE Plastics) have been developed. Valox shows improved performance at high temperature and is used in the electric industry (bobbins, switch components, connectors) and for medical and food applications. PBT/PC blends have outstanding resilience and are used for auto bumpers and other automotive applications. Worldwide consumption of PBT was ∼420,000 tons in 1999 (25).

Poly(trimethylene terephthalate). Like PET and PBT, PTT is based on terephthalic acid as the diacid monomer component, but the diol monomer is 1,3-propanediol, which has a number of carbon atoms intermediate between ethylene glycol and 1,4-butanediol. Because of the molecular structure, PTT properties (thermal and mechanical) are between those of the two other polyesters. PTT competes with PBT in engineering polymer applications (eg, snap fit parts) but finds its main use in fibers. Production in 1999 was ∼20,000 t/yr, under the trade name of Corterra (Shell), with a planned expansion to 110,000 t/yr (26).

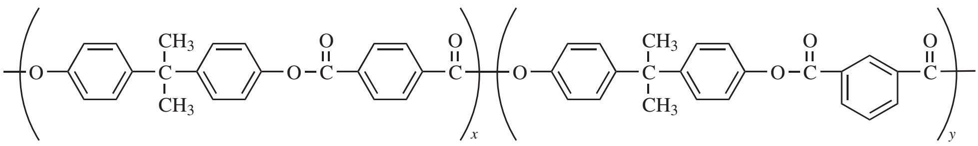


1,4-Butanediol

Poly(ethylene-co-1,4-cyclohexylenedimethylene terephthalate). PETG is commercialy available under different trade names: Eastar (Eastman Chemicals), Vivak, Ultros. Its structure is similar to PET, but part of the ethylene glycol units have been substituted with 1,4-cyclohexylenedimethylene units. It is a clear amorphous resin with a T_g of 82°C having good toughness (up to -40°C), a fair resistance to organic solvents and chemicals, and excellent gas barrier properties. Extrusion blow molding is the most convenient technique for the manufacture of liquid containers. Sheets, which exhibit an impact strength 10 times that of acrylics, can also be obtained by extrusion. The high transparency and gloss of PETG provides an excellent alternative to polycarbonate, at a lower cost. Other advantages are the good blendability and printability, superior in some cases to acrylics.

Applications are in store fixtures (shelf dividers, racks), material handling and storage, food packaging, medical lab equipment, interior sign and price markers, graphic devices, and industrial components.

6.3. Polyarylates. This class of fully aromatic polyesters (polyarylates) includes a large number of polymeric structures that differ for the diacid and the difunctional phenol used in the synthesis. However, in spite of the wide range of properties that can be attained by tailoring the structure through the variation of the monomeric units, the only commercial polyarylate is that formed by bisphenol A and isophthalic/terephthalic acid derived units.

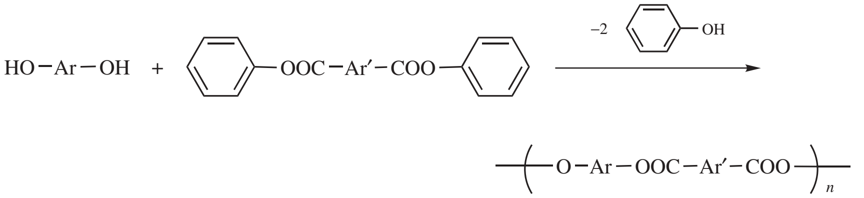


In recent years, two products dominated the market of polyarylates: Durel, produced for a while by Ticona and U-Polymer, produced by Unitika and commercialized in the United States by Amoco. Whereas the Unitika polymer has a isophthalic/terephtalic acid ratio of ~1, Durel has a higher isophthalic acid content (>80%).

Diphenols are scarcely reactive toward aromatic diacids (27), and only low molecular weight polymers can be achieved through their direct reaction. To increase reactivity and promote polycondensation, at least one of the monomers has to be properly activated. Thus, two processes have been conceived for polyarylate synthesis: interfacial polycondensation (preferred over the solution process) between diacyl chlorides and alkali metal diphenate (eq. 4) and the high temperature metal-catalyzed melt polycondensation between either diphenol acetates and aromatic diacids (eq. 5), or diphenols and diacid diphenyl esters (eq. 6).

$$\text{NaO}-\text{Ar}-\text{ONa} + \text{ClOC}-\text{Ar}'-\text{COOH} \longrightarrow -\!\!\left(\text{O}-\text{Ar}-\text{OOC}-\text{Ar}'-\text{COO}\right)_{n}\!\!- \qquad (4)$$

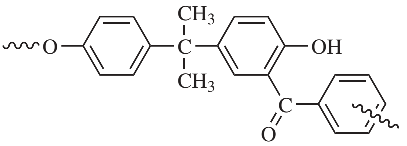
$$\text{CH}_3\text{COO}-\text{Ar}-\text{COOCH}_3 + \text{HOOC}-\text{Ar}'-\text{COOH} \xrightarrow{-2\ \text{CH}_3\text{COOH}} -\!\!\left(\text{O}-\text{Ar}-\text{OOC}-\text{Ar}'-\text{COO}\right)_{n}\!\!- \qquad (5)$$



(6)

Ardel polyarylate resins based on isophthalic/terephthalic acids are amorphous, transparent, amber materials, whose properties are dependent on the diacids ratio (generally not far from 1:1). They are tough resins, with excellent flexural recovery and high rigidity, exhibiting a mechanical and electrical behavior similar to polycarbonate but better heat resistance, as shown by the high value of HDT. Properties are reported in Table 10.

A characteristic of polyarylate is its inherent uv stability, which arises from the spontaneous formation of a protective surface layer of uv-absorbing *o*-hydroxybenzophenone structural units (see below).



This chemical modification is promoted by sunlight and does not involve the bulk of the polymer. In this way, mechanical properties are not only unaffected, but, unlike PC, are also maintained after prolonged weathering. Polyarylates have a fair heat stability but a low hydrolytic stability; for this reason, they must be carefully dried before processing. Solvent resistance is fair. Processing techniques for PAR are the same as those used for polycarbonate. The material does not exhibit outstanding moldability, but it can be easily shaped into rods, sheets, films, and slabs. PAR can be blended with other resins, such as polyamides to increase the solvent resistance, or poly(phenylene sulfide) to improve the dielectric properties and hydrolytic stability. Thermomechanical properties of poly(ethylene terephthalate) and poly(butylene terephthalate) can be

Table 10. **Properties of Polyarylates**

Property	ARDEL D-100
density, g/mL	1.21
flammability	V0
oxygen index (LOI), %	36
refractive index	1.64
water absorption, 24 h, 23°C	0.26
dielectric constant, 1 MHz	1.64
dielectric strength, kV/mm	0.4
dissipation factor, 1 kHz	0.004
volume resistivity, 23°C, dry, $\Omega \cdot$cm	2×10^{14}
HDT at 1.8 MPa, °C	174
thermal conductivity, 23°C, W/(m $\cdot$ K)	0.21
elastic modulus, GPa[a]	2.1
tensile strength, MPa[b]	70
flexural modulus, GPa[a]	2.1
flexural strength, MPa[b]	75
compressive strength, MPa[b]	84
elongation at break, %	60
notched Izod, 3.2 mm, J/m[c]	205
hardness (Rockwell)	R125

[a] To convert GPa to psi, multiply by 145,000.
[b] To convert MPa to psi, multiply by 145.
[c] To convert J/m to lbf $\cdot$ ft/in., divide by 53.38.

improved by melt mixing with a polyarylate and controlling the degree of transesterification of the polyesters chains.

Typical applications are as automotive trim and headlight housings, exterior lighting, solar energy components, semiconductor components, appliance parts, snap lock connectors, and fire helmets. The world production remained very low, of the order of 1000 t/yr.

6.4. Liquid-Crystal Polyesters. Among the polyesters, a unique class of wholly aromatic copolymers exhibits the peculiar behavior of mesomorphism or liquid crystallinity. Liquid-crystal polymers (LCPs) are rodlike macromolecules that are oriented in the melt state and organized into a para-crystalline state as a consequence of their structure. Such orientation is further promoted by shear. On cooling, the strong orientation is preserved and the resulting material exhibits an exceptionally high stiffness and strength. These copolyesters are obtained by the catalyzed melt polycondensation of monomers derived from biphenols (eg, 4,4′-biphenol), aromatic diacids (eg, terephthalic acid), and/or aromatic hydroxyacids (eg, *p*-hydroxybenzoic acid, 6-hydroxy-2-naphthoic acid). Either the carboxylic or the hydroxylic function needs to be activated in order to reach high molecular weights; usually the (di)acetate ester of the (bi)phenol is used as starting monomer (28,29).

LCPs were introduced on the market in 1984. Several different copolyesters and also copolyesteramides have been developed and some of them have also been industrially produced at some stage. At present, three main families of resins are available: Xydar (developed by Amoco Performance Products, now BP Amoco), Vectra (developed by Hoechst Celanese Co. and now commercialized by Ticona), and Zenite (Du Pont). Xydar resins are copolyesters based on biphenol, whereas Vectra A resins contain naphthalene units that impart the rod-like structure; Vectra B resins are copolyesteramides. The resins are generally opaque and brown or cream-colored.

Mechanical properties of LCPs are strongly dependent on the orientation and, thus, on the processing parameters adopted during molding. Tensile strength and elastic modulus is extremely high in the flow direction. Mechanical properties are retained after exposure to radiation and weathering. Flame resistance is inherent (UL 94 V-0 rating), dielectric strength is good, and dimensional stability is excellent. The resistance to aggressive solvents, ie, acids, bases, polar organic solvents, chlorinated solvents, and aromatic hydrocarbons, is very high. Properties are significantly lost only after prolonged contact with concentrated sulfuric acid, boiling alkali, or high temperature steam. Properties of some LCPs are reported in Table 11.

Processability is easy due to the very low melt viscosity, but high temperatures must be applied (285–340°C for Vectra and 370–450°C for Xydar). Thin walls and complex paths are easily filled; low warpage allows manufacturing of high precision parts, where close tolerances are required. Typical applications are as electric and electronic components (such as connectors) and medical devices. Also, aerospace applications can be conceived.

In 1998, the world consumption of LCPs was over 10,000 t, in comparison with a global capacity of 19,000 t (30).

Table 11. **Properties of Some LCP Resins**

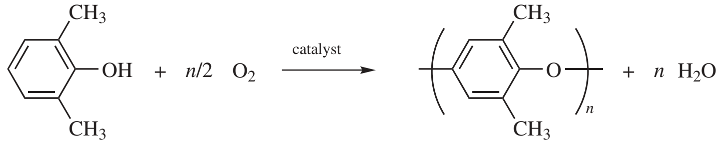
Property	Vectra A	Vectra B	Xydar (30% GF)
density, g/mL	1.40	1.40	1.6
flammability	V0	V0	V0
oxygen index (LOI), %	45	50	
water absorption, 24 h, 23°C, %	0.02	0.03	<0.1
dielectric constant, 1 MHz	3.0	3.1	3.9
dielectric strength, kV/mm	47	37	39
dissipation factor, 1 kHz	0.02	0.01	
volume resistivity (23°C, dry), $\Omega \cdot$cm	10^{15}	10^{15}	
HDT at 0.45 MPa, °C	220		
at 1.8 MPa, °C	235	235	271
specific heat, J/(kg · K)	1.0	1.0	
thermal conductivity, 23°C, W/(m · K)	0.18	0.18	
thermal expansion coefficient, K^{-1}	$-5–75\times10^{-6}$	$-5–40\times10^{-6}$	
upper working temperature, °C	200–220		220
elastic modulus, GPa[a]	2–10	2.5–20	15.8
tensile strength, MPa[b]	55–165	87–188	135
flexural modulus, GPa[a]	7.4		13.5
flexural strength, MPa[b]	146		172
compressive strength, MPa[b]	70	84	
elongation at break, %	3	1.3	1.6
Izod, 3.2 mm (unnotched), J/m[c]	520	415	96
hardness (Rockwell)	M60	M100	
abrasion (10^3 cycles), mg	56	56	

[a] To convert GPa to psi, multiply by 145,000.

[b] To convert MPa to psi, multiply by 145.

[c] To convert J/m to lbf · ft/in., divide by 53.38.

6.5. Poly(phenylene ether). The most common and commercially available poly(phenylene ether) is poly(2,6-dimethyl-1,4-phenylene ether) (trade name PPO, General Electric Co.), obtained through oxidative coupling polymerization of 2,6-dimethylphenol in the presence of catalyst (eq. 7). It was first commercialized in 1965. GE plastics remained the only producer until the early 1980s, when other producers like BASF, Hüls, and some Japanese companies (viz, Mitsubishi) entered the market.



(7)

Other phenol monomers (2,6-diphenylphenol, 2-methyl-6-phenylphenol) have been used to prepare homo- or copolymers, but they are not produced any more because they have never had a great market share, and the only important commercial poly(phenylene ether) remains PPE. Catalysts used in industrial plants are based on copper(I)–amine complexes; a toluene solution of 2,6-dimethylphenol reacts with oxygen under conditions suited to avoid formation of explosive mixtures. The reaction is interrupted at the desired polymerization degree by adding nitrogen to the system, removing the copper catalyst with a chelating agent in water solution, and precipitating the polymer from the organic solution.

The T_g of poly(2,6-dimethyl-1,4-phenylene ether) is ~210°C. It has a low crystallinity of ~10%, with a melting point ~265°C. Typical weight average molecular weight is 35–45,000, with a polydispersity index M_w/M_n slightly >2. Neat poly(2,6-dimethyl-1,4-phenylene ether) is very difficult to process due to its high melting temperature, high melt viscosity, and aptitude to oxidation. For this reason, the neat polymer is scarcely used in practice. On the other hand, poly(2,6-dimethyl-1,4-phenylene ether) is miscible over the entire range of composition with polystyrene (PS). The PPE–PS blends (trade name Noryl, General Electric Co.) present an excellent combination of properties, as reported in Table 12. Blends with polystyrene homopolymer are somewhat brittle; to improve the toughness, blends with high impact polystyrene have been developed. The Noryl EF alloy family is the most recent development in this class of materials, consisting of PPO-expandable polystyrene beads.

Noryl resins are cream or pale gray colored, opaque materials exhibiting good flexural fatigue properties, low humidity absorption (as low as 0.07%), and an excellent melt-flow behavior that allows a wide processing temperature range. Dimensional stability at elevated temperatures and dielectric properties at any frequency are also outstanding. The resistance to aromatic and chlorinated solvent is poor and limits some applications. Filled, pigmented, and flame-retarded grades (containing phosphorus-based halogen-free additives) are available.

Noryl blends are suited to injection molding processes on conventional machines equipped with general purpose screws. The high melt strength allows fabrication of cellular products through foam molding with gas-injection (ie, nitrogen) or chemical blowing agents. Also, blow molding is possible due to the

Table 12. **Properties of PPE Modified with PS**

Property	PPE–PS	PPE–PS (30% GF)
density, g/mL	1.06	1.29
flammability	HB	HB
oxygen index (LOI), %	20	26
water absorption, 24 h, 23°C, %	0.1–0.5	0.06–0.33
dielectric constant, 1 MHz	2.7	3.1
dielectric strength, kV/mm	16–20	15
dissipation factor, 1 kHz	0.004	0.01
volume resistivity, 23°C, dry, $\Omega \cdot$cm	2×10^{16}	10^{17}
HDT at 0.45 MPa, °C	137	165
specific heat, J/(kg $\cdot$ K)		1.0
thermal conductivity, 23°C, W/(m $\cdot$ K)	0.22	0.28
thermal expansion coefficient, K^{-1}	60×10^{-6}	$25–30\times10^{-6}$
upper working temperature, °C	80–120	90–160
elastic modulus, GPa[a]	2.5	8.0–9.0
tensile strength, MPa[b]	55–65	100–120
elongation at break, %	50	2–3
notched Izod, 3.2 mm, J/m[c]	200	80
hardness (Rockwell)	M78/R115	L108
abrasion (10^3 cycles), mg	20	35

[a] To convert GPa to psi, multiply by 145,000.

[b] To convert MPa to psi, multiply by 145.

[c] To convert J/m to lbf $\cdot$ ft/in., divide by 53.38.

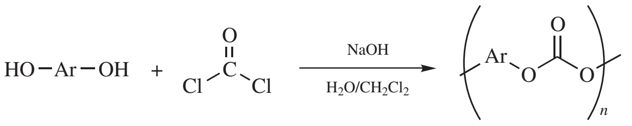
melt strength to produce large parts. Finally, Noryl sheets can be easily extruded and thermoformed.

Applications include internal appliances components, structural components in office products, housings (personal computers and printers), automotive coil forms, instrument parts and wheel covers, and electrical switch boxes and connectors. Noryl EF beads can be used in car interior applications, eg, door paddings, instrument panels, knee bolsters, and pillar trims.

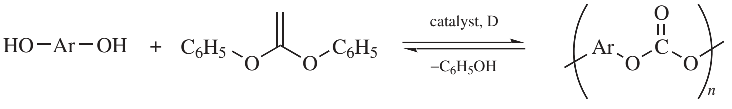
Another important family of PPO blends is Noryl GTX. They are PPO–polyamide blends, also used in the automotive market (mainly bodypanels and under-the-hood). Blends with other thermoplastic (polycarbonate, ABS) have been experimented with to bring the color stability to the level of other housing polymeric materials, but with poor success. Properties of various PPO-containing blends are compared elsewhere (9) (see Polyethers, aromatic).

Worldwide consumption of PPE blends was ~305,000 t in 1998 (31).

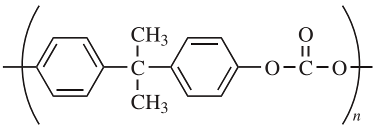
6.6. Polycarbonate. Polycarbonates (PCs) are obtained industrially by interfacial polycondensation of phosgene and aromatic diols (see eq. 8 for the typical molecular formula) in chlorinated solvent (usually methylene chloride)/aq NaOH system (32); monofunctional phenols are typically used as chain terminating agents and molecular weight controllers. The sodium bisphenolate attacks the phosgene molecule at the water–methylene chloride interface, eliminating sodium chloride and the polymer chain grows in the organic solvent. The latter is separated from the reaction mixture at the end of the reaction and evaporated. The polymer, recovered in the form of powder, is usually melted and pelletized; some companies supply polycarbonate in powdered form. The solution process, which was the first one commercially pursued, has been abandoned.


(8)

More recently a melt-phase process has been developed based on the transesterification reaction of diphenyl carbonate with aromatic diols (eq. 9). Due to the pressure of environmental issues connected with the use of phosgene and chlorinated hydrocarbons, the melt process will probably obtain increasing attention in the future (33,34).


(9)

The most widespread polycarbonate is bisphenol A polycarbonate (BPA–PC), due to the large commercial availability of bisphenol A; in some applications where higher heat distorsion, improved optical properties or flame resistance, greater weatherability are required, other aromatic polycarbonates based on different diphenols or containing diacid comonomers (isophthalate or terephthalate) have been proposed (35), but their market shares (<100 t/yr for polycarbonate–polyesters) are far from reaching the BPA–PC volumes (>1 million tons) (36).


Bisphenol-A Polycarbonate (BPA–PC

BPA polycarbonate was first commercialized at the end of the 1950s; Bayer AG (trade name Makrolon), General Electric (trade name Lexan), Dow Chemical and Mitsubishi Chemical Industries are the main commercial supplier of polycarbonate resins, both BPA–PC and modified grades. BPA–PC is a colorless crystalline polymer, but due to its extremely low crystallization rate, the commercial pelletized product is amorphous; it has an excellent moldability, structural strength, and toughness, even at low temperatures (down to −40°C) and a high transparency. Other outstanding properties are the broad temperature resistance and the ease of colorability and compounding with inorganic fillers and other polymers (eg, ABS). Properties are reported in Table 13. Its drawbacks are the poor chemical resistance (to alkali, hydrocarbons, ketones, and halogens), the sensitivity to environmental stress cracking, and the poor wear and fatigue behavior.

Table 13. **Properties of PC Resins**

Property	Neat	20% GF
density, g/mL	1.2	1.34
flammability	V0–V2	V1/V0
oxygen index (LOI), %	25–27	25–36
refractive index	1.585	
water absorption, 24 h, 23°C, %	0.1	0.1
dielectric constant, 1 MHz	2.9	3.2
dielectric strength, kV/mm	15–67	35
dissipation factor, 1 kHz	0.01	0.007
volume resistivity, 23°C, dry, $\Omega \cdot$cm	10^{14}–10^{16}	$>10^{15}$
HDT at 0.45 MPa, °C	140	147
specific heat, J/(kg · K)	1.2	1.13
thermal conductivity, 23°C, W/(m · K)	0.19–0.22	
thermal expansion coefficient, K^{-1}	$66–70 \times 10^{-6}$	$30–40 \times 10^{-6}$
upper working temperature, °C	115–130	115–165
elastic modulus, GPa[a]	2.3–2.4	6
tensile strength, MPa[b]	55–75	90
compressive strength, MPa[b]	>80	
elongation at break, %	100–150	3
notched Izod, 3.2 mm, J/m[c]	600–850	100
hardness (Rockwell)	M70	M91
abrasion (10^3 cycles), mg	10–15	

[a] To convert GPa to psi, multiply by 145,000.

[b] To convert MPa to psi, multiply by 145.

[c] To convert J/m to lbf · ft/in., divide by 53.38.

Processing can be carried out through the traditional transformation machines, such as extruders and injection molding machines. For extrusion blow-molding processes, special grades having high melt strength have been developed: to achieve this objective, low amounts of polyfunctional monomers, such as trimellityl trichloride, are incorporated in the polymer chain. On the other hand, high melt flow polycarbonate grades are needed to produce some complex or high precision parts or to reduce process cycle times (37). PC based polymer blends that are commercially available are mainly PC–ABS, PC–polyesters, PC–ASA, PC–polyetherimide; all these blends may be processed with the same machines used for pure PC.

Polycarbonate finds many applications in substitution of glass, steel, wood, and other materials (38,39). Some examples of applications are in architectural glazing (eg, for roofings), for helmets and safety shields manufacture, lighting devices, housings, kitchenware (microwaveable), compact disks, and sterilizable medical devices (syringes, catheters etc). PC blends are used for computer housings and panels (PC–ABS), in the automotive industry (PC–polyesters and PC–ASA), in construction (PC–ASA). PC–polyetherimide is especially used where higher heat resistance or low flammability are required (automotive reflectors, aircraft interiors).

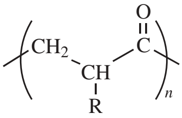
Glass-filled PC, which exhibits improved stiffness and creep, is used for electrical enclosures manufacture. Carbon filled PC is used for conductive film manufacture. In 1998 the annual world consumption reached 1.2 million tons, including 15% of PC blends (40).

6.7. Aliphatic Polyketones.

Aliphatic polyketones (PK) contain ketone groups along a main aliphatic chain. As engineering polymers, only perfectly alternating olefin/CO copolymers can be considered; polymers containing <50% CO groups are photodegradable and consequently not suitable for engineering applications.

Perfectly alternating ethylene–CO copolymers are obtained in rather severe conditions (typically, 100–200°C at a total gas pressure of 100–200 MPa) using complex catalyst systems based on groups 8–10 (VIII) transition metals. Most of the patented catalysts are based on Pd complexes with ligands ranging from acetate to 1,3-bis(diphenylphosphine)propane (41,42).

The ethylene–CO copolymer is a white, highly crystalline powder. The DSC curve shows a T_g around room temperature (25–35°C) and a T_m of 260°C. Because the thermal stability of the polymer is not fully guaranteed near the melting temperature, some percent (5–10% mol) of propylene is introduced randomly in the chain as a third monomer. Its presence causes the lowering of the T_m down to 200–220°C, without affecting the thermal stability, thus rendering the material processable. Consequently, the molecular structure of aliphatic polyketones can be sketched as follows:



where R=H or CH_3 (~10% of cases). Polyketones have been introduced at the industrial level by Shell Chemical in 1994, under the trademark Carilon. A plant with a starting capacity of 10 kt/yr ran at Carrington (UK) up to January 2000, when the stop of production was announced. BP Amoco is the follower in the field, but its Ketonex is only at the pilot plant stage.

The properties of aliphatic polyketones derive from their tight packing, favored by hydrogen bonds between chains. They are considerably rigid, and exhibit excellent elastic recovery, good sliding and abrasion properties, and impact resistance at low temperature. The peculiar molecular and crystalline structures confer to such materials a high hydrolytic stability, good chemical resistance against dissolution, degradation and swelling, and finally excellent gas permeation resistance. Properties are reported in Table 14.

Aliphatic polyketones found application mainly in automotive (snap-on assemblies, spring elements, fuel tanks and lines, grabs, clamps, and clips), electrical and electronics (connectors and switch gears), and medical fields (disposable breathing systems, test tube racks). Glass-fiber reinforced and lubricated grades have been offered on the market.

6.8. Poly(ether ketones).

Poly(ether ketones) (PEK) include a variety of aromatic high performance polymers characterized by the presence of ether bridges and ketone groups in the main chain, linking together arylene groups. Currently, the only product manufactured worldwide is Victrex PEEK, launched

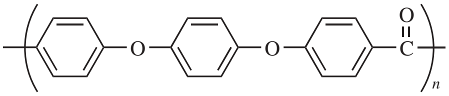
Table 14. **Properties of Aliphatic Polyketones**

Property	Neat	20% GF
density, g/mL	1.24	1.60
flammability	HB	V0
oxygen index (LOI), %	21	
water absorption, 24 h, 23°C, %	0.5	0.45
dielectric strength, 1 mm, kV/mm	18	
volume resistivity, 23°C, dry, $\Omega \cdot$ cm	10^{13}	10^{13}
glass-transition temperature (T_g), °C	15	15
melting temperature (T_m), °C	220	220
HDT at 0.45 MPa, °C	210	210
at 1.8 MPa, °C	100	
thermal expansion coefficient, K^{-1}	1.1×10^{-4}	
elastic modulus, GPa[a]	1.4	8
flexural modulus, GPa[a]	1.4	
elongation at break, %	350	3
notched Izod, 3.2 mm, J/m[b]	20	112
hardness (Rockwell)	R 105	
friction coefficient	0.2	
melt flow index, g/10 min	2.2–5.4	

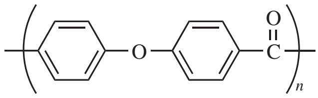
[a] To convert GPa to psi, multiply by 145,000.

[b] To convert J/m to lbf · ft/in., divide by 53.38.

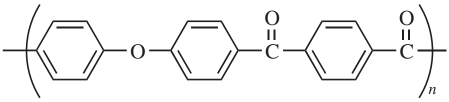
by ICI in 1978 and produced annually in an amount of ~ 2000 t (43). PEEK has the following chemical structure:



and is believed to be produced by polycondensation of 4,4′-difluorobenzofenone and a K-derivative of bisphenol (44). The reaction is carried out at high temperature (up to 300°C) in a high boiling solvent like diphenylsulfone. It is produced in batchs, with rather high production cost. Similar products, bearing various sequences of ether and ketone groups bridging together arylene rings can be synthesised in similar ways (44). Some of these structures have been commercialized.



PEK



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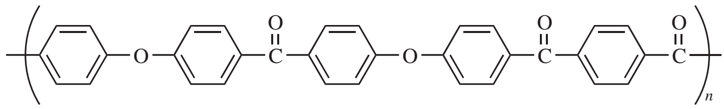


PEKEKK

Table 15. **Properties of PEEK**

Property	Neat	30% GF
density, g/mL	1.32	1.50
flammability	V0	V0
oxygen index (LOI), %	35	
water absorption, 24 h, 23°C, %	0.5	0.1
dielectric constant, 10 kHz	3.2	3.7
dielectric strength, 1 mm, kV/mm	24	
dissipation factor, 1 MHz	0.003	0.004
volume resistivity, 23°C, dry, $\Omega \cdot$cm	10^{16}	10^{16}
glass-transition temperature (T_g), °C	143	143
melting temperature (T_m), °C	334	334
HDT at 0.45 MPa, °C	>260	
at 1.8 MPa, °C	160	315
specific heat capacity, J/(kg · K)	320	
thermal conductivity, 23°C, W/(m · K)	0.25	
thermal expansion coefficient, K^{-1}	$50–110\times10^{-6}$	
upper working temperature, °C	250	
elastic modulus, GPa[a]	3.7–4.4	9.7
tensile strength, MPa[b]	70–110	156
flexural modulus, GPa[a]	3.7	
flexural strength, MPa[b]	170	
elongation at break, %	50	2
notched Izod, 3.2 mm, J/m[c]	83	90
hardness (Rockwell)	M105	

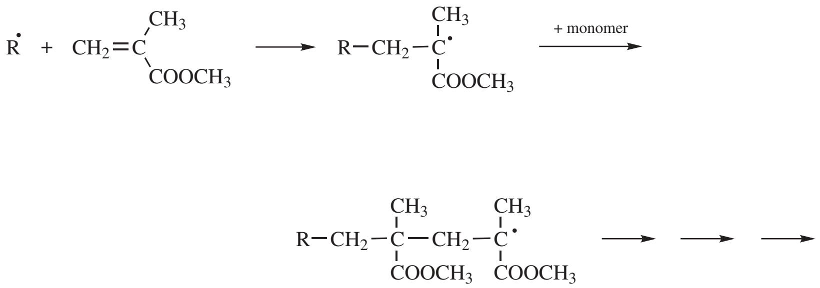
[a] To convert GPa to psi, multiply by 145,000.
[b] To convert MPa to psi, multiply by 145.
[c] To convert J/m to lbf · ft/in., divide by 53.38.

The first polymer of this group (PEK) was commercialized by Raytheon in the 1970s under the trade name of Stilan. Equivalent materials were commercialized by Hoechst Celanese and Amoco, while PEKEKK and PEKK were commercialized by BASF and Du Pont, respectively. Their T_g values are in the range 150–165°C, while T_m values are in the range 370–390°C. PEEK has a pale amber color, is usually semicrystalline and opaque. It has excellent thermal, mechanical, and tribological resistance and is insoluble in the most of solvents, with the exception of strong protonating acids like concentrated H_2SO_4 and HF. It is also soluble >220–230°C in benzophenone and Cl-naphthalene. Properties of PEEK are reported in Table 15.

A review (45) and a book (46) on the chemistry and properties of poly(ether ketones) has been recently published. PEEK is present in the market also in reinforced grades (glass or carbon fibers) as well as in yarns or in powder for coatings. Fibers are marketed by ICI under the trade name Zyex. PEEK found application in the transport, teletronics, and aerospace sectors, with the fabrication of injection molded engineering components and circuit boards. Recently, PEEK materials also found some space in medical technologies. For this purpose, their biological and toxicological safety has been certified (43).

6.9. Acrylic Resins. Poly(methyl methacrylate) (PMMA) is the only industrial product based on acrylic resins that has found rigid applications. The production started at Darmstadt in Germany in 1927, under the leadership of Otto Röhm, cofounder of Röhm & Haas. The first application was as an intermediate sheet in safety glass, followed during the Second World War in vacuum formed aircraft canopies.

PMMA is made industrially by four different processes, ie, bulk casting, bulk polymerization, suspension polymerization and emulsion polymerization, all based on free-radical chemistry (see METHACRYLIC POLYMERS). The reaction scheme follows the four classical basic steps of free-radical polymerization, ie, initiation, propagation, chain transfer, and termination. Initiation consists in the generation of free radicals from thermolysis of peroxy compounds or azo compounds (like 2,2′-azobisisobutyronitrile, AIBN).Then propagation follows:



$$\dot{R} + CH_2{=}C(CH_3)(COOCH_3) \longrightarrow R{-}CH_2{-}\dot{C}(CH_3)(COOCH_3) \xrightarrow{+\text{ monomer}}$$

$$R{-}CH_2{-}C(CH_3)(COOCH_3){-}CH_2{-}\dot{C}(CH_3)(COOCH_3) \longrightarrow \longrightarrow \longrightarrow$$

Chain transfer by means of long-chain alkyl mercaptans allows control of molecular weight. Termination occurs by head-to-head combination, or by disproportionation, consisting of the transfer of a hydrogen atom from a growing chain to another.

Only bulk casting and polymerization are suitable for rigid applications, whereas suspension polymerization is primarily used for obtaining molding powders and ion exchange resins. Emulsion polymerization is suitable for nonengineering applications of interest for paint, paper, textile, and leather industries. Finally, solution polymerization gives products for coatings, adhesives, impregnates, and laminates.

Initiation is favored by thermolysis of peroxides or by redox reaction (mainly in the emulsion process). The tacticity of PMMA depends on the method and conditions of polymerization and can be accurately controlled (47). T_g ranges from 45°C for isotactic PMMA to 110°C for atactic and 160°C for syndiotactic PMMA. Commercial materials contain different tacticity percentages and consequently have an intermediate T_g.

PMMA exhibits excellent optical properties, clarity and transparency, and it is used widely as a glass substitute in many sectors. Because of its high refractivity index, sophisticated applications in advanced sectors (optical lenses, prisms, fibers, etc) are also possible. The high surface gloss and good scratch resistance of PMMA favored its penetration in the sanitary ware field. By the addition of up to 60% of inorganic filler (aluminum hydroxide, calcium carbonate, etc), synthetic marble-like resin products can be are prepared. Properties of PMMA are reported in Table 16.

Molecular weights of commercial materials, regulated by chain-transfer agents, are of 70,000–200,000 Da for molding and extrusion applications and 1 million Da and more for cast sheets. Commercial materials often contain a

Table 16. **Properties of PMMA**

Property	PMMA
density, g/mL	1.19
flammability	HB
oxygen index (LOI), %	17–20
refractive index	1.49
dielectric constant, 1 kHz	3.0
dielectric strength, 1 mm, kV/mm	15
dissipation factor, 1 kHz	0.014
volume resistivity, 23°C, dry, $\Omega\cdot$cm	1×10^{14}–6×10^{17}
glass-transition temperature (T_g), °C	104
HDT at 0.45 MPa, °C	107
at 1.8 MPa, °C	96
specific heat capacity, J/(kg · K)	0.452
thermal conductivity, 23°C, W/(m · K)	0.003
thermal expansion coefficient, K^{-1}	8.3×10^{-5}
upper working temperature, °C	82–94
elastic modulus, GPa[a]	3.1
tensile strength, MPa[b]	72
flexural modulus, GPa[a]	3.1
flexural strength, MPa[b]	110
compressive strength, MPa[b]	124
elongation at break, %	4.9
hardness (Rockwell)	M93

[a] To convert GPa to psi, multiply by 145,000.

[b] To convert MPa to psi, multiply by 145.

limited percentage of comonomers like methyl acrylate, ethyl acrylate, or acrylonitrile, with the aim of increasing chain flexibility and toughness. Melt viscosity and T_g are correspondingly reduced.

In the late 1980s, Röhm & Haas introduced on the market a PMMA modified by *N*-methylamine imidization, having a higher T_g (150–180°C, depending on the imidization degree) and sold under the trade name of Kamax (9).

The worldwide capacity of PMMA stands ~1,600,000 t (48).

7. Sulfur-Containing Polymers

7.1. Poly(phenylene sulfide).

Poly(phenylene sulfide) (PPS) is obtained by condensation polymerization of *p*-dichlorobenzene with Na_2S, operating in a dipolar aprotic solvent like *N*-methylpyrrolidinone or *N*-methylcaprolactam (eq. 10).

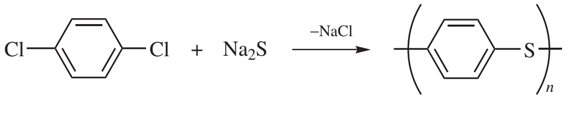


Table 17. **Properties of PPS Resins**

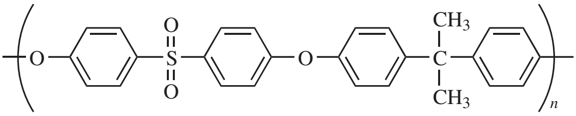
Property	Neat	30% GF
density, g/mL	1.35	1.60
flammability		V0
oxygen index (LOI), %		46
water absorption, 24 h, 23°C, %	0.01	0.02
dielectric constant, 1 MHz		3.8–4.2
dielectric strength, kV/mm		27
dissipation factor, 1 kHz	0.001	
volume resistivity, 23°C, dry, $\Omega\cdot$cm	10^{16}	$>10^{13}$
glass-transition temperature (T_g), °C	90	90
melting temperature (T_m), °C	280	280
HDT at 0.45 MPa, °C	111	
at 1.8 MPa, °C		265
thermal conductivity, 23°C, W/(m · K)		0.29–0.45
thermal expansion coefficient, K^{-1}		$22–45\times10^{-6}$
upper working temperature, °C		200–260
elastic modulus, MPa	3.7	11.7
tensile strength, MPa		124–160
elongation at break, %	4	1.9
notched Izod, 3.2 mm, J/m		80
hardness (Rockwell)		R123

To convert MPa to psi, multiply by 145.To convert J/m to lbf · ft/in., divide by 53.38.

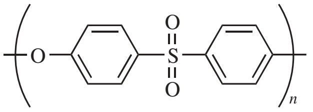
The polymer chain consists of alternating benzene rings and sulfur bridges. Because branching is uncommon, crystallinity is generally high, and depends on its thermal history. The first production process was set up by Phillips Petroleum in 1953; the low molecular weight of the product was increased by postreaction cross linking. Thirty years later, processes capable of producing linear PPS having the desired molecular weight were pioneered by Kureha in Japan. Both types (linear and crosslinked) are produced today, for a total installed capacity of 35,000 t in 1999 (49). Thus, PPS is actually the most significant high performance polymer (in terms of tonnage). Due to the lack of properties shown by the neat resin (particularly low T_g and toughness) it is commercialized only as a filled or reinforced compound. Properties are reported in Table 17 for the neat resin and 30% GF filled.

PPS is commercialized by a half-dozen producers, mostly in Japan (Toray, Kureha, Dainippon). Phillips (trade name Ryton) and Ticona (trade name Fortron) are the main producers. PPS is mainly used for injection molding. Due to its excellent melt viscosity, monofilaments, multifilaments, fabrics, and fibers are also produced for technical uses. PPS is applied for precision mechanical parts, electrical components, and components for use in aggressive environments. Among manufactured parts are engine components, valves, high pressure nozzles, fuel manifolds, exterior light reflectors, coil bobbins, and flow measuring units for hot and cold water.

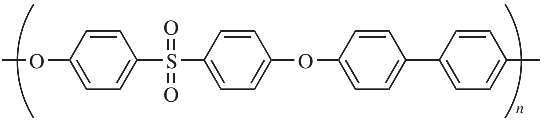
7.2. Polysulfones. Polysulfones are a group of aromatic resins containing sulfone and ether linkages. The commercially relevant structures are as follows, and also include PES and PAS:



PSU

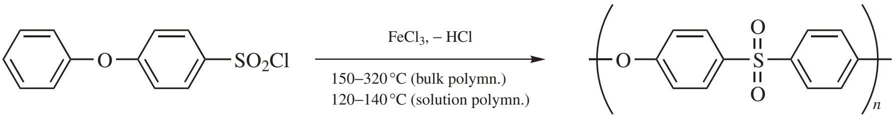


PES



PAS

The first commercial PSU resin was Udel in 1966, followed in 1972 by Radel, a PAS resin. Both were introduced its the market by Union Carbide. In 1986, the business was acquired by Amoco. The first PES resins (Victrex PES, now withdrawn from the market) was marketed by ICI in 1971. They are made by batch processes employing one of two main methods, ie, a polysulfonylation process (Friedel–Craft electrophilic aromatic substitution) or nucleophilic aromatic substitution of activated aromatic dihalides. The first route (1) was used in the early industrial plants, but it is at present almost abandoned in favor of the polyetherification route (2). Representative synthesis reactions are as follows:



Amorphous polymers are generally obtained, yellowish in color and transparent. Molecular rigidity is conferred by sulfone units, while ether links give some molecular flexibility, useful in processing. PES materials are more similar to PEI, while PSU materials have a different property profile. A survey on synthesis and properties of polysulfones has been published (50). Properties of representative commercial grades of PSU, PES, and PAS are reported in Table 18.

World consumption in 1998 was ~20,000 t, 70% of this was constituted by PSU (51). Applications are mainly in the electrical and electronics components, medical equipment requiring repeated sterilization procedures, household equipment, automotive applications, also under-the-bonnet. A very interesting application is in synthetic membranes, where polysulfones found market space for blood dialysis, water treatments, and food preparation, due to their superior separating capacity. Injection molding and extrusion grades are available for all polysulfone families. PSU and PES are available also as glass-reinforced grades (up to 30% by weight).

Table 18. **Properties of Polysulfones**

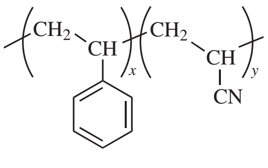
Property	PSU	PES	PAS
density, g/mL	1.24	1.37	1.29
flammability	V0	V0	V0
oxygen index (LOI), %		34–41	
refractive index	1.63	1.65	1.67
water absorption, 24 h, 23°C, %	0.3	0.4	0.37
dielectric constant, 1 MHz	3.03	3.54	3.45
dielectric strength, 1 mm, kV/mm	17	15	15
dissipation factor, 1 kHz	0.001	0.0022	0.0006
volume resistivity, 23°C, dry, $\Omega \cdot$ cm	5×10^{16}	10^{17}	
glass-transition temperature (T_g), °C	190	220	220
HDT at 0.45 MPa, °C	181	214	214
at 1.8 MPa, °C	174	204	207
thermal conductivity, 23°C, W/(m · K)	0.26	0.16	0.35
thermal expansion coefficient, K^{-1}	5.6	4.9	5.6
upper working temperature, °C	175	200	
elastic modulus, GPa[a]	2.48	2.65	2.34
tensile strength, MPa[b]	70	83	70
flexural modulus, GPa[a]	2.69	2.90	2.41
flexural strength, MPa[b]	106	111	91
elongation at break, %	>50	>50	>50
notched Izod, 3.2 mm, J/m[c]	69	85	693
hardness (Rockwell M or R)	R120/ M69	M127	

[a] To convert GPa to psi, multiply by 145,000.
[b] To convert MPa to psi, multiply by 145.
[c] To convert J/m to lbf · ft/in., divide by 53.38.

8. Nitrogen-Containing Polymers

Plastics based on styrene as a monomer include standard polystyrene (homopolymer), expanded polystyrene, high impact polystyrene, SAN and ABS. The first three hydrocarbon materials are considered commodity plastics. In contrast, the last two are regarded as engineering plastics because of their better performances and more demanding applications.

8.1. Styrene-Acrylonitrile Copolymer. The chemical structure of SAN is represented in below (see Acrylonitrile Polymers Survey and San).



SAN

SAN was initially put on the market in the mid-1930s, but the polymer became attractive for the end-users only after the development of the modern injection molding machines in the 1950s. The most widespread process for

SAN manufacture is bulk continuous polymerization, which in recent years has become overwhelming in importance for the emulsion and suspension processes. Bulk polymerization offers advantages in economics and product quality (mostly optical properties). In spite of the fact that styrene and acrylonitrile form an azeotropic system at 62 mol% (76 wt%) of styrene, the final composition of SAN copolymers can be varied by changing the composition of the feeding monomers. In this way it is possible, eg, to prepare polymer grades richer in acrylonitrile and having an improved resistance toward solvents. The typical properties given in the following are those of the azeotropic copolymer.

SAN is an amorphous, transparent resin having a T_g ~105°C. Its water absorption is ~0.3%.The polymer is not colored, but because the monomer units are randomly distributed along the chain, the occurrence of consecutive acrylonitrile monomer units causes a pronounced yellowing after prolonged exposure at high temperatures.

Outstanding properties are the high rigidity and hardness (up to 80°C), and good resistance to instantaneous and sustained loads and to cyclic temperatures. Chemical resistance is good, particularly against stress cracking. Heat resistance and dimensional stability are excellent, whereas the fatigue behavior is not satisfactory. Mechanical properties are affected by composition and, to a minor extent, by molecular weight. Tensile strength, flexural strength and impact strength reach a maximum (100 and 80 MPa and 28 J/m, respectively) around the azeotropic composition. SAN has a good resistance to apolar solvents (aliphatic hydrocarbons, greases, oils, petrol, fats), but a lower resistance to polar solvents than polystyrene; the nitrile groups are also sensitive to acids and alkali. Properties are reported in Table 19.

Several grades of SAN are available on the market: general purpose, easy-flow grade for thin walls and super clarity grade with high gloss. The main producers are Bayer, BASF, and Dow Chemical.

All conventional processing techniques are conveniently applied to SAN, which can be shaped easily into complex parts. SAN may absorb water (moisture absorption increase with acrylonitrile content), therefore it needs to be dried to avoid surface defects on part surfaces. Processing temperatures range typically from 200 to 270°C, with mold temperatures between 40 and 80°C. Some final properties (eg, tensile and impact strength and barrier properties) can be improved by controlling the orientation during processing.

SAN is used for the manufacture of housings for electronic and electric devices (computers, batteries), casings of domestic appliances (refrigerators), chair shells, domestic tools, instrument lenses, medical syringes, toys, etc. Glass-filled grades are used in automotive and appliances. Packaging materials (food, pharmaceuticals, cosmetics) are another important application. Special grades of SAN with improved weatherability, uv stability, and vapor barrier properties have also been developed. The demand for SAN in Western Europe is estimated ~100,000 t/yr (52).

8.2. Butadiene–Acrylonitrile–Styrene Polymer. Due to the inadequacy of SAN materials for several applications, a range of materials referred to as ABS polymers came out on the market in the early 1950s. ABS was obtained in the early times through mechanical blending of SAN with a acrylonitrile–butadiene rubber copolymer. The resulting materials were rather poor from

Table 19. **Properties of Styrene Copolymers**

Property	ABS	SAN	SMA
density, g/mL	1.05	1.08	1.07
flammability	HB	HB	
oxygen index (LOI), %	19	19	
refractive index		1.57	
water absorption, 24 h, 23°C, %	0.3–0.7	0.2–0.3	0.3
dielectric constant, 1 MHz	3.2	2.7	3.3
dielectric strength, kV/mm	20–25		20
dissipation factor, 1 kHz	0.02		0.001
volume resistivity, 23°C, dry, $\Omega \cdot$cm	$>10^{15}$	10^{16}	5×10^{15}
HDT at 0.45 or 1.8 MPa, °C	98	93	
at 0.45 or 1.8 MPa, °C	89	85	120
thermal conductivity, 23°C, W/(m · K)	0.17		0.17
thermal expansion coefficient, K^{-1}	80×10^{-6}		
upper working temperature, °C	70–100		
elastic modulus, GPa[a]		3.3	2.0
tensile strength, MPa[b]	41–45	65	40
flexural modulus, GPa[a]		3.6	2.5
flexural strength, MPa[b]		110	60
elongation at break, %	45	2.3	40
notched Izod, 3.2 mm, J/m[c]	30–35	0.19	2
hardness (Rockwell)	R100–110	M75	R110
melt Index, g		8.9	

[a] To convert GPa to psi, multiply by 145,000.

[b] To convert MPa to psi, multiply by 145.

[c] To convert J/m to lbf · ft/in., divide by 53.38.

the point of view of compatibility, low temperature behavior, and surface characteristics. This process has been almost totally abandoned.

The methods applied currently for ABS preparation are based on the radical grafting of styrene and acrylonitrile monomers onto butadiene rubber (see Acrylonitrile–Butadiene–Styrene Polymers). The synthesis is more commonly carried out through emulsion techniques, but also emulsion–suspension, emulsion–mass, and mass technologies are applied. Mass polymerization has gained increased attention in the last years due to the reduced costs and greater cleanliness (with some disadvantages in terms of flexibility). The mass-suspension process is much less important due to the difficulties in obtaining the desired morphologies and to reactor waste disposal issues. Radical grafting leads to a very peculiar morphology: the polymer consists of a matrix of SAN in which rubber globules bearing grafted SAN chains are present. Some small particles of free-SAN are included in the rubber domains, and the rubber is partially cross-linked.

The butadiene content of ABS usually ranges from 10 to 25% by weight (for some special grades up to 45%), and the styrene/acrylonitrile ratio can be controlled as in the case of SAN.

ABS is a translucent-to-opaque resin exhibiting a high gloss. Careful control of the rubber particles morphology even allows the attainment of transparent materials. The presence of rubber gives ABS a good toughness and a high

Table 20. **Producers and Trademarks of ABS materials**

Producer	Pure grade	Blend with PC	Blend with PBT	Blend with PVC	Blend with others
GE Plastics	Cycolac	Cycoloy	Cycolin	Cycovin	
Dow	Magnum	Pulse			Prevail[a]
Bayer	Lustran Novodur	Bayblend			Triax[b]
EniChem	Sinkral	Koblend			
Hoechst	Cevian				
Toray	Toyolac	Toyolac			
Condea	Vista			Suprel	
Shin-A	Claradex				
Nova	Cycogel				
Schulman	Polyfabs			Polyman	

[a] With polyurethane.

[b] With PA.

ductility compared to SAN, even at low temperatures. Rigidity and hardness are comparable to SAN. Chemical resistance (water, salts, alkalies, acids do not affect the properties), impact and abrasion resistance, dimensional stability, and surface hardness are also good; the polymer is very sensitive to uv radiation. Properties are reported in Table 19.

All the common molding technologies can be applied to ABS, which is available in different neat, filled, and fire retarded grades; also, several blends (in particular that with polycarbonate) have been commercially developed. Electroplating is used with some special grades for finishing. Producers of ABS and ABS-based blends are reported in Table 20, with the respective trade marks.

ABS is used mainly in the automotive industry, electrical and electronic equipment, and home appliances. Prolonged exposure to sunlight causes discoloration, but outdoor applications are wide nonetheless. Some examples of ABS parts are vehicle components (instrument panels and other interior components), casings and cabinets, communication equipments, pipes and pipe fittings, shower trays, and baths.

The world consumption of ABS was 4 million tons in 1998 (53).

8.3. Styrene–Maleic Anhydride Copolymer. Styrene–maleic anhydride (SMA) copolymer is an alternate copolymer obtained by radical bulk or solution polymerization of the two monomers. Obviously, SMA does not contain N in the chemical formula, but is located here as a styrene copolymer of minor importance. The high content of maleic anhydride make the polymer outstandingly resistant to aliphatic and aromatic hydrocarbons. Polar organic solvents and alkalies attack the material. The polymer is transparent and has a T_g 120°C. Properties are reported in Table 19. As for SAN, the applications are in the automotive industry, casings, and appliances.

8.4. Polyamide Resins (Aliphatic). *Polyamides.* The history of polyamides began in 1935, when nylon-6,6 was synthesised by Carothers and coworkers at Du Pont laboratories. The name nylon was never registered as a trademark, however, it became very popular and is now universally used instead of the chemical name polyamide. Whereas nylon fibers were produced starting

Table 21. **Commercial Aliphatic Polyamides and Their Constituents**[a]

PA[b]	Acid		Lactam
6,6	hexandioic (adipic)		
4,6	hexandioic		
6,9	nonandioic (azelaic)		
6,10	decandioic (sebacic)		
6,12	dodecandioic		
6	ϵ-aminocaproic	or	ϵ-caprolactam
11	ω-aminoundecanoic		
12	ω-aminododecanoic	or	dodecanelactam (laurolactam)

[a] $PA_{x,y}$ from diamine +dicarboxylic acid; PA_x from lactam opening or amino-terminated acid condensation.

[b] The first number of couples designates the number of carbon atoms in the diamine, eg, 6 denotes hexamethylene diamine.

from 1939, moldings were put on the market only ~1950. Polyamides contain the amide −CONH− group as a common feature. They are obtained in two main ways, by polycondensation of a diacid with a diamine or alternatively by the opening of lactam rings. In the latter case, a ω-aminoacid can be alternatively used as starting monomer. Several polyamides differing in the length of aliphatic segments in the chain have reached the industrial stage. They are conventionally denoted by numbers, corresponding to the numbers of carbon atoms in each segment (see POLYAMIDES, PLASTIC). In Table 21, commercial aliphatic polyamides are reported, with the corresponding monomers.

From a commercial point of view, PA6,6 and PA6 are the most important materials. PA6,6 is prepared by the reaction of adipic acid (hexandioic acid) and hexamethylenediamine in boiling methanol. This operation causes the precipitation of the 6,6 salt, thus assuring the right stoichiometry for the next step. A 60% water solution of the salt is treated at 220°C in a sealed autoclave, in order to obtain polymerization. Traces of acetic acid are added to limit the molecular weight. The temperature raises to 270–280°C, and the pressure reaches 1.7 MPa (17 atm). After reduction to atmospheric pressure, the polymer is extruded under oxygen-free nitrogen. Similar procedures are used for PA4,6, PA6,9, PA6,10, and PA 6,12, in the presence of the appropriate reagents (Table 21). PA6 is obtained starting from ϵ-caprolactam, by both batch and continuous processes. Typically, the reaction is carried out at 250°C in the presence of water as catalyst and acetic acid as molecular weight regulator. PA12 is prepared in a similar way (at 260°C), whereas PA11 is prepared by stirring the molten acid at 220°C.

Generally, aliphatic polyamides are white, semicrystalline materials. Their properties vary greatly with degree of crystallinity, which in turn is strongly dependent on processing conditions. It is easy to obtain moldings of PA6 having 60% or, on the contrary, 10% crystallinity. Amorphous, transparent materials can also be obtained, by suppression of the crystallization process. Typical properties of several polyamides are collected in Table 22. They exhibit high strength and stiffness, lubricity, resistance to abrasion, and chemical resistance. Because of the presence of amide groups, water absorption is relatively high, and its occurrence lowers mechanical and electrical properties. Properties of PA6,6

Table 22. **Properties of Aliphatic Polyamides**

Property	PA6,6	PA6	PA4,6	PA11	PA12
density, g/mL	1.14	1.13	1.18	1.04	1.02
flammability	V2	V2	V2	V2	HB-V2
oxygen index (LOI), %	23	25	24	22	21
refractive index	1.53	1.53			
water absorption, 24 h, 23°C, %	2.3	2.7	1.3	0.8	1.6
dielectric constant, 1 MHz	3.4	3.6	3.8–4.3	3.0	3.5
dielectric strength, 1 mm, kV/mm	25	25	20	20	26–30
dissipation factor, 1 kHz	0.2	0.2	0.35	0.05	0.03
volume resistivity, 23°C, dry, $\Omega \cdot \text{cm}$	10^{13}	5×10^{12}	10^{13}–10^{15}	10^{14}	10^{12}–10^{14}
glass-transition temperature (T_g) (dry), °C	50	60–70		45	40
melting temperature (T_m), °C	264	215	295	185	175
HDT at 0.45 MPa, °C	200	200	220	150	130
at 1.8 MPa, °C	100	80	160	55	48
specific heat capacity, J/(g · K)	1.47	1.59			0.71
thermal conductivity, 23°C, W/(m · K)	0.25	0.26	0.30	0.19	0.19
thermal expansion coefficient, K^{-1}			1×10^{-4}	1×10^{-4}	
upper working temperature, °C	80–180	80–160	100–200	70–130	
elastic modulus, GPa[a]	3.3	2.6–3.0	3.1–3.3	1.7	2.2
tensile strength, MPa[b]	82	78	55–100	44	50–55
flexural modulus, GPa[a]		3.1			
elongation at break, %	300	300	50	320	290
notched Izod, 3.2 mm, J/m[c]	40–110	30–250	80	96	40–110
hardness (Rockwell)	M89	M82	M92	M60	R84–107
friction coefficient	0.2–0.3	0.2–0.3	0.27	0.2–0.3	

[a] To convert GPa to psi, multiply by 145,000.

[b] To convert MPa to psi, multiply by 145.

[c] To convert J/m to lbf · ft/in., divide by 53.38.

and PA6 are rather equivalent. PA6 is slightly easier to process because of higher melt viscosity. PA6 shows higher impact strength, but lower tensile strength. Its water absorption is the highest of all polyamides. PA11 and PA12 have similar properties (PA12 slightly inferior).They absorb less water with respect to PA6,6 and PA6. Consequently, dimensional stability and electrical properties are improved. PA4,6 is colored (from yellowish to red). It maintains properties at high temperatures. Some books are dedicated to the synthesis and properties of polyamides (54,55).

Extrusion and blow molding are also common processing techniques. Films find large application in packaging of foodstuff and pharmaceutical goods. Glass-fiber filled grades are widely fabricated, obtaining materials able to replace metal parts for their rigidity, creep resistance, low coefficient of friction, and high HDT. Toughened polyamides are also offered for high impact resistance purposes.

Table 23. **Producers of Aliphatic Polyamides**

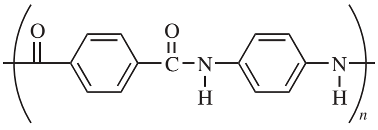
Company	PA 6	PA 6,6	Other PA	Trade names
Allied Signal	y	y	n	Capron
Ashley Polymers	y	y	6,10 6,12 11 12	Ashlene
ELF-Atochem	n	n	11 12	Rilsan, Orgalloy
BASF	y	y	y	Ultramid
Bayer	y	y	y	Durethan
Nyltech	y	n	y	Sniamid, Technil
Du Pont	y	y	11 6,12	Zytel, Minlon
DSM	y	y	4,6 6,10	Akulon, Stanyl
Ems	y	y	12 6,12	Grilon, Grilamid, Grivory
Hüls	n	n	12 6,12	Vestamid, Trogamid
Mitsubishi Kasei	y	n	n	Novamid
Radici	y	y	y	Radilon
Rhodia	y	y	y	Technyl
Ticona		y		Celanese
Toray	y	y	6,10	Amilan
UBE	y	y	y	UBE-Nylon

PAs are applied in mechanical engineering, mainly in the sectors of transportation and electrical/electronic appliances. Gears, bearings, valve seats, nuts, bolts, rivets, wheels, and casings are typically fabricated by injection molding, taking advantage of several properties like low viscosity at processing temperatures.

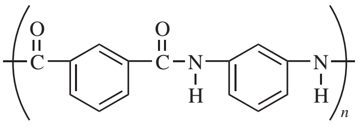
By 1998, the total consumption of polyamides had risen to 5.8 million tons worldwide (56). Approximately 1.6 million tons were used as molding compounds for injection molding or extrusion, the remaining as synthetic fibers in textiles, carpets, and nonwovens. Of this amount, >90% concerns PA6 and PA6,6; the remaining fraction is mostly PA11 and PA12. Producers are rather numerous and most of them produce both PA6 and PA6,6. A list of producers with the corresponding trade names is reported in Table 23.

Semiaromatic polyamides (eg, derived from *m*-xylylenediamine and adipic acid) are also present in the market in relatively low amounts. Poly(*m*-xylylene adipamide) was introduced as MDX-6 by Mitsubishi. It is also marketed by Solvay as Ixef. Polyphthalamides (PPA) and fully aromatic polyamides (aramids, ArPA) are treated separately in the following sections.

8.5. Aromatic Polyamides. Aromatic polyamides (aramids, ArPA) are a family of high molecular weight wholly aromatic polyamides, including poly(*p*-phenylene terephthalamide) and poly(*m*-phenylene isophthalamide). The chemical structure of these polymers is shown in below.



poly(*p*-phenylene terephthalamide)



poly(*m*-phenylene isophthalamide)

Poly(*m*-phenylene isophthalamide) [trade names Nomex (Du Pont) and Conex (Teijin)] and poly(*p*-phenylene terephthalamide) [trade names Kevlar (Du Pont) and Twaron (Akzo)] were discovered in the 1960s, but it was only in 1971, after the development of a suitable synthetic method and processing technique that these two materials became commercially viable. Almost a dozen different routes of synthesizing aramids have been pursued by industrial and academic researchers (57), but only the original processes are currently applied (58). They are based on the condensation of an acyl dichloride with an aromatic diamine in a suitable solvent. The solvent is critical especially in poly(*p*-phenylene terephthalamide) preparation, because of the high insolubility of the aramid. *N*-methylpyrrolidinone/calcium chloride or hexamethylphosphoramide/*N*-methylpyrrolidinone mixtures are good reaction media; the latter is no longer in use because of the carcinogenicity of hexamethylphosphoramide. Water must be excluded from the polymerizing system to avoid hydrolysis of the acyl chloride. After coagulation of the formed polymer, neutralization, washing, and filtration, the final product is dried. For poly(*m*-phenylene isophthalamide) the interfacial process is also possible, although less advantageous because lower molecular weights are obtained.

Aramids are crystalline, infusible, very insoluble materials. They are commercially available only in the form of fibers (Nomex also in sheets), generally spun from pure sulfuric acid solutions using the air-gap technique. Aramid solutions are generally fluid and opaque because they form lyotropic liquid-crystalline phases. Poly(*p*-phenylene terephthalamide) chains exist in the all trans conformation and reach a high degree of orientation with strong interchain hydrogen bonding (Fig. 2). Consequently, after spinning the chains maintain

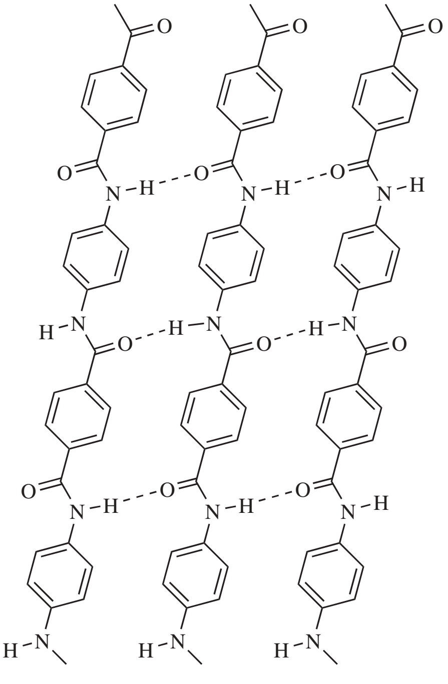


Fig. 2. Interchain hydrogen bonding in aromatic polyamides.

their orientation alignment along the flow direction and impart to the fiber an exceptionally high modulus. In fact, Kevlar is about five times stronger than steel by weight. Its modulus is ~60 GPa after spinning and is more than doubled after thermal treatment under tension, due to the increase of crystallinity.

Mechanical properties are remarkably better along the fiber longitudinal direction than in the axial direction. On the other hand, the fibrillar structure is the cause of poor shear and compression properties, thus making Kevlar elastic in tension and ductile in compression. Elongation at break and thermal shrinkage are low.

In contrast, poly(*m*-phenylene isophthalamide) is less oriented and its tensile properties are more like those of conventional textile fibers. Thermal stability, radiation, temperature, and flame resistance are very high; Kevlar decomposes in air at >430°C without melting, Nomex above at 350°C. Density is very high, especially for Kevlar, which is among the highest for organic polymers. Properties of Kevlar and Nomex are compared in Table 24.

One of the most important applications of Kevlar is in ballistics and defense sectors, for body armors, anti-mine boots, and helmets. In fact, to break the material, a fracture must traverse over different planes, and this makes for difficult penetration by projectiles or cutting objects. It is also widely used in composites for aircraft structural body parts and cabin panels. In addition, it is used for rope reinforcement, reinforcement for automotive and industrial hoses, and belts.

Nomex fibers can be converted to continuous filaments yarn, staple, spun yarn, floc, paper, needle felt and fabric, suited for protective devices (racing drivers suits, firefighter suits, flight suits, space suits, fire blankets), filtration media (hot gas filtration, laundry filters), electrical paper and pressboards (transformers, microwave ovens, electric motors), and mechanical parts of various kind (engine nacel, helicopter blades, aircraft parts).

Poly(*p*-benzamide) is another aramid that was, for a time, considered as a possible alternative to poly(*p*-phenylene terephthalamide). However, due to the problems of monomer synthesis, polymerization, and spinning process (59), its manufacture has been discontinued.

Table 24. **Properties of Aromatic Polyamides**

Property	Nomex	Kevlar[a]
density, g/mL	1.38	1.44
oxygen index (LOI), %	29	
water absorption, 24 h, 23°C, %	9	
melting temperature (T_m), °C		500
specific heat, J/(kg · K)	1200	1.4
thermal conductivity, 23°C, W/(m · K)	0.13	0.04
thermal expansion coefficient, K^{-1}	20×10^{-6}	-2×10^{-6}
upper working temperature, °C	200–300	180–245
elastic modulus, GPa[b]		60
tensile strength, MPa[c]		2760
elongation at break, %		3.7

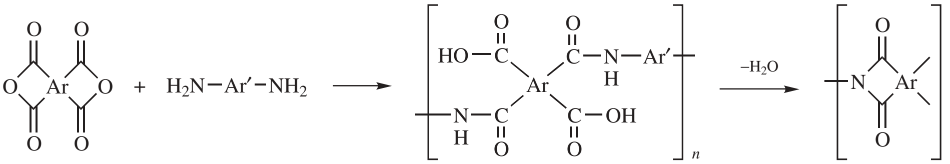
[a] In fiber form.

[b] To convert GPa to psi, multiply by 145,000.

[c] To convert MPa to psi, multiply by 145.

8.6. Polyimides. Polyimides (PI) contain cyclic imide groups in their molecular structure, the branched nature of which facilitates the build up of multiring structures. Due to their importance in advanced fields like electronics and aerospace, polyimides have been, and continue to be, the subject of extended research efforts, the result of which have been reported in several books and reviews (60–66). Here, thermoplastic, processable polyimides are mainly considered. This excludes some thermosetting materials prepared by polyaddition and based on bimaleimide and bisnadimide structures.

Polyimides are obtained from the condensation of an aromatic dianhydride with an aromatic diamine. Generally, a two-step method is followed, obtaining in the first step a poly(amic acid), followed by the dehydrative cyclization of the latter (thermally or chemically induced):



The first reaction is operated at room temperature in an organic solvent like dimethylformamide (DMF) or *N,N*-dimethylacetamide.

The high transition temperatures and melt viscosities exhibited by aromatic polyimides do not allow their processing in the melt with conventional methods like extrusion or injection molding. To obtain processable materials, different methods were pursued. The first method exploited the fact that they are prepared in two steps, supplying semi/fabricated shapes as films or coatings at the stage of the poly(amic acid). The final user assumes the responsibility of the final polymerization. A second method to obtain processable materials is through the use of comonomers, leading to polymers such as polyamideimides and polyetherimides.

Several approaches have been adopted to achieve fully imidized polymers that are soluble or melt processable:

Introduction of flexible segments (eg, aliphatic) to reduce chain stiffness.

Introduction of bulky side groups, to keep separate the polymer chains and hinder dense packing and crystallization.

Use of monomers containing angular bonds, to suppress coplanarity of molecules.

Use of 1,3-substituted monomers instead of 1,4-substituted monomers, to lower molecular ordering.

A wide list of monomers taken into consideration for such purposes has been reported in a review (63). Obviously, lowering of T_g and T_m can diminish mechanical properties, chemical resistance, and/or thermal resistance. The amount of structural modification should allow an optimized property balance. Polyimides are generally colored and exhibit excellent thermal properties, high

Table 25. **Properties of Polyimide**

Property	
density, g/mL	1.42
flammability	V0
oxygen index (LOI), %	53
refractive index	1.66
water absorption, 24 h, 23°C, %	0.2–2.9
dielectric constant, 1 MHz	3.4
dielectric strength, 1 mm, kV/mm	22
dissipation factor, 1 kHz	1.8×10^{-3}
volume resistivity, 23°C, dry, $\Omega \cdot$cm	10^{18}
glass-transition temperature (T_g), °C	370–400
HDT at 1.8 MPa, °C	360
specific heat capacity, kJ/(kg · K)	1.09
thermal conductivity, 23°C, W/(m · K)	0.1–0.35
thermal expansion coefficient, K^{-1}	$30–60 \times 10^{-6}$
upper working temperature, °C	250–320
elastic modulus, GPa[a]	2.0–3.0
tensile strength, MPa[b]	70–150
elongation at break, %	8–70
notched Izod, 3.2 mm, J/m[c]	80
hardness (Rockwell)	E52-99
friction coefficient	0.42

[a] To convert GPa to psi, multiply by 145,000.

[b] To convert MPa to psi, multiply by 145.

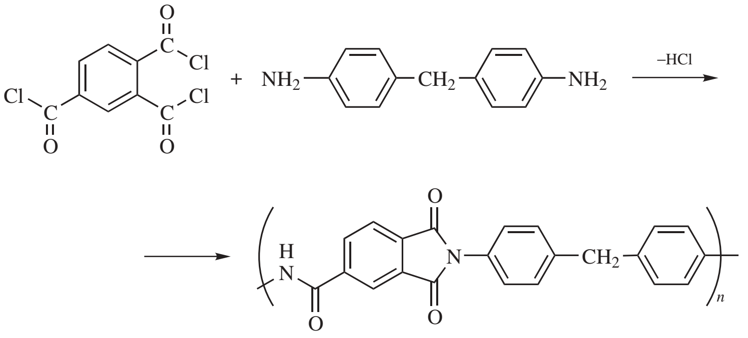
[c] To convert J/m to lbf · ft/in., divide by 53.38.

radiation resistance, low flammability, high wear resistance, and low creep. Properties of a representative polyimide are reported in Table 25.

The first commercial films obtained by the polycondensation of pyromellitic anhydride (PMDA) with 4,4′-oxydianiline (ODA) were introduced by Du Pont in 1965, under the trade name of Kapton. Also, moldable Vespel products are based on PMDA–ODA structures, whereas Avimid contains a fluorinated monomer. Of the other commercial polyimides reported in Table 3, Upilex and Apical are based on biphenylene, Matrimid contains an indane structure, and Aurum is a poly(ketoetherimide).

Due to the high price, applications are limited to very demanding cases, eg, in aerospace. Films are used for capacitors, insulation, printed circuit boards, engine components, and bearings. Fillers are added to enhance electrical or thermal properties.

8.7. Polyamideimides. Polyamideimides (PAI) are a class of amorphous thermoplastic polyimides, prepared by solution condensation of trimellitic trichloride with various aromatic diamines, such as *p*-phenylenediamine, oxydianiline, or methylenedianiline, as sketched in equation 11. Amide links alternate with imide links along the polymer chains. PAI was commercialized in the early 1970s by Amoco Chemical Co. under the trade name of Torlon. Similar products were also produced by Rhone-Poulenc and Becks, a subsidiary of BASF.



(11)

PAI resins have an amber-to-gray color. Due to their molecular rigidity and hydrogen bonding, they present several interesting properties, in particular high tensile strength and stiffness, excellent dimensional stability and creep resistance (among the best for thermoplastics), good solvent (aliphatic, aromatic, chlorinated, fluorinated hydrocarbons), and chemical resistance (dilute acids, aldehydes, ketones, ethers, esters). Only the resistance to alkalis is poor. Electrical insulation properties as well as flame resistance are also very good. Properties are reported in Table 26.

Commercial products can contain a filler, mainly graphite or glass fibers. These fillers tend to increase the modulus, dimensional stability and wear, and

Table 26. **Properties of PAI Resins**

Property	Neat	30% GF
density, g/mL	1.42	1.68
flammability	V0	
oxygen index (LOI), %	45	52
water absorption, 24 h, 23°C, %	0.3	0.17
dielectric constant, 1 MHz	3.7	5.4
dielectric strength, 1 mm, kV/mm	23	
dissipation factor, 1 kHz	0.026	0.042
volume resistivity, 23°C, dry, $\Omega\cdot$cm	2×10^{17}	0.08×10^{17}
Glass-transition temperature (T_g), °C	285	285
HDT at 1.8 MPa, °C	278	282
specific heat capacity, J/(kg · K)	1000	
thermal conductivity, 23°C, W/(m · K)	0.26	0.54
thermal expansion coefficient, K^{-1}	25×10^{-6}	31×10^{-6}
upper working temperature, °C	200	260
elastic modulus, GPa[a]	4.5	
tensile strength, MPa[b]	110	190
flexural modulus, GPa[a]	5	20
compressive strength, MPa[b]	180	220
elongation at break, %	15	7
notched Izod, 3.2 mm, J/m[c]	140	70
hardness (Rockwell)	E72	E86
friction coefficient (to steel)	0.2	

[a] To convert GPa to psi, multiply by 145,000.
[b] To convert MPa to psi, multiply by 145.
[c] To convert J/m to lbf · ft/in., divide by 53.38.

friction properties. PAIs possess a high melt viscosity, so special screws are necessary for injection molding. Compression moldable powder is also available for fabricating small, simple parts. Fabricated parts can require a postcuring operation in order to optimize properties and durability in service. Postcuring is favored by the presence of trimellitic anhydride end groups. PAIs are used in demanding applications like connectors, gears, relays, ball bearings, engine components (piston skirts and rings, valve stems), marine winches, switches. Due to the high prices (∼30–50 US$/kg) the market of PAIs is rather small, <1000 t.

8.8. Polyphthalamides. PPA are a class of semiaromatic polyamides introduced in the market by Amoco in 1991, under the trademark Amodel. The chemical nature of PPA has not been fully disclosed, but it is believed to be the result of polycondensation of hexamethylenediamine and a mixture of terephthalic and isophthalic acids. The presence of isophthalic acid is necessary to lower the melting temperature, which in the corresponding polymer containing only the terephthalic isomer is 370°C above the decomposition temperature.

Most commercial PPA grades contain fiber reinforcements (glass or mineral). Flame retardant grades (up to V0 rating at 0.8 mm thickness) are available. Properties of an unfilled resin and of a 40% glass-fiber reinforced resin are reported in Table 27.

Interesting properties with respect to other high performance polymers are the thermal resistance, toughness, chemical resistance, ease of processing

Table 27. **Properties of PPA Resins**

Property	Neat	40% GF
density, g/mL	1.15	1.54
flammability		HB
oxygen index (LOI), %		23
water absorption, 24 h, 23°C, %	0.65	0.16
dielectric constant, 1 MHz		4.3
dielectric strength, 1 mm, kV/mm		21
dissipation factor, 100 Hz		0.005
volume resistivity, 23°C, dry, $\Omega \cdot$ cm		1×10^{16}
glass-transition temperature (T_g), °C	127	127
melting temperature (T_m), °C	310	310
HDT at 0.45 MPa, °C		290
at 1.8 MPa, °C	120	275
thermal expansion coefficient, K^{-1}	2.9 FD/4.6 TD	
elastic modulus, GPa[a]	2.4	11
tensile strength, MPa[b]	76	174
flexural modulus, GPa[a]	2.6	10.6
flexural strength, MPa[b]	128	262
compressive strength, MPa[b]		228
elongation at break, %	30	2.6
notched Izod, 3.2 mm, J/m[c]	960	43
hardness (Rockwell)	R110	R125

[a] To convert GPa to psi, multiply by 145,000.

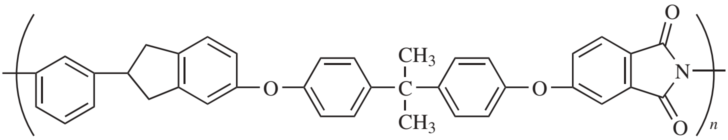
[b] To convert MPa to psi, multiply by 145.

[c] To convert J/m to lbf · ft/in., divide by 53.38.

(mainly by injection molding), and dimensional stability. Water absorption is very much decreased compared to aliphatic polyamides. PPA has found application in mechanical engineering, for the fabrication of fasteners, pump housings, motor end frames, connectors, engine parts, electric motor brush holders, pump and fan impellers, cooling circuits, etc.

8.9. Polyetherimide. Polyetherimides are thermoplastic polymers containing imidic moieties, which impart the outstanding thermal, mechanical, and electrical properties to the material, and ether groups, which facilitate the processability.

Ultem (General Electric) is the only polyetherimide still on the market and is synthesized through a multistep process from bisphenol A, *m*-phenylenediamine, and 4-nitrophthalic anhydride. It is a fine example of polymer synthesis that can be made by reactive extrusion (67).



Ultem

Ultem is an amorphous, amber colored resin with a T_g of 215°C, exhibiting very high flexural and tensile strength, inherent flame resistance with low smoke evolution, high stability toward heat and uv radiation, good resistance to acids, dilute alkali and hydrocarbons. Resistance to other solvents (ketones, jet fuel, hydraulic fluids) has been further improved in some modified polyetherimides used in prepreg systems developed for aerospace applications (68). Chlorinated solvents cause stress cracking.

Mechanical properties are maintained at elevated temperatures. For example, flexural modulus only decreases from 3.3 to 2.1 GPa at 180°C. However, absorbed moisture has a negative effect on the retention of mechanical properties at elevated temperatures. Reinforcing with glass fibers leads to a further improvement of mechanical behavior, due to the excellent adhesion of the polymer to the inorganic filler. The tensile strenght of the 40% glass-fiber filled resin increases by a factor of ~1.6. Electrical properties are stable over a wide range of conditions and the dissipation factor is low, which makes possible the use of Ultem at frequencies up to 1000 MHz without problems. Properties of PEI are reported in Table 28.

Ultem is easily processed at temperatures ~340°C by injection-, compression-, and blow-molding. Due to its high melt strength, extrusion in the form of films and sheets is possible. A prolonged drying (4 h) prior to transformation is recommended. Advantages on the flow behavior have been obtained by modified grades containing 1.5 wt% PPE.

Main applications of PEI are in automotive components (under-the-hood, electrical, heat-exchange components), electrical and electronics (circuit boards, switches, connectors), and aerospace (lighting, seating, wiring, microwave oven trays). Other fields of application are as medical reusable tools, requiring

Table 28. **Properties of a PEI Resin**

Property	ULTEM 1000
density, g/mL	1.27
flammability	V0
oxygen index (LOI), %	47
water absorption, 24 h, 23°C, %	1.2
dielectric constant (1 MHz)	3.1
dielectric strength, kV/mm	30
dissipation factor (1 kHz)	0.0013
volume resistivity, 23°C, dry, $\Omega \cdot$cm	7×10^{15}
glass-transition temperature (T_g), °C	215
HDT at 0.45 MPa, °C	200
specific heat, J/(kg $\cdot$ K)	2.0
thermal conductivity, 23°C, W/(m $\cdot$ K)	0.22
thermal expansion coefficient, K^{-1}	56×10^{-6}
upper working temperature, °C	170–200
elastic modulus, GPa[a]	2.9
tensile strength, MPa[b]	85
flexural modulus, GPa[a]	3.3
flexural strength, MPa[b]	145
compressive strength, MPa[b]	140
elongation at break, %	60
notched Izod, (3.2 mm), J/m[c]	50
hardness (Rockwell)	R125
abrasion (1000 cycles), mg	10

[a] To convert GPa to psi, multiply by 145,000.

[b] To convert MPa to psi, multiply by 145.

[c] To convert J/m to lbf $\cdot$ ft/in., divide by 53.38.

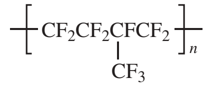
repeated sterilization procedures (eg, surgical probes); in high frequency printed wiring boards, where the low dissipation factor at high frequency plays a key role; and as fibers for dry filtration, aircraft fabrics, and protective clothing. In many applications, Ultem can be a substitute for other engineering plastics, such as acetal resins (eg, in clamp connectors for printed circuit boards in aircrafts), and inorganic materials (aluminum, ceramics, etc).

Commercialization of PEI started in 1982. World capacity in 1998 was 12,000 t/yr (69).

9. Fluorine-Containing Polymers

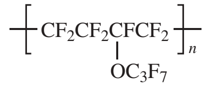
The interest in fluoropolymers as engineering polymers resides in their excellent chemical inertness, heat resistance, electrical insulation properties, and low friction coefficient. Under this profile, four materials are here considered, ie, PTFE, and various perfluorinated copolymers (FEP, ETFE, and PFA); they have the following molecular structures (scheme FP1):

$-\!\!\left[CF_2CF_2 \right]_n\!\!-$ PTFE $-\!\!\left[CF_2CF_2CH_2CH_2 \right]_n\!\!-$ ETFE



$$\left[\mathrm{CF_2CF_2}\underset{\mathrm{CF_3}}{\underset{|}{\mathrm{C}}}\mathrm{FCF_2}\right]_n$$

FEP



$$\left[\mathrm{CF_2CF_2}\underset{\mathrm{OC_3F_7}}{\underset{|}{\mathrm{C}}}\mathrm{FCF_2}\right]_n$$

PFA

In all cases, their properties depend on the strong C−F bonds.

PTFE is a white-to-translucent polymer discovered at Du Pont in 1938, but its commercialization was delayed by the second World War and began in 1947 under the trade name of Teflon. Two main manufacturing techniques are used, suspension polymerization, which produces a granular resin, and emulsion polymerization, which produces a coagulated dispersion. In the latter case, water is used as reaction medium; further, the presence of an initiator and an emulsifying agent are necessary. Polymerization of tetrafluoroethylene is also violent when initiated at low temperature. Inhibitors are therefore used for better control of the reaction, which is carried out in industrial plants at 80–90°C.

PTFE is highly crystalline and exhibits unique chemical inertness, chemical resistance, and electrical insulation properties, as well as a very low coefficient of friction. Properties of fluoropolymers are collected in Table 29.

Table 29. **Properties of Fluoropolymers**

Property	PTFE	FEP	ETFE	PFA
density, g/mL	2.18	2.13–2.17	1.70	1.8
flammability	V0	V0	V0	
oxygen index (LOI), %	95	95	30–32	
refractive index	1.38	1.344	1.403	
water absorption, 24 h, 23°C, %	<0.005	0.004	<0.02	0.03
dielectric constant, 1 MHz	2.1	2.1	2.6	2.1
dielectric strength, 1 mm, kV/mm	50	20 (@3.2 mm)	25	
dissipation factor, 1 MHz	3×10^{-4}	7×10^{-4}	8×10^{-4}	
Vol. resistivity, 23°C, dry, $\Omega\cdot$cm	$>10^{18}$	$>10^{18}$	$>10^{16}$	10^{16}
melting temperature (T_m), °C	325	260	270	302–306
HDT at 0.45 MPa, °C	121	70	104	74
at 1.8 MPa, °C	54	50	74	
specific heat capacity, kJ/(kg · K)	1.0	1.1	1.9–2.0	
thermal conductivity, 23°C, W/(m · K)	0.24	0.24	0.24	
thermal expansion coefficient, K^{-1}	12×10^{-5}	6×10^{-5}		12×10^{-5}
upper working temperature, °C	180–260	150–200	150–160	260
elastic modulus, GPa[a]	0.3–0.8	0.6	0.8	
tensile strength, MPa[b]	10–40	20–30	45	31
flexural modulus, GPa[a]	0.4–0.6	0.6	0.96	0.7
flexural strength, MPa[b]	∞			
compressive strength, MPa[b]	4	21–23	50	
elongation at break, %	200–300	150–300	250–350	300
notched Izod, 3.2 mm, J/m[c]	160	240	>1067	
hardness (Rockwell)	D50–65	D55–57	D75 R50	D60
friction coefficient	0.05–0.08	0.27	0.4	

[a] To convert GPa to psi, multiply by 145,000.

[b] To convert MPa to psi, multiply by 145.

[c] To convert J/m to lbf · ft/in., divide by 53.38.

Due to its chemical inertness and high molecular weight (in the range $4 \times 10^5 - 9 \times 10^6$ Da, necessary for achieving sufficient mechanical properties) PTFE cannot be melt processed. Consequently, unconventional techniques have been set up, like those derived from powder metallurgy for granular PTFE, and from lead cold processing for coagulated dispersions. PTFE grades are commercialized in several physical forms, ie, coarse cut, pelletized or presintered resins, fine powders, and aqueous dispersions (latices). Fillers like glass fibers, graphite, or powdered metals are eventually added.

The development of fluorine-containing copolymers also resulted from the attempt to provide materials combining the peculiar properties of PTFE with a processability similar to that of other thermoplastics (70). Du Pont introduced FEP on the market in 1956, ETFE and PFA in 1972. The latter are the easiest to process.

Fluoropolymers are widely used for fabricating bearings, seals, gaskets, packings, valve, and pump parts. They are also used for wire insulation, vessel lining, and laminates for printed circuitry. Because large objects made with PTFE cannot be fabricated, metal objects are conveniently coated by a PTFE layer.

The worldwide capacity for fluoropolymers was estimated at 135,000 t in 1998 (71), including polymers not treated here such as poly(vinylidene fluoride). The market request in the same year was only 85,000 t. Some 40% of such amount is composed by PTFE granules.

10. Interpolymer Competition

Looking at the tables reporting the properties of engineering thermoplastics, it is clear on one side that they cover a wide range of figures, and, on the other side, that many overlapping situations occur. To select the right polymeric material for a specific application is a hard job, because the market of commercial polymers has become so crowded. Books have appeared to guide the materials engineer in the selection of thermoplastic materials, with the help of a dedicated software (7).

Four main groups of technical considerations must be made in order to make the right choice, ie, mechanical, electrical, environmental, and appearance. In addition, cost and specifications (eg, imposed by a government body or by a corporation) are two other elements of importance. Environmental considerations include the operating temperature, the chemical environment, the weathering exposure, and humidity degree. Appearance includes style, shape, color, transparency, and surface finish of the fabricated object. Mechanical and electrical considerations must include both short- and long-time values, and also the effects of environment on such properties. Also, appearance can vary under service conditions. The necessary information must be provided by different actors, that is the material supplier, the processor, the processing equipment supplier, and the product designer/producer.

Depending on the particular application, numerous properties should be considered during the selection of the best candidate. Further, every property has a different importance, and thus a different weight on the final choice.

Property values reported here are representative; several of them vary over a wide range depending on several factors, like the nature and amount of fillers, the possible occurrence of copolymerization, etc. Also, some data are not available in the current literature and others are difficult to describe with just one figure, which is particularly true for rheological data reported in data sheets as flow curves, viscosity vs temperature curves, etc. Similar difficulties arise for creep curves (related to long-term mechanical resistance) and shrinkage and warpage of fabricated parts, which are strongly dependent on the geometry and thickness of the part itself. The Internet has made it easier to access data about polymer grades actually produced (Table 30).

In the final selection of the best material for the fabrication of a specific object, a compromise is generally made, choosing the material that shows an

Table 30. **www Sites Containing Data Sheets of Engineering Thermoplastics**

URL (uniform resource locator)	Information source
General	
http://matls.com/	MatWeb, The online materials information resource
http://polydatabase.com/index2.htm	
Wholesalers	
http://www.boedeker.com/mguide.htm	Boedeker Plastics Inc.
http://www.goodfellow.com/static/A/start.html	Goodfellow
http://www.panpolymers.co.uk/fprodb.htm	Pan Polymers
http://members.aol.com/vpisales/tpguide.html	Venture Plastics
http://www.actech-inc.com/engmrgt.htm	Actech Inc
http://www.plasticsandmetals.com/plastics.html	Cal Plastics and Metals
http://www.plasticeng.com/copy_of_plasticeng/engineeringmaterials.htm	Plastics Engineering Inc.
Producers	
http://www.dow.com/Homepage/index.html	Dow Chemicals
http://www.shellchemicals.com/home/1,1098,-1,00.html	Shell Chemicals
http://www.ticona.com/	Ticona (Celanese AG)
http://www.basf.com/	BASF
http://www.dupont.com/	DuPont
http://www.bayer.com/	Bayer
http://polymers.alliedsignal.com/	Allied Signal
http://geplastics.com/	General Electric Plastics
http://dsmepp.com/	DSM

optimized balance of the most relevant properties. In addition to some particular properties, like transparency and the question of processability (which involves complex issues as rheology, shrinkage, and surface finishing), in most of applications of engineering thermoplastics, the following characteristics and properties are considered: price, mechanical properties, thermal properties, electrical properties, and chemical resistance.

10.1. Price. The price of a thermoplastic resin is basically determined by the cost of preparation, which in turn strongly depends on the cost of reagents (monomers, catalyst, etc), the complexity of the manufacturing process, and the dimension of production plants. Aliphatic polyketones, eg, are made from very cheap raw molecules as ethylene, propylene, and CO; their cost is determined by the need for expensive catalysts, based on Pd complexes, and the relatively complex production plant. On the other hand, PEN, that can be easily prepared in the same reactors used for PET, suffers from the difficult availability of its basic monomer, dimethyl 2,6-naphthalene dicarboxylate. Most engineering polymers contain aromatic monomers, difficult to synthesize and polymerize, with slow and sophisticated mechanisms (condensation, substitution, oxidative coupling).

Roughly, commodities are priced 0.5–1 US$/kg, engineering polymers are in the range 1–5 US$/kg, and high performance polymers and in the range 5–50 US$/kg. The current prices fluctuate following market conditions and can be found as a price range, for most materials, in technical journals like *Plastics Technology*. In Figure 3, the prices of engineering thermoplastics are reported as a function of annual production volume, confirming, with a few exceptions, the inverse relationship between the two parameters. The price is reported in U.S. cents per volume unit, which is more significant than the corresponding price per mass unit. The unfilled materials have a density ranging from 1.02 g/mL for COCs to 2.18 g/mL for PTFE. However, the density of most engineering ther-

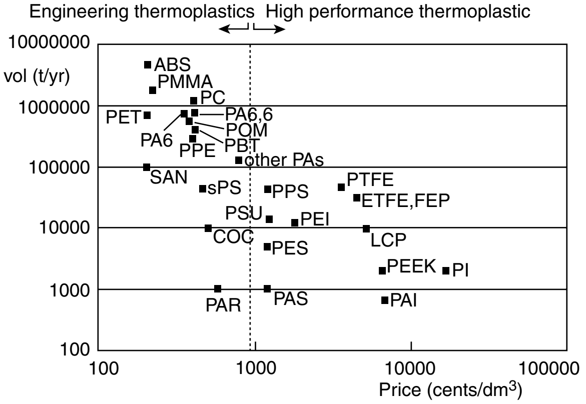


Fig. 3. Production volumes and prices for volume units for thermoplastics considered in this compilation. The dashed line represent an arbitrary border between engineering and high performance thermoplastics. In some cases, reinforced resins have been considered, ie, PPS: 10% glass fibers (GF); PSU,PA11: 30% GF; PAS: 40% GF. Acronyms are those listed in Table 1.

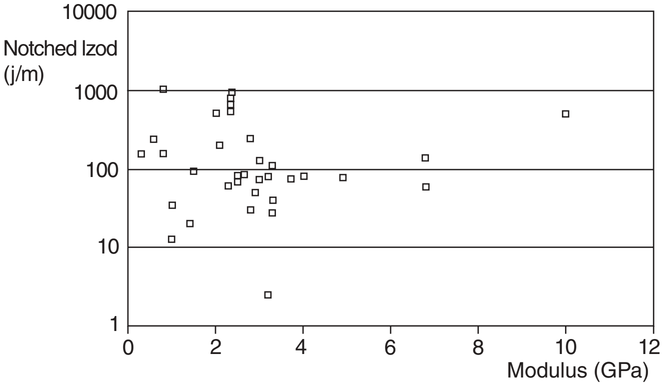


Fig. 4. Modulus vs notched Izod of engineering thermoplastics. To convert J/m to ft.lbf/in., divide by 53.38. To convert GPa to psi, multiply by 145,000.

moplastics falls ~1.15−1.45 g/cm^3. The price/volume relationship does not work when a low volume material can be produced in a captive way in a plant used also for producing a higher volume polymer, which is the case of polyarylates, some aliphatic polyamides, and polysulfones.

The most representative mechanical properties are elastic (or tensile) modulus, tensile strength, flexural modulus, and toughness. Flexural modulus is particularly interesting, because it represents the stiffness of the material. Unfortunately, data are not available for all materials. However, because flexural modulus values are mostly of the same order of magnitude of tensile modulus values, the latter can be used for comparison purposes. Toughness is approximately described by Izod impact strength. Figure 4 reports elastic moduli and Izod strengths of engineering thermoplastics. Data ranges are particularly wide for toughness data. This figure shows that for any application a wide number of combinations of stiffness and toughness is available in the field of engineering thermoplastics. Further, reinforcing practice with fibers, minerals, or other fillers is largely applied in order to enhance the mechanical and thermal properties. Most of the materials treated here are offered on the market in a large number of reinforced grades. Such a practice also influences the cost of the material, and this is particularly relevant when the cost of the matrix is higher than the cost of the filler. Figure 5 shows the increase of modulus values that can be obtained by adding glass fibers to several polymers.

Heat deflection temperature does not correspond to the practical use temperature, however it has been widely used in the plastics industry to compare the physical response of materials to temperature at a single load level. In Figure 6, HDT values at two different loads are reported vs tensile strengths. Both groups of data roughly show a proportional trend that can be ascribed to the fact that in many cases the molecular structure of the chain influences in the same sense the mechanical and thermal properties.

The electrical properties of engineering thermoplastics are generally excellent. In specific applications, like cable and wire coatings, electrical or electronic parts, etc, demanding values are requested. On the other side, electrical conductivity can be increased by adding particular fillers like metallic powders.

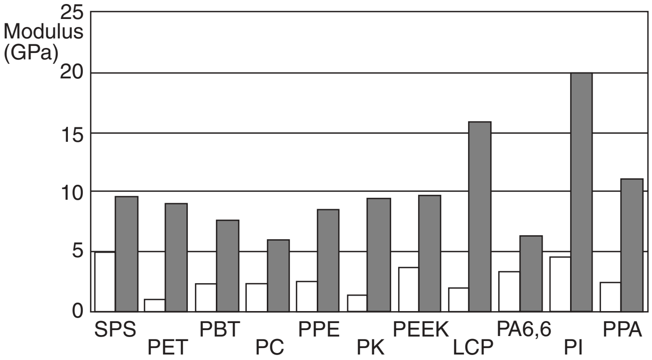


Fig. 5. Modulus increases obtained by reinforcing thermoplastic matrices with glass fibers. GF contents are at 30% by weight, but those of PC and PK are at 20%. PPE values are referred to a PPE–PS blend. To convert GPa to psi, multiply by 145,000.

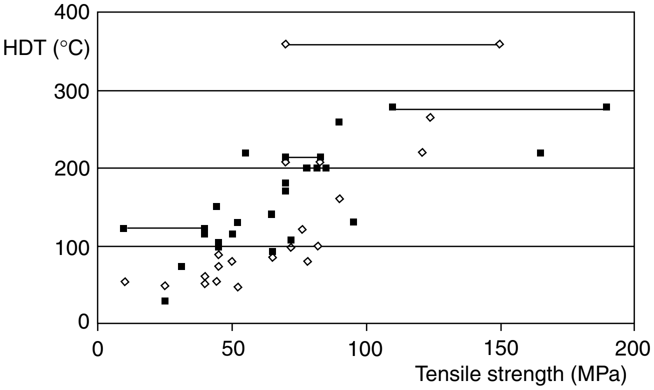


Fig. 6. Tensile strength vs HDT of engineering thermoplastics. Full squares represent HDT values obtained at 0.45 MPa, empty rhombi at 1.8 MPa. Horizontal bars between two tensile strength values represent a range. To convert MPa to psi, multiply by 145.

10.2. Chemical Resistance. Chemical resistance belongs to environmental considerations, because the accidental or expected exposure of a material to the action of chemicals or solvents can have relevant short- and long-term influence to the other properties. Table 31 summarizes the resistance of polymers to the most common families of chemicals and solvents. As expected, fluoropolymers show the best response against the whole range of chemicals considered. Chemical resistance values reported in this table are indicative, because they can be significantly affected by exposure length and temperature. In practice, chemical resistance testing under end use conditions are suggested.

10.3. The Future. Thermoplastic materials have now pervaded every important aspect of human life, from food management (through packaging) to clothing (through synthetic fibers), ground and air transportation, office equipment, health (medical instruments and devices, artificial prostheses), entertainment (audio and video reproduction components), sports goods, etc. Applications of thermoplastic materials, both commodities and engineering thermoplastics,

Table 31. **Chemical Resistance of Engineering Thermoplastics**[a]

Material	Acid dilution	Acid conc	Alkali	Alcohol	Hydrocarbon (aromatic)	Greases and oil	Ketones
SPS	G	G	G	G	F	G	G
POM		P	P	G	G	G	F/G
PET		G	P	G	F	G	G
PBT		G	F	G	G	G	G
PEN		G	F	G	G	G	G
PAR				F	F	F	F
LCP	G	F	G	F	G	G	G
PPE		F/G	G	F	P	F	F
PC		F/G	P	G	P	G	P
PK	G	P	G	F	G	G	G
PEEK	G	F	G	G	G	G	G
PMMA	G	F	G	F	P	P	P
PPS	G	F	G	G	G	G	G
PSU		G	G	G	P	G	P
PES		G	G	G	P	G	P
PAS		G	G	G	P	G	F
ABS		G	F		P		P
SAN		P	P	F	F	G	F
PA6,6	P	P	G	G	G	G	G
PA6	P	P	G	G	G	G	G
PA11	P/F	P	G	F	G	G	G
PA12	P/F	P	G	F	G	G	G
ArPA		F	F/G	G	G	G	G
PI	G	G	P	G	G	G	G
PAI	G	G	P	G	G	G	G
PPA	G	F	G	F	G	G	G
PEI		G	F/G		G		
F-polymers	G	G	G	G	G	G	G

[a] P = poor; F = fair; G = good.

will continue to expand at the expense of other materials like glass, metals, wood, and ceramics. Moreover, the time between the laboratory synthesis of a new polymer and its industrial production remains high (72), thus discouraging the introduction of new materials. The expected expansion of the engineering thermoplastics market is on the order of 12% per year in the next 3 yrs (73). Interestingly, the most significant threat to engineering polymers comes from some commodities, like polypropylene, which in some reinforced (but also unreinforced) grades reach the performance of some engineering materials.

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