Kirk-Othmer Encyclopedia of Chemical Technology.

COMPOSITE MATERIALS, THERMOPLASTIC POLYMER-MATRIX

Thermoplastic resins have received considerable attention in the past few years as the matrix material in organic resin-based composites. Whereas thermosetting materials date back 5000 years, when Egyptians used a straw-reinforcing agent in a clay matrix to form bricks, thermoplastic composites are relatively recent. Although their use in advanced composites is not widespread, thermoplastic composites are used extensively in commercial applications ranging from automobiles to durable goods (1) (see Engineering Plastics).

Thermoplastic polymers are usually linear molecules with no chemical linkage between the molecules. The molecules are held together by weak secondary forces, such as van der Waals or hydrogen bonding, and as such are readily deformed by the application of heat or pressure. Thermoplastic resins can be amorphous, that is, structureless, or semicrystalline, in which some of the molecules form an ordered array. A material is usually considered semicrystalline if as little as 5% of the polymer is in the crystalline form. Semicrystalline resins exhibit a higher modulus, but amorphous materials are tougher; amorphous materials are usually more solvent sensitive but can be processed at lower temperatures. One of the most important advantages of thermoplastic resins is their toughness, that is, high impact strength and fracture resistance, which, unfortunately, is not linearly translated into properties of the composite. Other advantages of thermoplastic polymers include long shelf life at room temperature; postformability, that is, thermal reforming; ease of repair by thermal welding or solvents; and ease of handling, that is, they are not tacky.

Although in a broad sense, a composite is a material that contains two or more distinct phases, this discussion is restricted to those materials in which one of the phases, usually the fibers, serves as a reinforcing or strengthening agent (see Composite Materials, survey). Materials in which a relatively inexpensive material, such as talc or calcium carbonate, is added to reduce the overall cost of the expensive thermoplastic polymer are not included. Advanced or high performance composites contain more than 50 wt % fibers, whereas other composites or commodity composites (reinforced plastics) contain 20–40 wt % reinforcing agent. The distinction is real, and different resin properties, hence different chemistries, are required for these materials. In general, the specific chemistry of the resin system cannot be separated from the processing method used to prepare the final composite. Although the fundamental structure of the polymer is the same regardless of the method used to synthesize it, significant differences in the form and reactivity of the final material can be observed.

Because the early thermoset resins used in advanced composites were quite brittle and tougher resins were needed, thermoplastic resins seemed to have great potential as composite matrix materials. In addition to being tough, they have a long shelf life and are thermally reformable. However, the primary user of advanced composites, the aerospace industry, has a large investment in capital equipment that utilizes tacky, drapable, carbon–epoxy composites, which are processed as prepregs at temperatures from 121° to 177°C at high pressures in an autoclave. Considerable effort has been expended to develop thermoplastic resins that can be processed with the existing equipment, that is, resins that can be (*1*) coated directly onto fibers to prepare conventional prepregs; (*2*) spun into thermoplastic resin fibers that can be woven together with the reinforcing fiber, that is commingled, and subsequently consolidated; (*3*) cured from a partially polymerized polymer and coated directly onto the fiber to form a prepreg similar to that used for thermosets; or (*4*) prepared as small particles that can be coated onto the reinforcing fiber from either solution or by electrostatic attraction and subsequently heated to form a continuous phase on the fiber.

One of the principal advantages of true thermoplastic polymers is their ability to consolidate or flow at elevated temperatures; however, this quality also limits their upper-use temperature. Amorphous materials begin to flow or creep above the glass-transition temperature, T_g, whereas crystalline resins must be heated above the melting point, T_m. As a rule of thumb, T_g is approximately $\frac{2}{3}T_m$ (Kelvin temperature), so that crystalline polymers may begin to degrade at the temperatures required for processing. Even a relatively low temperature material such as polypropylene, which melts between 168 and 175°C must be heated to approximately 180–190°C to process the composite. In many instances the processing window is quite narrow owing to a lower temperature limit set by the melting point and an upper temperature limit set by the rate of thermal degradation.

Much of the recent work on the synthesis of new resin systems has centered on two important problems: (*1*) methods to form thermoplastic resins at relatively low temperatures while maintaining high temperature capability; and (*2*) development of low viscosity resins that readily flow into and around an existing preform structure but rapidly polymerize to a stable thermoplastic resin when heated. For example, materials with reactive end groups or cyclic compounds that readily form high molecular-weight polymers during processing are being developed for both conventional and high performance composites.

In spite of the many advantages of and large data base on thermoplastic resins, the development of advanced thermoplastic composites has been much slower than the development of thermoset composites. Because of their high melt or solution viscosities, the incorporation of the reinforcing phase into the thermoplastic matrix has limited the development of thermoplastic composites. A great deal of work has been devoted to the development of materials and processing methods to circumvent these problems. Although fibers can be coated in several ways, it is necessary to prepare the polymer in a form suitable to the particular processing method. Thus it is necessary to prepare a given generic material by a different synthesis route in order to obtain the final resin in the desired form.

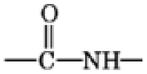
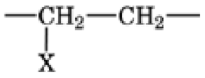
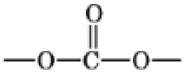
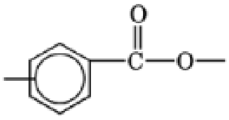
Thermoplastic composites can be classified according to use, cost, performance, or processing methods. In the following discussion of the chemistry of the resin systems utilized in composites, three classes are considered:

(1) Resins used in conventional composites (usually commodity materials) and typically containing 10–40 wt % reinforcing agent.
(2) Resins used in advanced or high performance composites, which contain more than 50 wt % reinforcing agent and are the typical aerospace materials.
(3) Pseudothermoplastic resin systems, which are formed as conventional thermoplastic materials and then cured or postcured in a manner similar to that used for thermosetting resins to enhance high temperature properties.

1. Commodity Resins

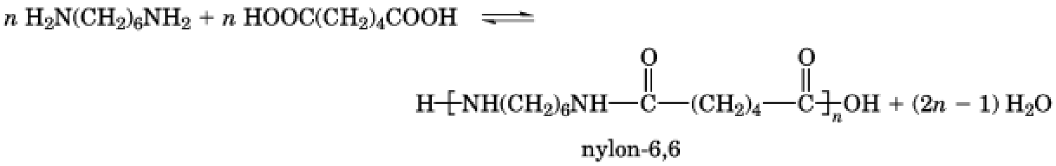
Most of the resin systems used in commodity composites are slight modifications of the standard commercial molding grade material. Usually certain selected properties, such as purity or molecular weight range or distribution, are enhanced or carefully selected. In addition, special additives, such as flow controllers, thermal stabilizers, or antioxidants, are often added by the resin manufacturer prior to shipment. Many of the conventional or commodity-type resins used in thermoplastic composites are listed in Table 1 and the preparation of each of these is described. All resins and blends described in the literature are not listed, and the synthesis described is not the only procedure available, but is usually the most common commercial process.

Table 1. Conventional Thermoplastic Resins

Chemical class	Repeat unit	Polymer	Morphology
polyamides	 $-\overset{O}{\overset{\|}{C}}-NH-$	nylon-6,6nylon-6	semicrystallinesemicrystalline
polyolefins	 $-\underset{X}{\underset{\|}{CH_2}}-CH_2-$	polypropylenepolystyrene and its copolymers	semicrystallineamorphous
polycarbonates	 $-O-\overset{O}{\overset{\|}{C}}-O-$	polycarbonate	amorphous
polyesters		poly(ethylene terephtha- late)poly(butylene terephthalate)	semicrystallinesemicrystalline
acetals	$-CH_2O-$	polyoxymethylene	semicrystalline

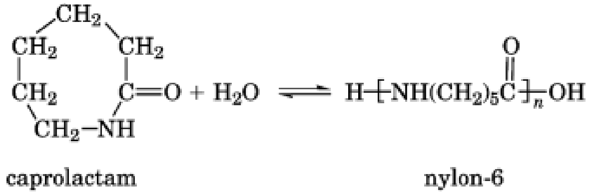
1.1. Polyamides

Nylon was the first commercial thermoplastic polymer produced on a large scale, as a direct result of the pioneering work of Carothers (2). Nylons contain repeating amide functionality (see Polyamides). The aliphatic polyamide nylon is one of the most important thermoplastic materials (3). It is used extensively as a molding compound and in fiber glass (both short and long fibers) reinforced composites. Nylon-6,6 [32131-17-2] and nylon-6 [25038-54-4] were first put into commercial production in 1938 and 1939, respectively. In view of the 50 years of commercial experience with nylons, a great deal is known about the chemistry of these materials and the various additives used to enhance specific properties. However, much of the specific knowledge remains proprietary information of the various suppliers. The molding grades form the basis for the composite grade material. There are two principal synthesis routes for the production of nylon: condensation of a diamine and dibasic acid (eq. **1**) or rearrangement of a lactam (eq. **2**).



$$n\ H_2N(CH_2)_6NH_2 + n\ HOOC(CH_2)_4COOH \rightleftharpoons H\!-\!\!\left[NH(CH_2)_6NH-\overset{O}{\overset{\|}{C}}-(CH_2)_4-\overset{O}{\overset{\|}{C}}\right]_{n}\!OH + (2n-1)\ H_2O \quad (1)$$

nylon-6,6



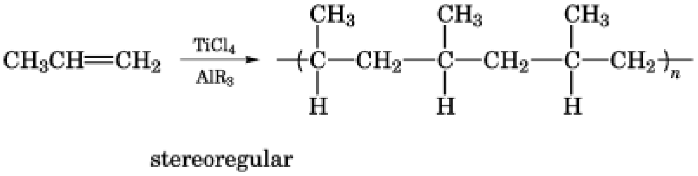
(2)

One of the primary factors in the use of nylons to prepare composites is their melt viscosity, which is controlled by the proper choice of molecular weight. Typical commercial nylons are available with molecular weights ranging from 11,000 to 40,000. The molecular weight chosen for a particular composite application represents a compromise between a low value, yielding a low viscosity to enhance fiber wetting, and a high value, to increase toughness and promote maximum crystallinity.

Many modifiers and additives have been described for use with nylon composites, but generally a small amount, 0.05–1 wt %, of a lubricity aid, such as sodium or zinc stearate (4) is added to enhance both resin flow during processing and removal from the mold after consolidation.

1.2. Polyolefins

The most common polyolefin used to prepare composites is polypropylene [9003-07-0], a commodity polymer that has been in commercial production for almost 40 years following its controlled polymerization by Natta in 1954 (5). Natta used a Ziegler catalyst (6) consisting of titanium tetrachloride and an aluminum alkyl to produce isotactic polypropylene directly from propylene:



$$CH_3CH{=}CH_2 \xrightarrow[AlR_3]{TiCl_4} \left(\overset{CH_3}{\underset{H}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2-\overset{CH_3}{\underset{H}{C}}-CH_2 \right)_n \qquad (3)$$

Polypropylene is available with many different reinforcing agents or fillers, such as talc, mica, or calcium carbonate; chopped or continuous strand fiber glass is the most common reinforcing agent used for composites. Many additives have been developed to enhance the thermal stability of polypropylene to minimize degradation during processing. One of the most important requirements of the polypropylene used in the manufacture of composites is that it be relatively pure and free of residual catalyst. Recent developments to form copolymers of polypropylene and polyethylene have great promise for relatively inexpensive, tough, thermoplastic composite applications (see Olefin Polymers).

Another polyolefin of interest is polystyrene, a clear, brittle plastic that, by itself, is rarely used in composites. However, several copolymers and alloys of polystyrene with acrylonitrile or butadiene have been used with fiber glass or glass spheres to form composites (7).

1.3. Acetals

Acetal resins (qv) are polymers of formaldehyde and are usually called polyoxymethylene [9002-81-7]. Acetal homopolymer was developed at Du Pont (8). The commercial development of acetal resins required a pure monomer. The monomer is rigorously purified to remove water, formic acid, metals, and methanol, which act as chain-transfer or reaction-terminating agents. The purified formaldehyde is polymerized to form the acetal homopolymer; the polymer end groups are stabilized by reaction with acetic anhydride to form acetate end groups (9).

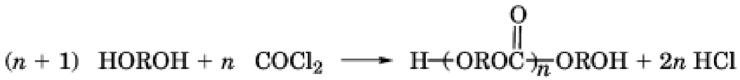
$$n\,\mathrm{CH_2O} \longrightarrow \mathrm{HOCH_2O{+}(CH_2O)_{\overline{n-2}}CH_2OH} \xrightarrow{\mathrm{(CH_3CO)_2O}} \mathrm{CH_3COO{+}(CH_2O)_{\overline{n}}COCH_3} \qquad (4)$$

The polymer also can be made from trioxane (the trimer of formaldehyde), usually as a copolymer with ethylene oxide. The $-CH_2CH_2-$ fragments in the copolymer chain prevent depolymerization; acetal copolymer was developed by Celanese (10).

Precise amounts of chain terminators are added during polymerization to produce final polymers having various molecular weights. Stabilizers and antioxidants are added to both the homopolymer and the copolymer to create the basic polymer grades. Although several fillers, such as talc or calcium carbonate, can be added to polyoxymethylene, the most common reinforcing agent for engineering applications is fiber glass. Reference 11 provides an excellent review of various fillers and reinforcing agents used with acetals.

1.4. Polycarbonates

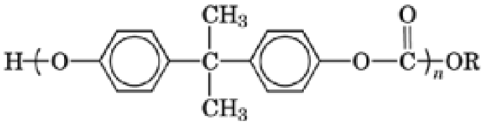
Polyarylates are aromatic polyesters commonly prepared from aromatic dicarboxylic acids and diphenols. One of the most important polyarylates is polycarbonate, a polyester of carbonic acid. Polycarbonate composite is extensively used in the automotive industry because the resin is a tough, corrosion-resistant material. Polycarbonates (qv) can be prepared from aliphatic or aromatic materials by two routes: reaction of a dihydroxy compound with phosgene accompanied by liberation of HCl (eq. **5**):



$$(n+1)\ \mathrm{HOROH} + n\ \mathrm{COCl_2} \longrightarrow \mathrm{H{+}ORO\overset{\overset{\displaystyle O}{\|}}{C}{)_{\overline{n}}}OROH} + 2n\,\mathrm{HCl} \qquad (5)$$

or transesterification of a dihydroxy compound with dialkyl or diaryl carbonates.

The most common commercial polycarbonate [24936-68-3] is prepared from 2,2-bis (4-hydroxyphenyl)propane, that is, bisphenol A [80-05-7], and has the general structure:



where R could be H or C_6H_5.

The principal industrial method of preparing this material is a two-phase reaction in which the polymerization reaction occurs at the interface (12, 13). The disodium salt of bisphenol A in aqueous alkaline solution reacts with the phosgene in an inert chlorinated solvent, such as methylene chloride. The mono- or dichloroformates condense and in a second stage are polymerized to a high molecular-weight polymer using a basic catalyst, such as triethylamine. The degree of polymerization depends on the degree of mixing and the pH of the aqueous phase. The molecular weight of the polymer is controlled by adding a chain terminator such as phenol. The usual molecular-weight range used for the manufacture of composites is 20,000–35,000. When used to prepare composites, polycarbonate must be dry and free of both acid and basic impurities to minimize depolymerization and degradation during processing. Most polycarbonate composites contain between 5 and 30 wt % fiber glass reinforcing agent, but composites with up to 40 wt % can be made. E-glass is the material of choice because it is alkaline free.

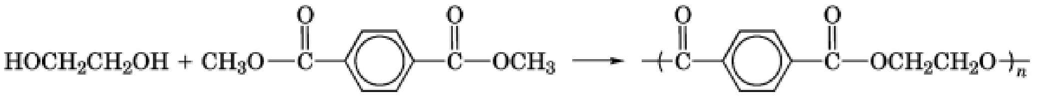
Workers at the General Electric Co. have described a new procedure using low viscosity cyclic intermediates to prepare polycarbonate composites (14, 15). This work is discussed in the section dealing with novel methods.

1.5. Polyesters

Polyesters (qv) are widely used as the matrix for conventional composites. Two resins of particular importance because of the large amounts used are (poly(ethylene terephthalate) [25038-59-9] (PET) and poly(butylene terephthalate) [24968-12-5] (PBT). Although polyesters can be made from diacids and diols by direct condensation,

$$\mathrm{HO{-}\overset{\overset{O}{\|}}{C}R\overset{\overset{O}{\|}}{C}{-}OH + HOR'OH \rightleftharpoons {-}\!\left(\overset{\overset{O}{\|}}{C}{-}R{-}\overset{\overset{O}{\|}}{C}{-}OR'{-}O\right)_{n}\!{-}} \qquad (6)$$

they form relatively low molecular-weight polymers that have little commercial value. The most practical methods for the preparation of high molecular-weight polyesters involves ester-exchange reactions. PET is usually prepared by the reaction between ethylene glycol and the dimethyl ester of terephthalate acid in acid solution (16):



(7)

PET is a semicrystalline material with a nominal degree of crystallinity of approximately 60 vol %; however, because the rate of crystallization is relatively slow, it is desirable to add a nucleating agent, such as talc, to the resin (17). If a nucleating agent is not added, fabricated parts have a nonhomogeneous morphology and it is difficult to maintain dimensional stability. It is also possible to add a plasticizer, such as dibenzoate of neopentyl glycol, to lower the T_g and permit rapid crystallization throughout the part (18). Composites containing up to 40 vol % fiber glass are commercially available.

PBT is produced by the transesterification of dimethyl terephthalate with 1,4-butanediol by means of a catalyzed melt polycondensation (19). PBT is also semicrystalline and is an extremely tough resin. Several commercial resins use a blend of PBT with another resin, such as PET, polycarbonate, or nylon. Typically, composites of PBT contain 20–30 vol % fiber glass.

2. Advanced Composites

The term *advanced composite* normally implies a high volume fraction reinforcing agent, of the order of 60 wt %. Much research into the development of high temperature advanced thermoplastic composites has been conducted since the late 1970s. The primary goal of this work has been the development of high temperature tough materials. This development presents a twofold problem: (*1*) the synthesis of resins that are stable and do not degrade at the high temperatures of interest, and (*2*) incorporation of the resin system into a reinforcing agent so that a structural composite can be fabricated. The latter is the more difficult of the two problems.

Resins for advanced composites can be classified according to their chemistry; typical resins are polyaryletherketones, polysulfides, polysulfones, and a very broad class of polyimides containing one or more additional functional groups (Table 2) (see also Engineering plastics).

Table 2. Resins for Advanced Composites

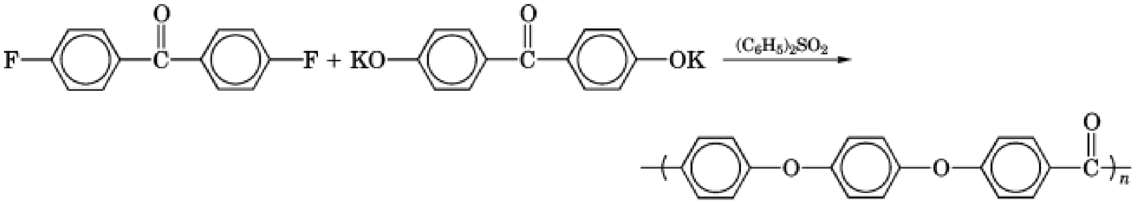
Chemical class	Resin	Morphology	T_{g}, °C	T_{m}, °C
polyetherketones	polyether ether ketone	semicrystalline	143	345
	polyether ketone ketone	semicrystalline	170	370
polysulfones	polysulfone	amorphous	200	
	polyethersulfone	amorphous	230	
polysulfides	polyphenylene sulfide[a]	semicrystalline	85	285
polyimides	polyimide[a]	semicrystalline	250–300	
	polyetherimide	amorphous	220	
	polyamide imide[a]		275	
	polybenzimidazoles[a]		230–290	
	fluorinated polyimides	amorphous	340	

[a] These materials are also referred to as pseudothermoplastics.

It is important to distinguish between true thermoplastics and pseudothermoplastics. Pseudothermoplastics are systems in which the chemistry continues during processing or an extra postcure step is added after the resin is consolidated. During the postcure process, the molecular weight may continue to increase, reactive pendent or end groups may cross-link, or volatile compounds such as reaction products or residual solvent may be expelled. In general, the properties change and can be likened to cross-linking or chain extension. Many of the so-called advanced thermoplastic resins are actually pseudothermoplastics. Although pseudothermoplastics are not completely reprocessible as are the true thermoplastics, usually they can be thermoformed a second or possibly a third time if necessary to correct defects in a structural component.

2.1. Polyarylether Ketones

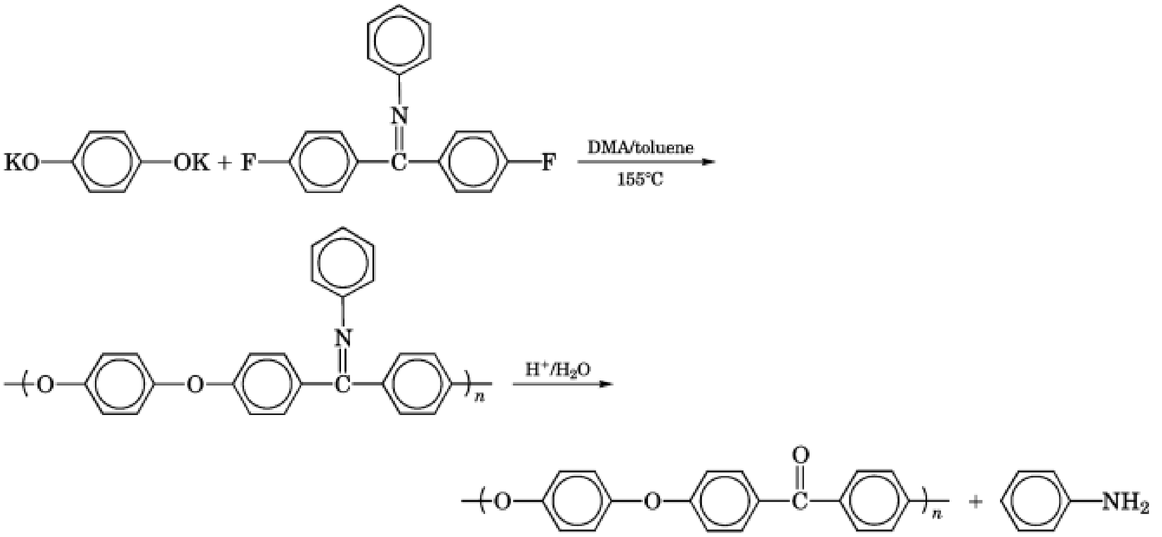
The aromatic polyether ketones are true thermoplastics. Although several are commercially available, two resins in particular, poly ether ether ketone [31694-16-3] (PEEK) from ICI and poly ether ketone ketone (PEKK) from Du Pont, have received most of the attention. PEEK was first synthesized in 1981 (20) and has been well studied; it is the subject of numerous papers because of its potential use in high performance aircraft. Tough, semicrystalline PEEK is prepared by the condensation of bis(4-fluorophenyl) ketone with the potassium salt of bis(4-hydroxyphenyl) ketone in a diaryl sulfone solvent, such as diphenyl sulfone. The choice of solvent is critical; other solvents, such as liquid HF, promote the reaction but lead to premature low molecular-weight crystals, which do not exhibit sufficient toughness (21).



(8)

A commercial prepreg of PEEK and carbon fibers (manufactured and sold by ICI as APC-2) can be made by the hot melt process. Although the prepreg prepared in this manner has been used extensively, it is quite stiff and boardy and makes it difficult to form structures with complex shapes. The PEEK used to make the APC-2 composite is a high purity grade that contains no special additives. An excellent discussion of the effects of heat transfer during processing of APC-2 on the morphology of PEEK has been given (22).

More recently a method has been described to prepare fine (0.5–5 μm) particles of PEEK for use in powder prepregging (23). PEEK resin is too tough to be ground to a fine powder suitable for powder prepregging. This represents an excellent example where the choice of processing method, in this case the method of coating the resin onto the fiber, controls the synthesis procedure. In this synthesis (23) a fluorinated ketamine reacts with the potassium salt of dihydroxybenzene in dimethylacetamide–toluene solution at 155°C. The resulting ether ketamine polymer is hydrolyzed in acid solution to form PEEK polymer (eq. **9**). The size and shape of the particles is controlled by the acid concentration (that is, rate of hydrolysis) and agitation during the hydrolysis step. Uniform crystalline particles as small as 0.5 μm can be obtained.

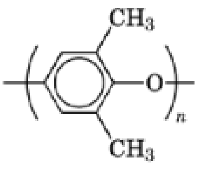


(9)

PEEK can also be spun into fibers, which are commingled with a reinforcing fiber to form a yarn (24). The PEEK fiber is not used as the reinforcing agent but, when heated above its melting point, flows around the reinforcing fibers (typically carbon) and forms the resin matrix. The commingled yarn is woven into the shape desired and consolidated at temperatures above the melting point of PEEK. The PEEK used in this material is resin grade, which is slightly less pure than the PEEK used in APC-2. The overall effect of this slight difference in purity between the resin used in APC-2 and the commingled yarn on the long-term performance of the composite is not known.

2.2. Poly(phenylene ether)

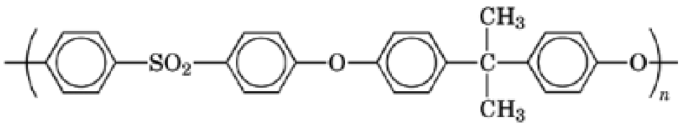
The only commercially available thermoplastic poly(phenylene oxide) PPO is the polyether poly(2,6-dimethylphenol-1,4-phenylene ether) [24938-67-8]. PPO is prepared by the oxidative coupling of 2,6-dimethylphenol with a copper amine catalyst (25). Usually PPO is blended with other polymers such as polystyrene (see Polyethers, Aromatic). However, thermoplastic composites containing randomly oriented glass fibers are available.



PPO

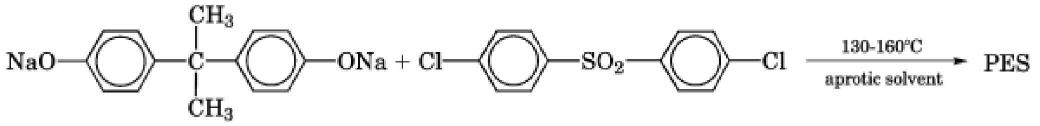
2.3. Polysulfones

The most common polysulfone is actually a sulfone ether, polyethersulfone [25135-51-7] (PES), and has the following structure.



PES

It is prepared from the polycondensation of the disodium salt of bisphenol A and 4,4-dichlorodiphenyl sulfone in a polar aprotic solvent such as dimethyl sulfoxide (26).



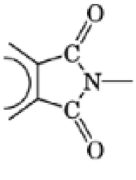
(10)

This material is a true amorphous thermoplastic with a T_g of 185°C and can be made into thermoforming composite with 20–40 wt % glass fiber (see Polymers containing sulfur).

2.4. Polyimides

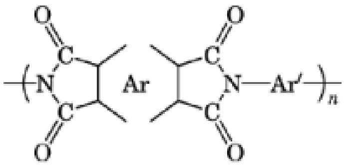
Polyimides (qv) represent a very broad class of materials ranging from thermosets to both amorphous and semicrystalline thermoplastics. Polyimides are used extensively as high temperature adhesives, as insulation for electrical wire, and for printed circuit boards. They have great potential for high temperature applications because of their thermo-oxidative stability, solvent resistance, and general ease of preparation. However, their use in resin matrix composites has been rather limited in spite of their great potential. Much has been written about polyimide resins for use in high temperature composites, but the amount of literature generated greatly exceeds their commercial value. Reference 27 is an excellent summary of some of the many studies on polyimides.

All polyimides contain the basic imide functionality:

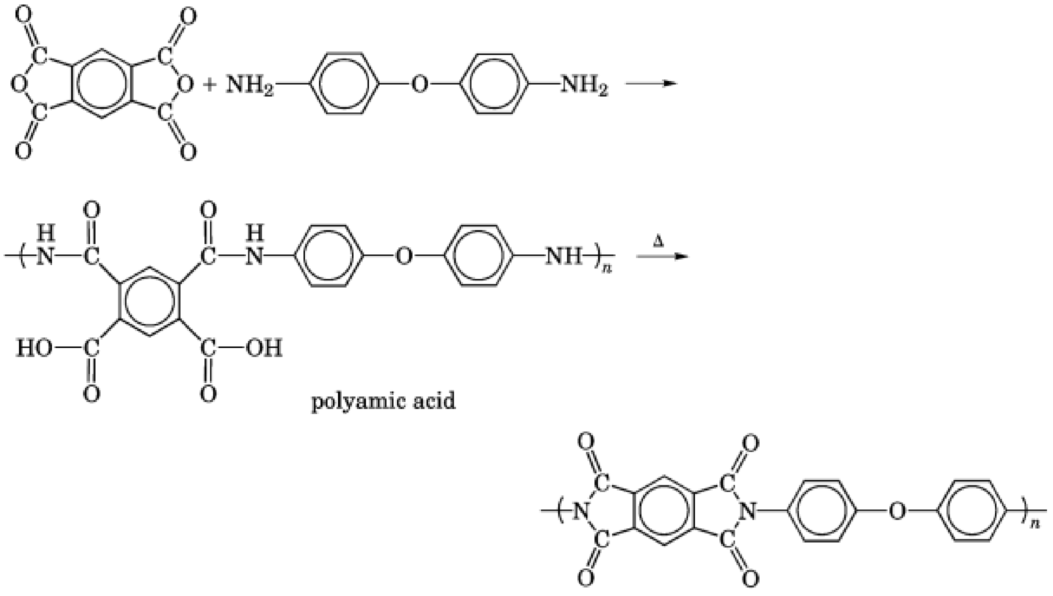


In addition they may contain ether, amide, carbonyl, sulfone, or other functional groups. References 28 and 29 provide excellent reviews of polyimide chemistry.

Aromatic polyimides are generally produced by the reaction of aromatic dianhydrides with aromatic diamines to yield a material with the general structure



where either the aromatic ring Ar or Ar′ can contain a functional group. The first commercial polyimide, poly(4,4′-oxydiphenylpyromellitimide) [25036-53-7], manufactured by Du Pont and sold under the trade name Kapton, is a high temperature imide-ether polymer prepared from pyromellitic dianhydride and 4,4′-diaminodiphenyl ether according to the following reactions (30):



polyamic acid

polyimide

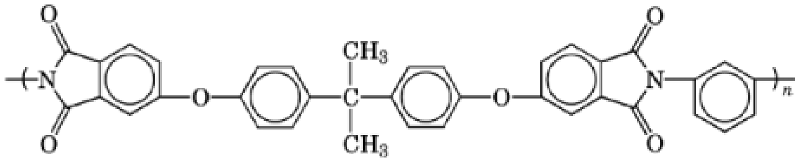
The polyimide shown is a true thermosetting resin, but the general reaction procedure, coupling the dianhydride with the diamine, is extremely important throughout polyimide chemistry. The intermediate polyamic acid polymers form the basis for many of the polyimide resins used in advanced composites.

Different dianhydrides reacting with different diamines can be used to prepare a wide variety of polyamic acids. Although the polyamic acid is a high molecular-weight polymer, it is soluble in solvents such as *N*-methylpyrrolidinone (NMP) and in this form can wet the reinforcing agent prior to the final imidization step. Because of the high temperature capability of polyimides and the desirable overall properties of thermoplastic resins, considerable effort has been devoted to the development of thermoplastic polyimide-based materials (29).

Even though linear aromatic condensation types of thermoplastic polyimides can be prepared according to the reactions described and are, at least in principle, melt processible, they are quite difficult to process because of the extremely high (315–400°C) temperatures and high pressures required. In some instances the polyamic acid (in an appropriate solvent) is used and the final imidization step conducted during processing. In this case, both the solvent and the volatile compounds formed during ring closure must be eliminated from the consolidated composites. The total volatile content may amount to 15–20 wt % of the resin systems. To eliminate this undesirable reaction, considerable research has been devoted to synthesizing low molecular-weight imide oligomers with reactive end groups, such as maleimide, norbornene, or acetylene, which can be condensed during the processing stage. In many cases, these resins undergo a small amount of crosslinking during processing, and they are best referred to as pseudothermoplastics.

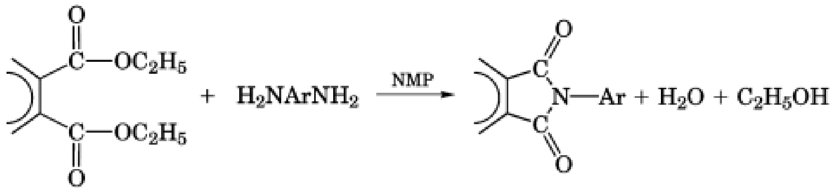
2.5. Polyether Imides

Polyether imides (PEIs) are amorphous, high performance thermoplastic polymers that have been in use since 1982. The first commercial polyether imides were the Ultem series developed by the General Electric Co. The first, Ultem 1000 [61128-24-3], is prepared from phthalic anhydride, bisphenol A, and meta-phenylenediamine and has the following structure:

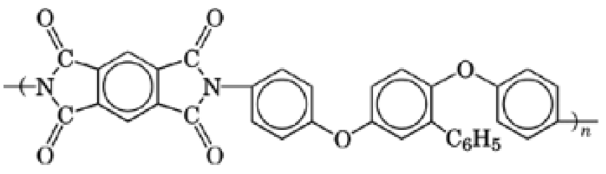


PEI resins reinforced with up to 40 wt % fiber glass are available. The American Cyanamid Co. uses an Ultem-type resin with carbon fibers to form their Cypac 1000 series prepregs (31). The moisture content of the resin must be less than 0.05% prior to melt processing to minimize thermal degradation.

Another series of PEI resins has been introduced by Du Pont, the Avimid series. The Avimid K-III [94148-82-0] resin was formulated to be a high temperature thermoplastic polyimide that could be processed with existing autoclave equipment designed for thermosets (32). The tack and drape of the prepreg are similar to those of the epoxies but the final resin is a tough thermoplastic. The exact structure and formulation has not been published but, in general, an aromatic diethyl ester of a diacid reacts with an aromatic diamine in a solvent such as *N*-methylpyrollidinone (NMP), that is,



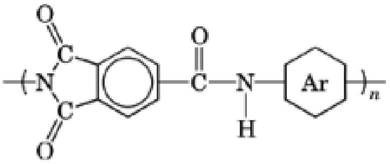
The structure of Avimid K-III is similar to



A significant problem associated with this resin system is the large amount, 14–16%, by weight of NMP solvent and condensation reaction by-products (water and ethanol). Special autoclave processing cycles are required to remove these volatile compounds from a finished part. During early stages of processing a semicrystalline polymer forms. The crystalline intermediate melts and the molten polymer consolidates into a tough amorphous material that does not crystallize upon cooling. The material is processed at approximately 360°C using a 1.5 MPa (200 psi) consolidation pressure. The final product is not a true thermoplastic but a pseudothermoplastic, which, however, can be postformed into simple geometries. Composites containing up to 60 wt % with either carbon or aramid reinforcing agents are available.

2.6. Polyamide Imides

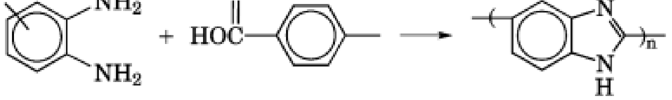
Polyamide imides (PAIs) are formed from the condensation of trimellitic anhydride and aromatic diamines (33). The polymer is called amide–imide because the polymer chain comprises amide linkages alternating with imide linkages, with the general chemical structure:



One commercial PAI is Torlon [42955-03-3], supplied by Amoco (33). Some PAI grades must be postcured after molding to fully develop their mechanical properties for long-term service and to keep parts from blistering or distorting during use at high temperatures. Several of the commercial grades of PAIs contain approximately 1 wt % polytetrafluoroethylene and can be used with either glass or carbon reinforcing fibers (34). The required postcure at 260°C can range from 5 to 30 days. Postcuring causes significant changes, most notably a large increase in molecular weight to form a pseudothermoplastic material, as noted previously.

2.7. Polybenzimidazoles

The polybenzimidazoles (PBIs) are generally produced by the high temperature, melt polycondensation reaction of aromatic bis-ortho-diamines and aromatic dicarboxylates (acids, esters, or amides) in a reaction such as that shown in equation **11** to form benzimidazole [51-17-2] as the repeating unit.



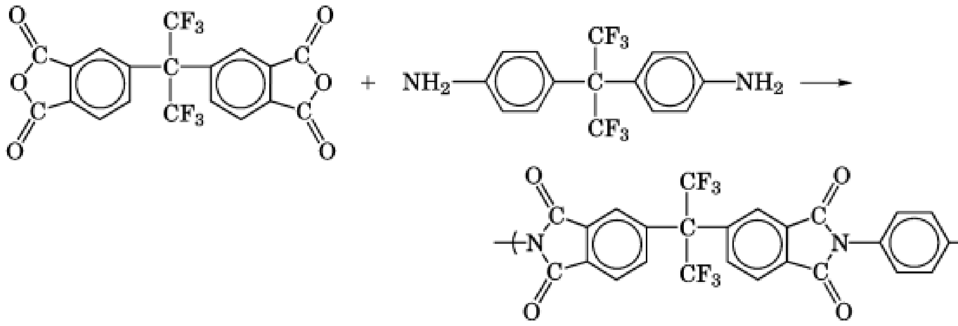
(11)

A large number of PBIs have been investigated since their first synthesis in 1961 (35); the particular polymer used in many commercial and developmental applications is poly(2,2′-*m*-phenylene)-5,5′-dibenzimidazole).

The distinction between thermoplastic and thermoset is particularly cloudy in the case of PBIs because they are formed and processed as thermoplastics but after processing exhibit properties that are more closely related to thermosetting materials. Hence they, too, are usually considered pseudothermoplastics.

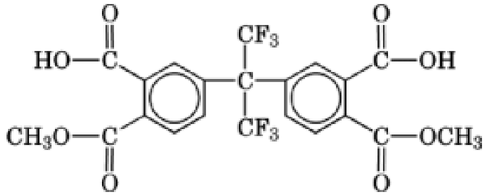
3. Fluorinated Polyimides

Often the substitution of fluorine atoms for hydrogen atoms in a polymer chain markedly increases the thermal stability of the base polymer; this is true for polyimides. A typical fluorinated polyimide is prepared from the reaction of 2,2-bis(3,4-dicarboxyphenyl)hexafluoropropane dianhydride and 2,2-bis-(4-amino phenyl)hexafluoropropane according to the following reaction (36):



(12)

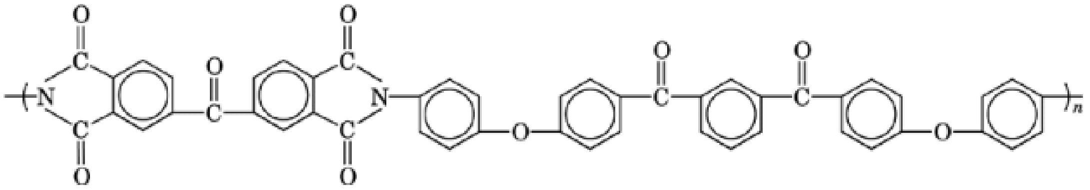
This material is manufactured by Du Pont and sold as resin NR-150B2. A carbon fiber prepreg using NR-150B2 is available and is a member of the Avimid series of composites, Avimid [70850-07-6]. The resin used in the prepreg also contains the following diester-diacid:



and a mixture of meta- and para-phenylenediamines with 5–10% solvent of NMP.

3.1. Semicrystalline Polyimides

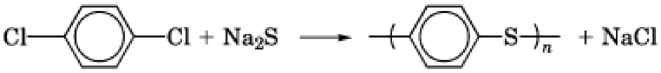
Semicrystalline polyimides containing carbonyl and ether groups have been synthesized by the group at the NASA Langley Research Center (37). One such material, designated LARC-CPI, which is an acronym for Langley Research Center–Crystalline Polyimide, [103320-42-9] has the following structure:



LARC-CPI has a T_g of 222°C and melts at 350°C (37). The high melting temperature illustrates one disadvantage of the high temperature thermoplastics: in order to process or melt consolidate the prepreg, it must be processed at temperatures greater than 360°C.

3.2. Poly(phenylene sulfide)

Poly(phenylene sulfide) (PPS)is a semicrystalline thermoplastic with a T_g of 85°C and a T_m of 285°C. The nominal degree of crystallinity is 50–65 vol %. It is produced commercially by the direct reaction of *p*-dichlorobenzene with sodium sulfide in a polar organic solvent (38).

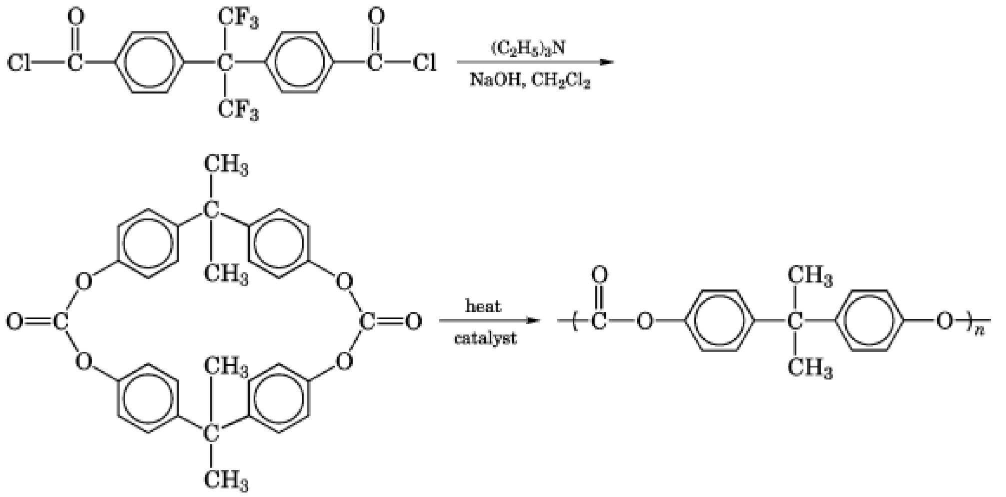


A composite utilizing the high molecular-weight extrusion grade PPS is available. Glass fiber (20–40 wt %), carbon fiber (40–60 wt %), or aramid (50–70 wt %) can be used as the reinforcing agent (38). Although the resin is considered a thermoplastic, continued heating above the melting point during processing produces an effect similar to that of the cure reactions in thermosetting resins and the resulting composite is pseudothermoplastic.

4. Novel Methods

One of the principal problems facing the use and further development of thermoplastic matrices for composites is the need to wet the reinforcing agent with the matrix to obtain a good strong bond. Amorphous thermoplastics must be heated above their T_g and crystalline materials must be heated above their crystalline melting points to flow. The upper temperature limit to which the polymer can be heated is controlled by rate of thermal degradation; thus, a relatively narrow processing window is imposed by the need to flow without degrading. In the usable temperature region, most thermoplastics are quite viscous (several hundred $\mathrm{Pa{\cdot}s}$) and high pressures are required for the resin to flow. Even then, in many cases the resin wets the fiber poorly. Recently, new methods have been described to circumvent this problem and still prepare a true thermoplastic composite. In one case relatively low molecular-weight, low viscosity cyclic compounds are injected directly onto preforms, the resin transfer molding process (RTM), and the polymerization conducted rapidly *in situ.* This requires a special low viscosity monomer coupled with a unique catalytic system that rapidly polymerizes the monomer but does not lead to excess thermal degradation at elevated temperatures.

The general concept of using cyclical monomers to produce high molecular-weight polymers is not new; silicones have been produced by this method for many years. However, most of the silicones are elastomers, and the extension of this method to structural thermoplastic composites is relatively new. This method (14) has been used at the General Electric Co. to prepare cyclooligomers of polycarbonate, which are subsequently used to form a composite via RTM. A mixture of cyclic carbonate oligomers was prepared by the triethylamine-catalyzed hydrolysis–condensation reaction of bisphenol A (bis-chloroformate) using methylene chloride and NaOH (15):



(13)

When the catalyst is triethylamine, the yield is nearly 100% cyclic oligomers; but if pyridine is used, the polymer is nearly 100% linear. A basic catalyst in the second step, such as lithium stearate or an organic titanate [bis-(acetylacetonato)diisopropoxytitanium], produces a polycarbonate with a molecular weight of 250,000–300,000 when polymerized at 300°C for 30 min. A fiber glass composite has been prepared using this basic procedure (39).

Another method that has great potential for the preparation of advanced prepregs and has been explored extensively requires fine powders. The reinforcing fibers are coated with fine particles of the resin and, when heated, the resin flows over the fiber. This method requires finely divided particles either in aqueous solution, in an inert volatile solvent, or as high dielectric material that can be charged and coated by electrostatic attraction to the fiber. Synthetic methods that make fine particles, similar to that described for PEEK (23), are needed.

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