2. Neat Thermoplastic Resins Properties

2.1 Introduction

Plastics are commonly classified into two classes, thermoplastics or thermosets, depending on their behavior when heated [4, 5, 6]. A thermoset polymer undergoes various degrees of cross-linking when cured by heat (or other means) [6]. The cross-linking reactions lead to the formation of an insoluble or infusible rigid product, a "set" product, in which chains are joined together to form a three-dimensional structure [5, 7]. In contrast, thermoplastic polymers do not undergo chemical changes during consolidation; changes are substantially physical [5, 6]. Generally, thermoplastics are melt fusible and can be consolidated by the application of heat and pressure only. They can be repeatedly softened by heating and hardened by cooling. There are however some polymers categorized as thermosetting thermoplastics or pseudo-thermoplastics [1, 6, 8]. They are considered as thermosets; they undergo some reaction chemistry during processing cycles. These materials require both curing and heat treatment for effective consolidation [6].

Thermoplastic polymers are not new; they have been known for a long time. It is only recently that the newer so-called high temperature or high performance thermoplastics have been introduced. The early thermoplastic polymers had predominantly aliphatic carbon backbones in which flexible carbon chains could be extended and rotated into many configurations with relative ease [4, 9, 10]. Rigidity was obtained by restricting the movement of the backbone chain either by crystallinity such as in polyethylene and polypropylene or by the introduction of side groups as in polystyrene or polymethylmethacrylate. The major limitations with these early thermoplastics which are still on the market are their low elastic modulus, low glass transition temperature (Tg) and poor solvent resistance. In the past few years, a range of thermoplastics based on aromatic polymers have been developed which surmount these limitations. The introduction of rigid aromatic rings instead of aliphatic chains increases the intermolecular forces, thus restricting the movement of the backbone chain [4, 10]. Hence, mechanical properties, high temperature capability and solvent resistance are greatly improved and can be often equivalent or even better than the best thermosets. For ease of processing, groups such as ether, carbonyl, thioether, amide, methylene, ester, isopropylidine and sulfone are incorporated between the aromatic rings to render the polymer chain more flexible [1, 10].

This section presents data on a number of these high performance thermoplastic resins which have the potential to be used as matrix material in fibre reinforced composites aimed at aircraft structural applications. The chemical structure, trade name and producers of these resins as well as their thermal and mechanical properties and solvent resistance are presented. A brief description of each polymer follows which highlights their important characteristics.

2.2 Properties of Neat Thermoplastic Resins

2.2.1 Chemical Structure and Some Physical Properties

Table 1 lists the high performance thermoplastic polymers that are discussed in the present report. Although this list is not exhaustive, it provides a good indication of the thermoplastics that have been and are being investigated for use as matrix materials for high performance composites. Most of these neat resins are either commercially available or nearly so, in either industrial or developmental quantities. Some of them are provided as a neat resin or filled with short fibres but not yet reinforced with continuous fibres in a prepreg tape or fabric form. Although it is included in the present list, polyphenylquinoxaline (PPQ) is not expected to be available in the form of fibre reinforced matrix because of its low modulus, high viscosity and its high cost.

Table 2 presents the chemical structure of some of these thermoplastics. The dominant aromatic character in their polymer backbone is clearly shown. Density, Poisson's ratio, Limiting Oxygen Index (L.O.I.) and viscosity are presented in Table 3. Density varies from 1.15 to 1.45 depending on the thermoplastic matrix; the polyamide J-2, a product from E.I. Dupont de Nemours, has the lowest density while N-polymer, a polyimide from Dupont and Eymyd, a polyimide from Ethyl Corporation, have the highest.

The melt viscosities of high-molecular weight thermoplastics are much higher than most thermosets. At processing temperature, thermosets have viscosities less than 1000 poise [2], which is much less than the viscosities presented in Table 3 for thermoplastics. The low viscosity of epoxy formulations results in high melt flow properties in the uncured state leading to good wetting of the fibres during prepreg manufacture [1]. Figure 1 shows the relationship between solution viscosity, melt viscosity, number average molecular weight and the glass transition temperature (Tg) presented in [9]. As shown, the desired high Tg leads inevitably to high melt viscosity. Unfortunately, the high melt viscosity of thermoplastics renders processing difficult as high processing temperatures are required to achieve a low melt viscosity for good consolidation and fibre impregnation; and the viscosity may still be too high for complete impregnation of continuous fibre bundles. Processing becomes difficult at melt viscosities above 5500 poise [9]. Melt viscosities of 10² to 10⁴ poise are desirable for the fabrication of composites [1]. It is then a question of compromise between processability of thermoplastic composites and their high temperature performance as reflected by Tg.

L.O.I. numbers found in Table 3 give an indication of the material's resistance to burning, which may be very important in certain applications. For example, aircraft interiors such as sidewall panels, storage bins, partitions, galley doors and ceiling panels have to meet certain combustibility requirements to comply to the more and more stringent U.S. Federal Aviation Administration (FAA) cabin safety regulations [57]. "L.O.I. is the minimum

TABLE 1. Selected High-Performance Thermoplastics

GENERIC NAME	MANUFACTURER	TRADE NAME
POLYKETONES		
Polyetheretherketone (PEEK)	Imperial Chemical Industries (ICI)	Victrex PEEK
Polyetherketone (PEK)	Imperial Chemical Industries (ICI)	Victrex PEK
Polyetherketoneketone (PEKK)	E.I. Dupont de Nemours	PEKK (1)
Polyetherketoneetherketoneketone (PEKEKK)	BASF	Ultrapek
Polyketone	Amoco Performance Products	Kadel
POLYARYLENE SULFIDES		
Polyphenylene sulfide (PPS)	Phillips Petroleum Company	Byton PPS
Polyarylene sullide (PAS)	Phillips Petroleum Company	Byton PAS-2 (2)
Polyphenylene sulfide sulfone (PPSS)	Phillips Petroleum Company	Byton S PPSS (2)
	i impo i cuoleum company	
POLYAMIDES		
Polyamide	E.I. Dupont de Nemours	J-2 (12)
Polyamideimide (PAI)	Amoco Performance Products	Torlon
POLYIMIDES		
Polyaryleneimide	E.I. Dupont de Nemours	K-Polymer
Polyaryleneimide	E.I. Dupont de Nemours	N-Polymer
Polyimide	Ethyl Corporation	EYMYD
Polyetherimide (PEI)	General Electric Company	Ultem
Polyetherimide	American Cyanamid	Cypac
Polyketoimide	Mitsui Toatsu Chemicals Inc. (MTC)	Larc-TPI, New-TPI
Polyketoimide	Rogers Corp.	Durimid

- (1) Is or will be available only as custom finished composite material parts
- (2) Not commercially available but nearly
- (3) Not expected to be commercially available as a matrix for composite material

(continued)

TABLE 1. Selected High-Performance Thermoplastics (cont'd)

GENERIC NAME	MANUFACTURER	TRADE NAME
POLYSULFONES		
Polysulfone (PSU)	Amoco Performance Products	Udel
Polyarylethersulfone	Amoco Performance Products	Radel A
Polyphenylsulfone	Amoco Performance Products	Radel R
Polyethersulfone (PES)	Imperial Chemical Industries	Victrex PES
POLYESTERS		
Liquid Crystalline (LCP)	Amoco Performance Products	Xydar
Liquid Crystalline	Hoescht Celanese	Vectra
POLYBENZIMIDAZOLES		
Polybenzimidazoles (PBI)	Hoescht Celanese	PBI (1)
Polyphenylquinoxalines (PPQ) (3)		

- (1) Is or will be available as custom finished composite material parts
- (2) Not commercially available but nearly so
- (3) Not expected to be commercially available as a matrix for composite material

Polymer	Chemical Structure	Reference
VICTREX PEEK	[-⊙-°°-⊙-∘-] _n	1, 2
VICTREX PEK	[-⊙-o-⊙-c-] o	11
РЕКК		2, 12
RYTON PPS	[-∞-s] _n	1, 2
J-2	$ \begin{bmatrix} H & 0 & 0 \\ H & -(S) - CH_2 - (S) - H & -(C) - R - C \\ -R - C & -R - C \\ -R & -C & -R - C \end{bmatrix}_{R} $	1
TORLON	$ \begin{bmatrix} R & O \\ I & I \\ N - C & O \\ C & N - (R) \end{bmatrix}_{n} $ $ R = -O - O - O - O - O - O - O - O - O - $	1, 2
N-POLYMER	$ \begin{bmatrix} N \\ C \\$	1, 2

TABLE 2. Chemical Structure of Some High Performance Thermoplastics

(continued)

Reference **Chemical Structure** Polymer 0 11 0 11 CF3 13 EYMYD CF3 ii O 11 0 0 0 ñ CH₃ 1, 2 UITEM CH₃ 11 11 O 0 0 II 0 0 Ĥ 11 1, 2 LARC-TPI ii O II O CH₃ 1, 14 UDEL CH, RADEL A 1 ∘₋] RADEL R 14 1, 14 SO2 VICTREX PES

TABLE 2. Chemical Structure of Some High Performance Thermoplastics (cont'd)

(continued)



TABLE 2. Chemical Structure of Some High Performance Thermoplastics (cont'd)

TABLE 3. Density, Poisson Ratio, L.O.I. and Viscosity of High-Performance Neat Thermoplastic Resins

Resin	Density (g/cm ³)	Poisson Ratio	L.O.I. (%)	Viscosity (poise)*	Reference
Victrex PEEK	1.30			34000	20
	1.27 - 1.32	0.42	35		21
	1.30		35		12
	1.30			35000	2
Victrex PEK	1.30		4 0		22
PEKK	1.30		40		12
	1.30			25000	2
KADEL	1.30				23
Ryton PPS	1.35		44		24
	1.36		44		25 - 30
	1.36			25000	20
Ryton PAS-2	1.40		46		28 - 30
	1.40	0.41			31
Ryton S PPSS	1.40	0.41			31
J-2	1.15				32
				10000	2
	1.15			10000	20
TORLON	1.40		43		33 .
	1.38			> 100000	2
K-POLYMER	1.31	0.365			34, 35
	1.31			>100000	2
N-POLYMER	1.43 - 1.45				36 - 38
	1.44			> 1000000	2
EYMYD	1.45				13
	1.39				39

Resin	Density (g/cm)	Poisson Ratio	L.O.I. (%)	Viscosity (poise)*	Reference
	4.07 4.00		4.7		4.0
	1.27 - 1.29		47		40
	1.27		4 7		41
	1.27			20000	2, 14
CYPAC	1.29				41
	1.28				42
	1.29 - 1.33				43
LARC-TPI (MTC)	1.40		47		44
				> 100000	2
DURIMID	1.37	0.36			45, 46
UDEL	1.24 - 1.25	0.37	30	-	1 4
	1.24			20000	20
RADELA	1.37		33		14
	1.37				23
RADEL R	1.29	· · · · · · · · · · · · · · · · · · ·	38		14
	1.28		> 42		47
VICTREX PES	1.37	0.40	38		14, 48, 49
XYDAR	1.35		42		50 - 52
VECTRA	1.40		35 - 50		53
CELAZOLE	1.30	0.34	58		17
5208**	1.27				54
5245C***	1.25	······································		< 1000	54

TABLE 3. Density, Poisson Ratio, L.O.I. and Viscosity of High Performance Neat Thermoplastic Resins (cont'd)

* Viscosity at processing temperature

** First generation epoxy

*** Bismaleimide (BMI) modified epoxy



Number Average Molecular Weight, in Thousands

FIG. 1a: Victrex PES Reduced Viscosity vs. Number Average Molecular Weight



FIG. 1b: Victrex PES Reduced Viscosity vs. Melt Viscosity



FIG. 1c: Victrex PES Glass Transition Temperature vs. Reduced Viscosity

FIGURE 1. Relationship Between Solution Viscosity (RV), Melt Viscosity, Number Average Molecular Weight (Mn) and Glass Transition Temperature (Tg) of Victrex PES [9]

concentration of oxygen in a test atmosphere adequate to sustain continued burning of the test specimen for a specified period of time or until a specified amount of material is consumed" [56]. The normal atmosphere contains 22% oxygen. All thermoplastics listed in Table 3 have L.O.I. values higher than the absolute minimum (28%) required to qualify the polymer "self-extinguishing" as per ASTM-D2863 [56]. Hoescht Celanese's polybenzimidazole (PBI) has a very high L.O.I. value of 58. Although it gives an indication of the flammability of the polymer, it is not the only criteria to observe when choosing a fire resistant material; ignition temperature, burning time, tendency to drip, smoke emission and safety of the combustion products, for example are also important considerations.

2.2.2 Thermal Properties

Thermal properties including glass transition temperature (Tg), melting temperature (Tm), processing temperature (Tp), heat deflection temperature (HDT) and continuous use service temperature (Ts) are presented in Table 4 while coefficients of thermal expansion (C.T.E.) are presented in Table 5. Included in Table 4 is the morphology of the polymers, i.e. amorphous or semi-crystalline. More detailed information on the morphological factors and the effects of morphology on physical properties of thermoplastic composites is given in Chapter 3.

The performance of thermoplastic composites in high temperature environments depends on the Tg of the polymer matrix and its morphology [74]. Below Tg, a polymer, either amorphous or semi-crystalline, is in a glassy state while above Tg, the material softens as the temperature increases and the material becomes rubbery. As shown in Figure 2, when heating a semi-crystalline polymer above Tg, the amorphous regions of the polymer can flow plastically and therefore heating is accompanied by a reduction in the polymer stiffness which may occur over a broader range of temperatures than that shown in the schematic of Figure 2 [74]. A 100% crystalline polymer would eliminate the Tg process and replace it with the melting process, but this excessive crystallization would impair the ductility of the resin [75]. At temperatures between Tg and Tm the semi-crystalline polymer consists of rigid crystalline regions dispersed in a soft amorphous matrix, so that the polymer is flexible. The properties of the semicrystalline thermoplastics are then significantly reduced, but to a lesser extent than in amorphous thermoplastics; they retain a portion of their load-bearing properties, but not above the melting temperature (Tm). Amorphous thermoplastics do not have a true melting temperature as melting is the disassociation of the crystalline structure [76, 77], but they go through a glass transition. Above Tg, amorphous thermoplastics exhibit substantial loss of their mechanical properties. According to Cogwell's practical experience [74], the long-term service temperature of the composite is 25 - 30° C below the Tg of the matrix; hence continuous use service temperature (Ts) for thermoplastics as reported in Table 4 from different sources

TABLE 4. Thermal Properties of High-Performance Neat Thermoplastic Resins

Resin	Morphology *	Tg (°C)	Tm (°C)	Tp (°C)	HDT (°C)**	Ts (°C)	Reference
				· ·			
Victrex PEEK	С	143	343	370-400	152		1
	C	143	334	350-380	160	250	21
	C	145	335			200	58
	C	143	334				22, 59
	C		334	370-400		250	60
	C	144	340				12
	C	144	340	380			2
Victrex PEK	C	165	365	005 110	165	250	61
DEVIC	C C	162	3/3	385-410	186	260	22
PEKK	C	156	338	000 070			12
		156		360-370		050	62
		150		0.70		250	63
		150	338	370			
Ultrapek		1/3	374				64
Kadel			240		160		03
Duton PPS		85	285	330	135		23
		85	205	330	135		25-30 65
	Ŭ Ŭ	00	200	215.240	115	200-240	20-00,00
	C	85	285	343	115	200-240	2
Byton PAS-2	Ā	215	205	315-343			28 - 30
191011170-2		215		325-330	198		1
		218		020 000			6.6
		222		343			31
		215		330			2
Rvton S PPSS		218		343			31
J - 2		156	• • •	290-305	154		1
	A	160		290-305	138		32
	A	156		300			2
Torlon					274		33
					278		23
		275		330-400	274	200	1
						220	22
	Α	288		350			2
K-Polymer		251		340-400			1
	A	250		360			35
		251		360		232	34
	A	250		350			2
N-Polymer	A		•	385-390			36, 67, 68
	A	340-370	• • •	370			37, 38
		360		350-400			1
	Α	350		375			2
Eymyd U-25	A	249	· · ·	343			39, 69
Eymyd U-35	A	432				427	69
Eymyd U-55	A	288		1			

(continued)

TABLE 4. Thermal Properties of High-Performance Neat Thermoplastic Resins (cont'd)

Resin	Morphology *	Tg (°C)	Tm (°C)	Tp (°C)	HDT (°C)**	Ts (°C)	Reference
Ultem		219-234	•••		200-216		40
	A	230	•				41
		217		340-400	200	170	1
		210		340-380	200		32
	А	217		343			2
Cypac	A	230		304-343			41
	A	217-275		350-385			42
	A	230-275		302-357		180	43
Larc-TPI (MTC)	С	261	270-340				44
	С	264	275-325	343			3
New-TPI	Α	250			238-260		70
		271				204	63
Durimid	A	255-256		340			40, 45
			1	320-350			45, 71
Udel	Α	185			174	160	14
				343-399	174		23
		190		300			3
Radel-A	A	217			204	180	14
				345-388	204		23
		220		330			3
Radel-R		220			204		23
	A						14
Victrex PES	Α	220			203	180	14
		230		315-370	203	180	1
					203	180	48
	А	260		330			2
Xvdar			421	360-430	355	240	1
· ·			358	360-398	337		50
			421		355		51
			358-364		332-347		52
Vectra			280		180-200		53
1000.0				300-340			16
			280-285	300-340			15
PBI	Α	430					24
		427			435		17
				430			72
				470			18
PPO		290		350-400			1
	Α	207-390					14
		288		400		260	19
3501-6***	·····	206		177			1
5245-C		226		177			54
							.

* C = crystalline, A = amorphous

** Heat distortion temperature at 1.82 MPa, ASTM D648

*** First generation epoxy

TABLE 5. Coefficient of Thermal Expansion (C.T.E.) of High-Performance Neat Thermoplastic Resins

Resin	C.T.E. (x 10-6/°C)	Temperature Range (°C)	Reference
Victrex PEEK	47		21
	108	> 150	21
Victrex PEK	57, 69	20 - 150, 150 - 200	22
	79, 84	200 - 250, 250 - 300	22
Ryton PPS	59.7	- 5 0	73
	04.0	23	73
	108.9	150	73
Torlon	35	23 - 149	33
N-Polymer	90	23 = 323	67
PEI Ultem	52 - 56	-20 - 150	40
Eymyd U-25	44	N/A	39
Larc TPI (MTC)	24 - 33	20 - 200	4 4
New TPI	50 - 55	N/A	70
Durimid	35	20 - 240	45.46
Udel	51	N/A	14
Radel A	49	N/A	14
Radel R	55	N/A	14
Victrex PES	5 5	N/A	14
Vectra	- 5	parallel to flow	53
		-50 - 200	
	40 - 75	transverse to flow	53
		-50 - 200	
PBI	23	24 - 149	17
	32	200 - 300	17



FIGURE 2. Semi-Crystalline Thermoplastic Polymers Retain Part of Their Properties above Tg [75]

(mainly manufacturers' datasheets) could be lower. Many of the thermoplastics listed in Table 4 have Tg greater than 200° C and then have use temperatures in the 170° C - 180° C range required for applications on supersonic fighter and supersonic commercial aircraft [1, 74].

Figure 3 presents the average Tg found in Table 4 for a number of thermoplastics. Except Phillips Petroleum's polyphenylene sulfide (PPS), a member of the polyarylene sulfide family, all Tg's are over 140° C. The polyimide family, Amoco's polyamideimide Torlon and polybenzimidazole (PBI) exhibit very high Tg's. Among them, N-polymer and PBI have the highest Tgs, both higher than 300° C and higher than 400° C in the case of PBI. It can also be observed that the latest compositions within the polyketone and polyarylene sulfide families have higher Tg's than their predecessors (Dupont's polyetherketoneketone (PEKK), ICI's polyetherketone (PEK), BASF's polyetherketoneetherketoneketone (PEKEKK) versus ICI's polyetheretherketone (PEEK) and Phillips Petroleum's polyarylene sulfide (PAS-2) and polyphenylene sulfide sulfone (PPSS) versus PPS) [3]. Unfortunately, as mentioned earlier, the desired high Tg of a high performance thermoplastic is generally associated with a high melt viscosity and a high processing temperature, often close to the decomposition temperature. As shown in Table 4, processing temperatures for thermoplastics vary from 290 to 470° C compared to 177° C for Hercules 3501-6 epoxy. In general, amorphous thermoplastics exhibit higher Tg values than the semi-crystalline polymers but fortunately they are processed in the same temperature range as semi-crystalline thermoplastics [77]. Processing temperature must exceed Tg in the case of an amorphous thermoplastic while it has to exceed Tm in the case of a semi-crystalline thermoplastic in order to achieve a low melt viscosity, good consolidation and proper morphology [1].

The thermal stabilities of different thermosets including epoxy and polyimide thermoset resin formulations as well as the thermoplastic resins PEEK and PPS have been measured and compared by Knight and Wright [78]. They have rated the relative thermal stabilities of these polymers in a decreasing order as follows: PEEK and PPS > polyimides > epoxies. Scola [79] examined the thermal-oxidative stability of polymer materials which are candidates for application in advanced composites in the temperature region of 287 - 343° C. Among these polymers were N-polymer, PPQ, Durimid (Larc-TPI produced by Rogers), Larc-TPI (produced by Mitsui Toatsu Chemicals (MTC)), Ethyl Corporation's Eymyd L-30N (based on the same resin formulation of Eymyd U-35), Ethyl Corporation's Eymyd L-20N (based on the same resin formulation to Eymyd U-25) and PBI. Figure 4 shows the thermo-oxidative stability of some of these polymers at 316° C. In terms of their thermo-oxidative stability in air for 1500 hours at 316° C, the author has rated the polymers as follows: N-polymer >>> PPQ > Durimid > Eymyd L-20N > Larc-TPI >>> Eymyd L-30N > PBI.



FIGURE 3. Glass Transition Temperature (Tg) of High Performance Thermoplastic Resins



FIGURE 4. Thermo-Oxidative Stability of High Temperature Polymers at 316°C in Airflow (100 cc/min) [79]

2.2.3 Mechanical Properties

Tables 6,7, and 8 contain the neat resin tensile, flexural and compressive properties respectively of the high performance thermoplastics. High resin strength values are desirable to minimize intra-ply cracking in the composite under impact conditions and to obtain good transverse properties [80]. Tensile and flexural strengths of thermoplastics listed in Table 6 and 7 are comparable and often better than those of 3501-6 epoxy and BASF 5245C bismaleimide modified epoxy. Hoescht Celanese's liquid crystalline polyester Vectra, polyamideimide Torlon and polybenzimidazoles exhibit the highest tensile and flexural properties. The tensile failure strains of Torlon are much higher than the other two (12% versus 1-3%). Tensile moduli should be above 3.1 GPa to achieve acceptable composite compression strength [3, 80, 84]. The tensile modulus of polysulfones in general falls below this value. Thermoplastic resins exhibit higher tensile strain to failure than thermoset resins. They can be then used more efficiently with newer high strain, high strength carbon fibres. It is observed from the few data available on compressive properties (Table 8) that PBI has outstanding compression strength while LCP Vectra exhibits poor compression strength.

A major requirement in the design of aircraft for high temperature performance is the use of a resin that retains adequate stiffness at the required temperature and in a wet environment. Modulus and strength values under hot and especially hot/wet environments are scarce but limited data are shown in Tables 9 and 10.

2.2.4 Toughness

Notched and unnotched Izod impact energies as well as G_{Ic} fracture toughness from compact tension tests for selected high performance neat thermoplastic resins are shown in Table 11. Like most plastics, these thermoplastics are notch sensitive; notched Izod impact energies are much lower than unnotched Izod impact energies. Sharp radii and molded notches must be avoided. Values above 53 J/m for notched Izod impact are indicative of tough materials [1]. Liquid crystalline polyester Vectra and Amoco's polyphenylsulfone Radel-R have especially high values (420-690 and 425-640 J/m respectively).

These fracture toughness measurements are not expected to correlate well with the G_{Ic} values [1]. Except for PPS, the G_{Ic} values are outstanding and range from 1 to 6.6 kJ/m². These are much higher than the values obtained from typical brittle epoxies cured at 177° C (0.1 kJ/m²) used as matrices in current high performance composites (e.g. Hercules Corp's AS4/3501-6) and even higher than the values observed for the second generation or toughened epoxies [1].

TABLE 6. Tensile Properties of High-Performance Neat Thermoplastic Resins

Resin	Tensile Strength	Tensile Modulus	Elongation at	Test Standard	Reference
	(MPa)	(GPa)	Break (%)	ASTM	
	<u> </u>				
Victrex PEEK	100	3.1	40		1
	92	3.6	50	D638	21
	100		28.5		81
	103	3.8	11		2, 12
Victrex PEK	105	4	5	D638	22
PEKK	102	4.5	4		2.63
Ryton PPS	82.8	4.3	3 - 5		1, 25 - 27
	79		2 - 20		29. 30
	65.5		1.6	D638	24
	80	3.91	3		2
Ryton PAS-2	100	2.8	7.3		1
	100 - 101		8		28 - 30
	90		5.4		31
Ryton S PPSS	92		5.4		31
J - 2	85	3.2	44.3		1
	103	3.2	25		2
Torion	152	4.5		D638	23
	166	3.7	12 - 15		1
	185		12	D1708	33
	136	3.3	25		2
	136 - 186	3.3 - 4.8	9.7 - 25.4		82
K-Polymer	102	3.8	14		1, 2, 34, 35
N-Polymer	110	4.1	6		2, 36, 67
	110		6		1, 37
Eymyd U-25	91.1	4.1	7.2		39
PEI Ultem	105	3	30 - 60	D638	1, 2, 40, 42
	100	3.1	6.4		83
PEI Cypac	95 - 102		15 - 20		42
Larc TPI (MTC)	113	4.5	3		8
	163	3.5	8.5		44
New TPI	78 - 92	2 - 4.9	10		70
Durimid	138 - 153	3.4 - 4.4	5 - 8	D1708	8. 45. 46
Udel	70.3	2.48	75	D638	14
	68.9 - 70.3	2.48			23
	76	2.41	76		2
Radel A	82.7	2.66	40	D638	14
	82.7	2.66		D638	23
Radel R	71.7 - 75.9	2.14 - 2.77	30 - 60	D638	14, 47
Victrex PES	84	2.4	40		14
	84		40 - 80	D638	1, 48
	76	2.4	7		2

(continued)

Resin	Tensile Strength	Tensile Modulus	Elongation at	Test Standard	Reference
	(MPa)	(GPa)	Break (%)	ASTM	
Xydar	126	8.3	5		50
	131	14.5	1.3		1
	116	9.7			51
	110	14	1.1 - 1.3		52
Vectra	165 - 188	9.7 - 19.3	1.3 - 3.0	D638	53
PBI	160	5.8	3	D638	17
PPQ	99.3 - 122.7	2.04 - 3.10	6.2 - 128		14
	117	2.6	8.5		1
3501-6	82.8	4.3	1.2		1
5245C	82.8	3.3	2.9		54

TABLE 6. Tensile Properties of High-Performance Neat Thermoplastic Resins(cont'd)

TABLE 7. Flexural Properties of High-Performance Neat Thermoplastic Resins

Resin	Flexural Strength	Flexural Modulus	Test Standard	Reference
	(MPa)	(GPa)	ASTM	
Victrex PEEK	110	3.9		1
	170	3.7	D790	21
Victrex PEK		3.7	D790	22
Kadel	169	3.7	D790	23
Ryton PPS	96	3.8		24
	152	3.4		25 - 27
	166	4.1		1
	147 - 149	3.4 - 4.1		28 - 30
Ryton PAS-2	177	3.2		28 - 30
	149	3.4		31
Ryton S PPSS	150	3.3		31
J - 2	125	3		1
Torion	207	4.3		1, 82
	244	5	D790	23
	212	4.6	D790	33
N-Polymer	117	4.2		1, 36, 37, 67
PEI Ultern	145	3.3		1, 40 - 42
PEI Cypac	128 - 130	3.0 - 3.1		41 - 43
Larc TPI (MTC)	159			44
New TPI	137	2.8 - 3.9		70
Durimid	193	4.3	D790	45, 46
Udel	106	2.69	D790	14, 23
Radel A	110	2.75	D790	14, 23
Radel R	85.5	2.3	D790	14
	104.1	2.62	D790	47
Victrex PES	129	2.6	D790	1, 14, 48
Xydar	131	11 - 14		1, 50, 51
	135 - 139	12.1 - 12.2		52
Vectra	169 - 245	9.0 - 15.2	D790	53
PBI	220	6.5	D790	53
5208	112	3.7		54
5245C	145	3.4		54

Resin	Compressive Strength (MPa)	Compressive Modulus (GPa)	Test Standard ASTM	Reference
Victrex PEEK	118		D695	21
Ryton PPS	110		D695	24
Torlon	172		D695	33
	276	3.1		82
PEI Ultem	140 - 150	3.3	D695	40
Durimid	236	3.6	D695	45, 46
Udel	96	2.6	D695	14
Victrex PES	108	2.1	D695	14
Vectra	70	6.3	D695	53
PBI	390		D695	17

TABLE 8. Compressive Properties of High-Performance Neat Thermoplastic Resins

TABLE 9. Tensile Properties of High-Performance Neat Thermoplastic Resins at Elevated Temperatures

Resin	Tensile Strength (MPa)				
	RT(a)	I <u>T</u> (b)	HT(c)		
Victrex PEEK Victrex PEK	100 105	66 (100) ^(d)	35 (150) 20 (250)		
Ryton PAS-2	90	63 (120)	54 (150)		
Ryton S PPSS	92	69 (121)	53 (150)		
Torlon	166	152 (100)	124 (149)		
N-Polymer	110	90 (100)	76 (149)		
PEI Ultem	105	90 (100)	76 (149)		
Udel	70	52 (100)	41 (149)		
Victrex PES	84	69 (100)	55(149)		
Xydar	131	62 (100)	35 (149)		
PBI	159	165 (93)	138 (204)		

(a) RT = Room Temperature (23 °C)

(b) IT = Intermediate Temperature (100 °C to 140 °C)

(c) HT = High Temperature (> 140 °C)

(d) number in parenthesis indicates the temperature at which the value has been measured

Resin	Flex	Flexural Strength (MPa)		Flex	Flexural Modulus (GPa)				
	RT ^(a)	I1(p)	HT(c)	RT	IT	н			
Victrex PEEK				3.9	3.0 (100) ^(d)	2.0 (149)	1		
Victrex PEK	1			3.7		0.3 (250)	22		
Ryton PAS-2	149	94 (121)	73 (150)	3.4	3.0 (121)	2.5 (150)	31		
Ryton S PPSS	150	98 (121)	75 (150)	3.3	3.0 (121)	2.6 (150)	31		
Torlon	207	193 (100)	166 (149)				1		
PEI Ultem	145		60 (200)	3.0		2.2 (200)	40		
				3.3	3.1 (100)	2.7 (149)	1		
Victrex PES				2.6	2.5 (100)	2.5 (149)	1		
				2.6		2.3 (180)	48		
Xydar	131		41 (232)	11.0		6 (232)	51		
				14.0	11.0 (100)	9.7 (150)	1		
5208	112	88 (93)	74 (132)	3.8	3.3 (93)	2.9 (132)	54		
5245C	145	115 (93)	107 (132)	3.4	3.2 (93)	2.8 (132)	54		
		1	L		1		1		

TABLE 10. Flexural Properties of High-Performance Neat Thermoplastic Resins at Elevated Temperatures

(a) RT = Room Temperature (23 °C)

(b) IT = Intermediate Temperature (100 °C to 140 °C)

(c) HT = High Temperature (> 140 °C)

(d) number in parenthesis indicates the temperature at which the value has been measured

Resin	Notched Izod	Unotched Izod	G _{ic} (kJ/m ²)	Test Standard	Reference
	Impact (J/m)	Impact (J/m)		ASTM	
Victrex PEEK	85		> 4 4.8 - 6.6		1 85
Victrex PEK	83 81	no break	2	D256 D256	2, 12, 62 21 86
	69			D256	22
PEKK			1		2, 12, 62
Kadel	85			D256	23
Ryton PPS	160		0.1 - 0.2		1
	16	100			24
	21	427			25 - 27
	21	576 - 578			28 - 30
Ryton PAS-2	43	1344 - 1348			28 - 30
	43				1
	31	1590			31
Ryton S PPSS	19	1380			31
J - 2	80.1		2.0		
Tarlan	142		2.0		2
1011011	143		3.4 - 3.5	D256	22
	140			D256	33
	145		34	0256	23
K-Polymer			18 - 19		1 2 34 35
N-Polymer	42		2.4		1.37
			2.5		2
Evmvd U-25			2.3		39
PEI Ultem	40 - 50	1300		D256	40, 42
	53.4		2.5		1
PEI Cypac	50	1300			42, 43
Larc TPI			1.7 - 1.8		1, 2
Larc TPI (MTC)	21.3 - 21.4				44, 87
New TPI	19.6 - 88.3				70
Durimid	53			D256	45.46
Udel	64 - 69	no break		D256	14
	64 - 69			D256	23
	64		2.4		1
Radel A	85	no break		D256	14
	85			D256	23
	640		3.5		1
Radel R	425 - 640	no break			14

TABLE 11. Impact and Fracture Toughness of High-PerformanceNeat Thermoplastic Resins

Resin	Notched Izod Impact (J/m)	Unotched Izod Impact (J/m)	G _{ic} (kJ/m ²)	Test Standard ASTM	Reference
Victrex PES	84 85	no break	1.9	D256	14, 48 1
Xydar	165 - 245 208 128	390 - 454 454	2.9		52 50 1
Vectra	420 - 520 690			D256	53 88
PBI	30	600		D256	17
5208 3501-6 5245 C	128 411		0.12		54 1 54

TABLE 11. Impact and Fracture Toughness of High-Performance Neat Thermoplastic Resins (cont'd)

TABLE 12. Creep Properties of Selected High-Performance Neat Thermoplastics

Resin	Tensile Creep	Reference
Vietrox DEEK	1.72% offer 168 br 150 °C 1450 ppi	-
VICITEX PEEN	2.83% after 1000 br 66 °C 5000 psi	90
Ryton PPS	0.8% after 1000 hr. 66 °C. 5000 psi	1
	1.74% after 1000 hr, 66 °C, 5000 psi	90
Torlon	4.8% after 1000 hr, 100 °C, 15000 psi	1, 33
	1.0% after 100 hr, 23 °C, 5000 psi	1
	1.7% after 100 hr, 240 °C, 5000 psi	1
Udel	1.0% after 20000 hr, 22 °C, 3000 psi	1
	1.8% after 300 hr, 100 °C, 3000 psi	1
	2.0% after 10000 hr, 149 °C, 1000 psi	1
Radel A	< 0.7% after 500 hr, 175 °C, 1000 psi	1
Victrex PES	~ 1.0% after 24 hr, 150 °C, 2200 psi	1

2.2.5 Non-Linear and Time-Dependent Behavior

Stress-strain behavior of all plastic materials depends on time, temperature and on the applied stress or strain [4]. The viscoelastic behavior of polymeric materials is primarily determined by molecular configuration; therefore the viscoelastic behavior of thermoplastic resins is likely to be quite different from that of thermoset resins [89]. The non-linear stress-strain behavior and time-dependent response are not very significant in the brittle thermoset resins found in normal use [1]. Thermoplastic resins exhibit significant non-linear stress-strain behavior [1]. The degree of non-linear viscoelasticity varies among the thermoplastics. Figure 5 illustrates stress-strain plots for PEEK at temperatures in the range 20 - 180° C. The curves are quite parallel and linear up to strain levels of 1%. There is a significant shift in the curves between 80 and 150° C as the Tg for PEEK is 143° C.

Data on the time dependence response of thermoplastic resins as measured by creep tests are very limited [59, 89]. Families of creep curves for specific conditions can be found sometimes in the manufacturer's datasheets for the oldest materials such as PEEK and PPS. The tensile creep data presented in Table 12 indicate that thermoplastics may undergo creep. Figure 6 presents tensile creep curves for PEEK in the temperature range 20 - 180° C under load. The modulus dependence on time increases with increasing temperature. Results of Xiao [89] presented in Figure 7 shows that the creep compliance of PEEK resin rises markedly near 120° C. Figure 8 illustrates yield stress as a function of time under load for PEEK resin for temperatures of 23 and 150° C. The influence of temperature is greater than that of time under load.

2.2.6 Chemical Resistance

It is well recognized that polymers in a chemical environment can absorb, react chemically, become plasticized, dissolve and be stress-cracked [91]. The chemical resistance of a polymer depends primarily on its chemical structure. For example, high molecular weight, chain branching, cross-linking and high degree of crystallinity reduce the solubility of polymers [91]. High performance thermoplastics developed in recent years are generally characterized by good heat and chemical resistance, better than the first generation of thermoplastics such as polycarbonates, polyurethanes and polystyrenes [91]. Table 13 shows the effects of solvents on some high performance thermoplastics. Although some amorphous thermoplastics such as Dupont's polyimide K-polymer and American Cyanamid's polyetherimide (PEI) Cypac have been found to be solvent resistant, in general, semicrystalline polymers are more solvent resistant than amorphous polymers due to the densely packed spherulites in the crystalline region which impedes diffusion of solvents into the polymer [1, 77]. The solvent resistance of thermoplastics may be improved by inducing limited







FIGURE 6. Tensile Creep Curves for PEEK (Subsequent to Interpolation of Experimental Curves) [59]



FIGURE 7. Temperature Dependence of Creep Compliance. (a) PEEK Resin, at 9.3 MPa (△), 4.6 MPa (○) and 2.3 MPa (□); (b) Transverse Tensile at 15 MPa. [89]



FIGURE 8. Tensile Creep Rupture for PEEK, Specimens Cut 90° to Flow [59]

TABLE 13. Solvent Effects on Selected High-Performance Neat Thermoplastics (a,b)

RESIN	HYDRAULIC	JP-4	ALCOHOLS	CHLORINATED	ETHERS	KETONES	ESTERS	AROMATIC	NMP/	20% H2SO4	H ₂ O UPTAKE
	FLUID		GLYCOLS	HYDROCARBONS				HYDRO-	DMA (c)	~ 7	SATURATION
								CARBONS			(%)
Victrex PEEK	ο	0	0	0		0	0	o		0	0.5
Victrex PEK											
PEKK	0	0									0.3
Ryton PPS	0	0	0	0	0	0	0	0	0	0	0.4 - 0.5
Ryton PAS-2	0	0	0	+		+	0	ο			
Ryton PPSS	0	0									
J - 2	+		+	+	+						5.0
Torlon	0	0	0	0	0	0	0	0	о	0	2.0 - 5.0
K-Polymer	0	0	0	0		0				······	2.2
N-Polymer	0	0				+ +	+ +	+ +			
Eymyd U-25		0									0.5
PEI Ultem	0	0	0	+ +	0	+	+	о	+ +	0	1.2
PEI Cypac	0	0		0		0				-	
LARC-TPI(MTC	C)							0		0	
Udel	+	0	0	+ +		+	+	+	+ +	0	0.6 - 0.9
Radel A	+	0	0	+ +		+	+	+	+ +	0	1.3 - 1.9
Radel R			0	+		+	+	+	+ +		1.1
Victrex PES	+	0	0	+ +	0	+	+	+	+ +	o	2.1
Xydar	0	0	0	0		0	0	0		0	0.2
Vectra	0		0								0.03
PBI	0			0		0	0	0	+ +	0	
PPQ				+ +					0		
3501-6	0	0	0								

(a) ++: dissolves, +: attacks or is absorbed, o: no effect

(b) these data come mainly from References 1, 14, 92 and from manufacturer's data

(c) DMA: dimethylacetamide, NMP: n-methylpyrrolidone

cross-linking into the polymer backbone through the use of annealing, postcures, or thermal reactions of terminal and pendant reactive groups (norbornene, ethynyl and phenylethynyl groups) [1, 92, 93], but these techniques often reduce fracture toughness.

In aircraft applications, structural composite parts must be resistant to the various fluids encountered in flight and maintenance operations such as fuel, fuel additives, deicing fluids, lubricants, paint strippers and hydraulic fluids [1, 94]. Composites must be resistant to swelling and delamination in the presence of these fluids. Some of the thermoplastics listed in Table 13, particularly the ones belonging to the polysulfones family, do not possess sufficient solvent resistance to be used in aircraft structural applications.

Knowledge of the resistance of thermoplastic composites to aircraft fluids and moisture is not as extensive as for epoxy based composites due to lack of experience. In order to apply high performance thermoplastics with confidence as quickly as possible, accelerated environmental testing such as that carried out in Reference 95 should be conducted to predict the effects of long time exposure to realistic anticipated climatic conditions and aircraft utilization scenarios (load, moisture and temperature) on mechanical properties. The issue is even more critical with semi-crystalline polymers [1]. In Reference 1, several unanswered questions have been identified: "With semi-crystalline thermoplastic composites, is the percentage of crystallinity constant with time under load? Is crystallinity constant with time in the presence of aggressive liquids such as hydraulic fluids or methylene chloride? For thermoplastics composites in general, what aging mechanisms will be significant?"

2.2.7 Water and Moisture Resistance

As shown in Table 13, maximum moisture content absorbed by thermoplastics when immersed in water is generally lower for semi-crystalline thermoplastics than for amorphous thermoplastics. The maximum moisture content values for semi-crystalline thermoplastics are about an order of magnitude lower than for epoxy.

Most data available either in the open literature or from manufacturers' datasheets present the behavior of thermoplastics when immersed in water; however, the response of thermoplastics to other moist environments must be understood. The effects on mechanical properties of thermoplastic composites of exposure to humid air (which is usually representative of the environment encountered in aircraft applications) as well as the determination of the moisture absorption charcteristics have been rarely addressed. Wang and Springer [96] have conducted tests to determine the moisture absorption characteristics of PEEK 150P (the commercial grade that is close to the polymer used in carbon/PEEK ICI's APC-2 composites) and APC-2 composite when exposed to humid air of different relative humidity and temperature. They have also evaluated the effects of moisture content and crystallinity on fracture toughness. The range of crystallinity was 30,34 and 43 % for PEEK polymer and 17 and 21 % for APC-2. They found that both PEEK polymer and APC-2 followed the Fick Diffusion Law [97] when exposed to humid air and that the maximum moisture contents and the diffusivities can be described by expressions similar to those developed for epoxy matrix composites. Maximum moisture content did not vary significantly with the degree of crystallinity of PEEK polymer and APC-2. Depending on the hygrothermal conditions, the maximum moisture content obtained for APC-2 varied from 0.1 to 0.2%, which is one tenth that of current carbon/epoxy (typically 2%). It varied from 0.2 to 0.4% for the PEEK polymer. For the conditions of the tests, the fracture toughness was found to be unaffected by crystallinity and by moisture content. The low moisture absorption exhibited by carbon /PEEK has been corroborated in [98]. Figure 9 shows that the equilibrium moisture level for the thermoplastic composite fabricated from the prepreg tapes and exposed to 95% relative humidity and 71° C were significantly lower when compared to the epoxy composite exposed to the same environmental conditions; i.e. 0.15% versus 2.32% respectively.

2.3 Characteristics of Some Thermoplastic Polymer Families

This section presents a brief description of the different chemical classes of thermoplastic polymers. The main characteristics of each class are overviewed. Emphasis is placed on neat thermoplastic resins, but occasionally information on fibre reinforced thermoplastics are also included as some thermoplastic resins are available only when reinforced with continuous fibres or data found in literature have been generated mainly on reinforced thermoplastics.

2.3.1 Polyketones

Although polyetheretherketone (PEEK) is the only polyketone of current commercial importance, there are other aromatic ketones newly introduced to the market that are of increasing interest. There are at least six producers supplying four types of aromatic ketones [63]: I.C.I. with PEEK (1981) and PEK (1986), E.I. Dupont de Nemours with PEKK (1988), Amoco Performance Products with PAEK, BASF with PEKEKK, Mitsubishi with its newly developed PEK material that is ready to be commercialized, and Hoescht which is in the early stage of introducing its own PEK. All of these polyketones are very attractive because of their balanced properties. They exhibit excellent chemical resistance, excellent toughness, good strength and rigidity, good load-bearing properties even at high temperature and in harsh environments, good radiation resistance, excellent fire safety characteristics and easy processability [63]. The price is also becoming reasonable compared to other high performance thermoplastics.

Polyetheretherketone (PEEK):

Among the new high performance thermoplastics, PEEK has been investigated the most over the last few years and still much attention is being devoted to PEEK and its composites. PEEK resins were introduced into the marketplace in different grades by Imperial Chemical



FIGURE 9. Moisture Absorption of Graphite Reinforced Thermoplastic and Epoxy When Exposed to 95% RH and 71°C [98]

Industries (ICI) in 1981 under the trade name of 'Victrex' PEEK [99]. It is a semi-crystalline polymer for which the maximum achievable degree of crystallinity is about 48%, although more typical values are generally lower than 30% [59]. The counterpart composite material, APC-1 (Aromatic Polymer Composite), containing 52% by volume of carbon reinforcing fibres was introduced into the market by ICI in 1982 [99]. APC-1 product has been replaced by an optimized system identified as APC-2 [10]. The major difference between the two is that APC-1 contained only 52% by volume of carbon reinforcing fibre while APC-2 contains 62% by volume thus enhancing its fibre dominated mechanical properties. In addition, a better fibre/matrix adhesion with APC-2 compared to APC-1 was found responsible for the better resistance to impact and crack initiation and propagation of APC-2 [100]. APC (ITX) is another member of the Aromatic Polymer Composite family being developed at ICI. It is based on a semi-crystalline polymer belonging to the polyketone family. It exhibits a Tg of 177° C which is 34° C higher than PEEK. APC (HTX), and APC (HTC) are other development grades of Aromatic Polymer Composite belonging to the same family as APC-2 (carbon fibre reinforced polyetheretherketone) [74, 75], but unlike to APC (ITX), they are not expected to enter the composite business due to processing difficulties.

Many data are available in the open literature and from ICI's datasheets on reinforced and unreinforced PEEK. There are numerous papers on various aspects of PEEK such as processing [101, 102] and joining [103, 104], rheological and morphological aspects [58, 105 -113], environmental resistance [96, 99], radiation resistance [114], physical and mechanical properties [10, 59, 115], thermal cycling [98], fatigue resistance [85, 116] creep properties [59, 89], toughness [96, 117 - 124] and damage tolerance [125 - 127, 185]. Very often, the evaluations of carbon fibre reinforced PEEK were done in conjunction with those of epoxy composites for comparison purposes. Nagure and shide [100], have summarized the synthliched studies up to 1986 on PEEK and its composites.

PEEK is inherently flame retardant with a L.O.I. of 35; and therefore flame retardants are not required [61]. Also, smoke emission of PEEK during a fire is amongst the lowest of any thermoplastics. PEEK exhibits excellent chemical and moisture resistance, and it withstands most solvents [91, 96, 99, 100]. It can be dissolved by concentrated sulfuric acid and attacked by other mineral acids, such as nitric, but only a limited number of solvents cause stress-cracking, and then only under severe stress conditions [91]. It is insensitive to moisture even when hot. Because of its balanced properties including good strength, high ductility, high temperature stability (Tg 143° C), excellent impact toughness and excellent resistance to moisture and solvents, PEEK may be used in a wide range of applications such as electrical and electronic parts, military equipment, automotive parts, wires and cables in nuclear plants, underground railways and oil wells, as well as advanced structural composites for aircraft.

Polyetherketoneketone (PEKK)

PEKK is a semi-crystalline thermoplastic that has been developed by Dupont. It exhibits lower melt viscosity than PEEK rendering the processing and the achievement of optimum consolidation of fibre reinforced composite laminates easier [12]. The Tg of PEKK is 10-12° C higher than PEEK. As with PEEK, PEKK demonstrates good flammability characteristics, good durability and property retention at elevated temperature when saturated with moisture and good resistance to aircraft fluids. The high tensile modulus of PEKK (4.5 GPa) contributes to its high composite performance [12, 62]. The compressive strength of unidirectional carbon/PEKK materials is among the very highest measured for high performance thermoplastic composites. Dupont's PEKK is available in the form of finished composite parts ordered by the customer.

Polyetherketoneetherketoneketone (PEKEKK)

PEKEKK has been developed by BASF and is marketed under the trade name Ultrapek [63]. PEKEKK is a polymer with 10-25% crystallinity that has been tailored for composite applications and is available as a commingled woven fabric form. Its Tg of 173° C is 30° C higher than the Tg of PEEK, but its Tm of 374° C is also higher. However, its melt viscosity at 400° C is virtually identical to that of PEEK 150G. Reinforced PEKEKK exhibits good mechanical properties, similar to APC-2 laminates, and excellent solvent resistance.

Polyetherketone (PEK)

PEK has been developed by ICI and is sold under the tradename 'Victrex' PEK. It is a semicrystalline polymer that exhibits a Tg of about 165° C which is 22° C higher than PEEK. Its heat deflection temperature is among the highest of the unfilled crystalline polymers and exceeds that of some amorphous thermoplastics. However, its melt viscosity is lower than that of PEEK [22]. As for other polymers of the ketone family, PEK has good balanced properties. It exhibits good tensile and flexural properties, and excellent chemical and radiation resistance as claimed in the manufacturer's datasheet [22].

2.3.2 Polyarylene Sulfides

Polyarylene sulfide polymers represent a family of thermoplastic materials with high aromaticity and divalent sulfur linkages (Figure 10) [128]. This combination results in polymers with excellent corrosion resistance, good thermal stability, inherent flame resistance and a good balance of physical properties.

Polyphenylene Sulfide (PPS)

PPS is the simplest member of the polyarylene sulfide family [25]. The polymer backbone is composed of a series of alternating aromatic rings and sulfur atoms. Being one of the first synthetic resins, together with the phenolics [24], PPS is very well documented in the open literature [1, 25, 26, 65, 90, 128 - 139] and several extensive datasheets from the

manufacturer, Phillips Petroleum Company, are available. A detailed review of PPS has been presented by Lopez and Wilkes [137]. Phillips Petroleum began the world's first commercial production of Ryton PPS in 1973 [24]. The PPS composite counterparts were introduced to the market place in 1983 [28, 30]. PPS is a semi-crystalline polymer with a degree of crystallinity as high as 60-65% after annealing [90, 134]. It exhibits inherent flame resistance. This polymer is very inert and offers excellent chemical resistance to several classes of chemicals including aqueous acids and bases, chlorinated solvents, amines, phenols, paint remover, hydrocarbons, fuels and aircraft hydraulic fluid [93, 134, 140, 141]. There is no known solvent for PPS below a temperature of 204° C [142]. It is not resistant to strong oxidizing agents, e.g. sodium hypochlorite and mineral acids. The main disadvantages with PPS are its low fracture toughness $(0.1 - 0.2 \text{ kJ/m}^2)$ and its low Tg (85° C) leading to fair retention of properties at elevated temperature. At 177° C, PPS unidirectional laminates retain 90% of their room temperature stiffness but only 30 % of their room temperature strength [28 - 30]. There is ongoing research and development reported in Reference 133 concerning a new grade of PPS resin for carbon and glass reinforced composite materials. The new grade has improved polymer toughness, morphological structure and interfacial adhesion resulting in improved laminate mechanical performance especially in the transverse direction. In addition, the new composite grade has a widened processing window.

Some of the market areas that have been defined so far include: valves and piping resistant to chemicals encountered in petroleum, chemical, marine and pulp and paper industries, automotive parts such as internal engine parts and underhood covers, helmets, seat backs, submersible pumps and condensing heat exchangers and aircraft components such as interior panels and doors, radomes and secondary structures [57, 143, 144].

Polyarylene Sulfide (PAS-2)

Polyarylene sulfide crystalline polymers, PAS-1 and PAS-B were investigated by Phillips Petroleum Co. [30, 128, 145]. They have been superseded and replaced by the amorphous polymer PAS-2 being developed also by Phillips Petroleum Co. [28 - 31, 128]. It is reported to be commercially available in the near future as a reinforced material. The impact resistance for PAS-2 is at least twice that of PPS while room temperature properties are quite comparable to those of PPS. The major difference between them is in the elevated temperature properties. PAS-2 composites have been shown to have greater high temperature properties than PPS composites. The 135° C higher Tg for the PAS-2 resin accounts for its excellent retention of mechanical properties at 177° C. As shown in Table 14, at 177° C, PAS-2 unidirectional composites retain 100% of their room temperature stiffness and over 70% of their room temperature strength. Although it is an amorphous polymer, PAS-2 exhibits excellent chemical resistant to various chemical environments [28].

 $(-Ar - S)_{x}$

Ar = Aromatic Structure

FIGURE 10. General Formula for Arylene Sulfide Polymers [128]

TABLE 14. 177°C Properties of PPS and PAS-2 Unidirectional Composites / 60% Weight Carbon Fibres [28]

Bronortu	PAS-2 Resin	PPS
Property	% Ret.	<u>% Ret.</u>
Long. Ten. Str.	85	37
Long. Ten. Mod.	100	94
Long. Flex. Str.	70	26
Long. Flex. Mod.	100	81
		1

Polyphenylene Sulfide Sulfone (PPSS)

PPSS is a polyphenylene sulfide sulfone being developed by Phillips Petroleum Co. to provide a more processable composite material than PAS-2 [31] but it is not commercially available. The characteristics of the neat resin PPSS are essentially the same as PAS-2 except for impact resistance. PPSS has a lower notched and unotched Izod impact energy. PPSS composites have equal chemical resistance to the PAS-2 composites but have better moisture resistance. Processing is easier and laminates have superior room temperature and elevated temperature properties to those of PAS-2 composites.

2.3.3 Polyamides

Polyamide J-2

J-2 polymer is an amorphous polyamide copolymer of low density being currently developed by Dupont [32]. It replaces early semi-crystalline J and J-1 polymers [146 - 148]. Neat resin as well as reinforced J2-polymer are not presently available as they are still under development. It appears that Dupont does not intend to provide J-2 polymer as a neat resin, nor as a composite, but rather as a finished part requested by the customer.

J-2 requires special attention regarding water absorption [32]. Saturation moisture level in water is high (5%) [1]. At temperature above Tm, water reacts through a hydrolysis reaction that reduces molecular weight and toughness of the resin. Impregnated tows and prepregs have to be enclosed in moistureproof packaging or in low humidity environment at room temperature; otherwise, pre-drying of the prepreg before use is indicated. However, J-2 can tolerate some moisture without impairing the mechanical properties. Solvent resistance is generally good. In most cases, specimens that have been exposed 14 days to hydraulic fluid. MEK, deicing fluid, isopropanol, jet fuel and trichloroethylene and one day in methylenechloride have retained 90% of their original flexural strength [32], although significant weight gain was reported in most cases. Preliminary results obtained by Krueger et al. [32] showed that J-2 reinforced with Kevlar fibres and produced by melt impregnation technology offers attractive property performance due to inherent fibre/matrix compatibility and good processing characteristics.

Polyamideimide (PAI) Torlon

Torlon is the tradename for the polyamideimide manufactured by Amoco. It is available in several grades including unfilled and filled with short fibres [23]. Torlon has a high Tg of 275° C and a high HDT of about 276° C. It exhibits strength amongst the highest of any commercial unreinforced plastic [33]. Neat Torlon resin is used for high temperature electrical connectors and other demanding electrical, electronic and aerospace applications because of its high strength, long term heat resistance, excellent electrical properties and with the ability to mold into complex shapes. It has been used in adhesive and coating applications including high temperature coatings for metal substrates, and adhesives for both metal and plastic materials [82].

The chemical resistance of Torlon is outstanding [1, 33, 82, 91]. It is resistant to hydrocarbons and halogenated solvents, but it is attacked by caustic solutions at elevated temperature, steam, some amino compounds and some oxidizing agents [33, 91]. The moisture absorption is high (2 to 5 %) and it is not recommended for use in steam. Aqueous systems at elevated temperature attack the polyamide components. In addition, Torlon is not easy to process [33, 149] because it has a high melt viscosity and it is reactive in the melt state. Hoechst Celanese is developing a new PAI with higher Tg and improved processability, moisture sensitivity and thermal-oxidative stability [149].

Prepregs of polyamideimide are supplied by Amoco Chemical Corporation under the product name Torlon-C [82]. Preliminary results on carbon fibre reinforced Torlon-C have demonstrated that laminates made of Torlon-C exhibit excellent mechanical properties and toughness characteristics [82].

2.3.4 Polyimides

Aromatic polyimides are very attractive mainly because of their outstanding thermal properties. Their Tg and continuous service temperature are high and they possess high thermal and thermo-oxidative stabilities. They also exhibit good mechanical properties and in general excellent chemical resistance. They are however generally expensive and difficult to process [150]. They are normally insoluble in most organic solvents and mostly infusible in melt processing. Research and development is leading to polyimides that are more tractable such as Larc-TPI, and easier to process while retaining their good properties [71, 150, 151]. In this report, polyimides include "pure polyimides" and the hybrids, such as polyetherimides (PEI) which involve the combination of the imide backbone with another linkage such as an ester [152]. There are three basic pure polyimides; 1) fully imidized thermoplastic polyimides (TPI) such as Larc-TPI, which are characterized by easy processability (but require high processing temperature due to the high melt viscosity [2]) and improved mechanical properties, 2) condensation-type TPIs involving condensation reaction between anhydrides and diamines such as Dupont's Avimid K and Avimid N, which are difficult to process as a result of extremely high melt viscosity but they are highly heat resistant and 3) thermoset polyimides which are easier to process than condensation TPI and possess better chemical resistance [91] but they are generally less heat resistant. Thermoset polyimides will not be discussed herein.

Polyimide K-polymer

Dupont's K-I polymer was the first of the K-polymer family to be developed [153]. It was superseded by the K-II polymer [154-156] which was later superseded by K-III polymer, now

called K-polymer. Dupont's Avimid K is the trade name of the composite counterpart of K-polymer. The physical and mechanical properties of K-polymer are essentially the same as K-II polymer but the melt flow is 15-20 times higher than K-II polymer thus improving the processing characteristics [34].

K-polymer is an amorphous polyimide matrix resin based on a combination of monomers in solution [34, 35, 157, 158]. It is produced by reacting an aromatic diethyl ester diacid with an aromatic diamine dissolved in a NMP (N-methyl pyrrolidine) solvent. The reaction proceeds with loss of water, ethanol and solvent that have to be removed during an autoclave molding cycle to produce high quality laminates. The processing parameter window is wide but the processing cycle time is very long (about 12 hours) to allow time for solvent and by-product removal. Successful laminates (assessed by C-scans and void volume content) varying in thickness from 8 to 96 plies have been processed [34, 35]. Large area, high quality laminates have been made with 22.8 mm thick ply build-up [158]. The resin has excellent resistance to a variety of fluids such as MEK, deicing fluids, hydraulic fluids, jet fuel and methylene chloride which is retained in the laminates. With its high Tg of 250° C, its excellent toughness, strength and stiffness, its high damage tolerance and excellent chemical resistance, Avimid K is a good candidate for primary structures in aeronautical and aerospace applications. It is being evaluated for applications in the primary structures of fixed wing aircraft and missiles [2, 34, 35].

Polyimide N-polymer

N-polymer is an amorphous polyimide based on NR-150B2 precursor solutions developed by Dupont [36, 67]. As for K-polymer, it is produced by reacting monomeric solutions in a solvent. It is one of the most thermally and oxidatively stable organic polymers known [2, 37, 38, 68] and therefore prepregs are made with the best thermally stable carbon fibres. Avimid N is the trade name for the composite material produced by Dupont. Laminates can maintain 50% of their original flexural strength for up to 50,000 hours at 260° C, 5,000 hours at 316° C and 1,500 hours at 343° C [2, 37, 38]. Avimid N has a high Tg of 360-373° C that can be increased to 400-410° C with post cure processes [36, 67, 68]. As for Avimid K, the processing cycle time is very long (about 12 hours). Because of the high Tg, the high toughness, the low coefficient of thermal expansion $(4.5 \times 10^{-6} / \circ C$ for the composite Avimid N), the excellent thermal-oxidative stability of Avimid N and its resistance to thermal cycling, it is used in composite tooling to fabricate quality parts from thermoplastic prepregs such as Avimid K or APC-2 [2, 36, 67]. As shown in Figure 11 and Table 15, Avimid N has superior flexural strength and modulus along with a low specific gravity and coefficient of thermal expansion compared to other tooling materials. 14.6 cm diameter filament wound pressure bottles have been produced successfully [38] in a joint program between E.I. Dupont and the Air Force Astronautics Laboratory (AFAL). Void content was found to be between 3 and 5% and results from burst tests compared favorably with a typical thermoset polyimide.



FIGURE 11a. Flexural Strength of Tooling Materials [67]



FIGURE 11b. Flexural Modulus of Tooling Materials [67]

TABLE 15. Density and Thermal Properties of Tooling Materials [67]

Material	Density (g/cm ³)	Specific Heat (cal/cm ³ - °C)	Thermal Mass (cm/cm/°C x 10 ⁻⁶)	Thermal Expansion Coefficient (cm/cm/°C x 10 ⁻⁶)	Thermal Conductivity (cal-cm/cm ² -sec- °K)
Avimid N	1.55	0.30	0.46	4.50	0.17
Monolithic Graphite	1.78	0.28	0.50	4.50	1.65
Ceramics	4.16	0.86	3.58	7.50	0.07
Steel	7.86	0.11	0.87	12.10	1.49
Aluminum	2.70	0.23	0.62	22.50	5.79

Polyimide Eymyd

Eymyd is the trade name of the polyimide resins that have been recently introduced into the market by Ethyl Corporation [13, 39, 69]. They are used as protective coatings, electronic coatings, solid film lubricants and as matrix for advanced composites. Ethyl Corporation sells three types of prepreg Eymyd products, U-25, U-35 and U-55. Of these three tacky and drapable prepregs, U-25 is the one to which the most research has been devoted. Processing conditions of U-25 have been optimized (temperature of 343° C. pressure of 1.4 MPa and processing cycle time of about 6 hours), while U-35 and U-55 are still difficult to process (high temperature and pressure and a long cure cycle). However U-35 and U-55 have higher Tg than U-25 (432 and 288° C versus 246° C respectively). The few data available on Eymyd composites indicate that they have good mechanical properties, excellent thermal stability and good resistance to aircraft fluids, but long processing times are required. They are potentially useful for airframe construction of high speed military aircraft, radomes, jet engine parts, missiles and spacecraft.

Polyketoimide Larc-TPI

Larc-TPI (Langley Research Center ThermoPlastic Imide) is an amorphous pseudothermoplastic that has been developed at NASA Langley Research Center [8, 87, 150, 151]. Through a licensing agreement with NASA, Mitsui Toatsu Chemicals (MTC) in Tokyo, Japan, and Rogers Corporation in the U.S.A. now commercially manufacture the resin Larc-TPI. Rogers Corporation produces it under the tradename Durimid. Recent work by Rogers Corporation to develop a new version of this polymer has led to improvements in neat resin properties. Properties of Durimid surpass those previously reported for Larc-TPI and Larc-TPI manufactured by MTC [8, 45]. MTC has developed and introduced into the market a new thermoplastic polyimide resin under the tradename "New-TPI" [70].

Larc-TPI is being used primarily as structural adhesive for bonding metals, composites, ceramics and films in the fields of electric/ electronic, special instruments and aircraft [150]. Development is underway to produce high quality prepreg with Larc-TPI [45, 71, 160]. Preliminary results have shown that some mechanical properties obtained with laminates made from reinforced Larc-TPI are as good as reinforced PEEK, PPS and K-polymer [45].

Polyetherimide PEI

Ultem is the trade name of a polyetherimide resin produced by General Electric Plastics (GE) [40, 41, 161, 162]. It has been selected for a number of interior parts for the Fokker company aircraft designated as Fokker 50 and Fokker 100 series because of its excellent flammability performance (L.O.I. of 47) and good mechanical properties [161]. The weakness of PEI Ultem is its poor resistance to several solvents [41, 162]. PEI Ultem is resistant to salt solutions, dilute bases, gasoline, aliphatic hydrocarbons, alcohols and mineral acids, but it is attacked by partially halogenated solvents such as methylene chloride or trichloroethane and

strong bases [91]. Recently, GE introduced a new polyetherimide, Ultern 6000, which offers higher temperature resistance and higher chemical resistance especially to partially halogenated solvents.

Cypac is the trade name of the polyetherimide neat resin introduced by American Cyanamid Co. in cooperation with GE Plastics [41 - 43, 163]. Several grades are available. Cypac X7010 is based on Ultern 1000 [43, 163]. Cypac X7000 and Cypac X7005 have been especially developed to overcome the poor solvent resistance of Ultern. Both materials retain the excellent mechanical properties and processing advantages of Ultern but the resistance to solvents such as MEK, hydraulic fluid and JP-4 is greatly improved. They exhibit similar properties but Cypac X7005 is a tackless and boardy prepreg that can be processed very rapidly while Cypac X7000 is a tacky, drapeable prepreg that has to be handled like conventional epoxies to allow solvent removal during processing. Cypac 7156-1 is an other amorphous polyetherimide under development for use as a matrix for composite materials [42, 43]. A higher Tg and better chemical resistance than the earlier Cypac versions are reported while retaining good processability and mechanical properties [42]. M&T Chemicals is also currently developing a grade of polyetherimide for composite materials [83].

2.3.5 Polysulfones

The aromatic polysulfones described in this paper include ICI's 'Victrex' PES, Amoco's polysulfone 'Udel', Amoco's polyarylethersulfone 'Radel A' and Amoco's polyphenylsulfone 'Radel R'. They have Tgs between 185 and 230° C and possible continuous use in the range of 150 to 200° C. They are available in many grades including unfilled resin and glass- and mineral-reinforced grades. In general, they exhibit slightly lower mechanical properties than most of the high performance thermoplastics included in this study, especially tensile and flexural modulus. However, they exhibit high unotched impact strength [14]. But, like most thermoplastics, they exhibit notch sensitivity as shown by comparing the values for notched and unotched Izod impact strength (Table 11). Care should be taken in design to avoid sharp radii and abrupt changes in cross-section.

Polysulfones exhibit excellent resistance to flame [14]. Radel R and PES show particularly low smoke emissions. Along with PEEK, PES has the lowest toxic gas and smoke emission of any thermoplastic [164]. Polysulfones exhibit good resistance to mineral acids, alkalis, salt solutions, and aliphatic hydrocarbons, but they are not resistant to many aircraft fluids and paint strippers such as hydraulic fluid, methylene chloride and MEK [1, 14, 93, 165]. They are attacked by chlorinated hydrocarbons and aromatic hydrocarbons. They also exhibit stress cracking and crazing in organic solvents. Solvents such as methylene chloride, ethyl acetate and MEK attack or dissolve them [93]. The solubility of polysulfones in common solvents can be ranked in this order: Udel > Radel A > PES > Radel R [14]. Udel 1700 is crazed, swollen or dissolved by chlorinated hydrocarbons, aromatic hydrocarbons, esters and ketones. PES, Radel A and Radel R are somewhat more resistant to aromatic hydrocarbons, esters, ketones and some chlorinated aliphatic hydrocarbons. Polysulfones are highly resistant to water [14]. They exhibit excellent hydrolytic stability and ability to retain mechanical properties in hot, wet environments. They are then often used in applications requiring prolonged exposure to steam and hot water such as medical and food service applications, microwave cookware and valves [14].

PES was the first member of the ICI's Victrex family [9]. The composite counterpart of Victrex PES is called APC(ITA) where ITA stands for Intermediate Temperature Amorphous. In Reference 19, successful post-forming of carbon reinforced PES panels and complex contours has been demonstrated. In this experimental study, Maximovich pointed out that a significant reduction of mechanical properties (reduction of 56% of the original flexural strength for example) at elevated temperature (177° C) occurred after having been exposed to a 24 hour water boil. They believe that this loss is attributed to plasticization of the matrix by absorbed water since the polymer is especially resistant to hydrolytic degradation.

HTA is an amorphous polymer in a developmental stage at ICI and APC(HTA) is the developmental grade of Aromatic Polymer Composite. HTA stands for High Temperature Amorphous; this resin belongs to the polysulfone family. It exhibits a substantial increase in Tg compared to PES (260 versus 230° C) [9, 75]. It can be processed with the same technology used for APC-2 except that there is no constraint over cooling rates since it is amorphous. Being an amorphous polymer, its solvent resistance is not as good as PEEK although it is superior to that of many other amorphous engineering plastics [75]. Some mechanical properties in APC (HTA) such as transverse strength, are lower than APC-2 due to the inferior bond between fibre and matrix compared to APC-2.

2.3.6 Liquid Crystalline Polymers

Low molecular weight liquid crystals (LC) have been known for about 100 years but liquid crystalline polymers (LCP) have gained considerable attention only in the last 30 years [50, 166]. LCP resemble closely the low molecular weight LC but they are polymeric and hence have properties similar to those of polymers. Figure 12 compares a LCP structure to an amorphous or semi-crystalline polymer structure. Amorphous and semi-crystalline polymers are both amorphous in the melt phase. Under cooling, an amorphous polymer will stay amorphous, while creation of ordered regions will take place in semi-crystalline polymer. In the solid state, regions with preferential alignment of molecules will be present in the semicrystalline material. In the case of a thermotropic LCP, an ordered state will exist in the melt and in the solid phase [50, 166]. Stiff rodlike molecules organize in LC domains in such a way that molecular alignment occurs in a preferred direction along their long axes. Lyotropic LCP as opposed to thermotropic LCP are another type of LCP. They cannot be melt processed as the molecules are too rigid and well packed. However, they exhibit order when they are dissolved.



FIGURE 12. Polymer Structures [166]

Aramid fibre such as Kevlar is a typical example of a lyotropic polymer. In general, the viscosity of LCP is much lower than that of conventional polymers at a comparable molecular weight [15, 16, 50, 166]. This lower melt viscosity combined with extremely low shrinkage and warpage offers processing advantages over conventional thermoplastics [15, 50].

In the past few years, a variety of LCPs has been developed [15]. Among them are Vectra and Xydar developed by Hoechst Celanese and Dartco respectively. Amoco bought the Xydar technology from Dartco and is now the producer of Xydar. These two aromatic polyesters exhibit liquid crystalline order in the melt leading to a high degree of molecular orientation and excellent mechanical properties. Neat unfilled resins are self reinforcing and exhibit unusually high modulus because of their LC nature. Fracture surfaces of these LCP appear typically to be fibre reinforced [51]. They have superior tensile properties to some fibre reinforced thermoplastics such as glass-filled polyethyleneterephthalate (PET). The impact strength of these polymers is very high as the materials have the strength of reinforced materials without the weak matrix/fibre bond [166]. However, the main disadvantages include poor compression strength and poor transverse properties caused by the anisotropy [50, 51]. As shown in Table 5, the coefficient of thermal expansion of these materials depends upon the degree of orientation in the polymer. Both Xydar and Vectra have lower viscosity than most of the high performance thermoplastic resins and have virtually zero mold shrinkage. Xydar has a higher melting point than Vectra and has better high temperature performance with a high heat deflection temperature of 337° C. Chemical resistance of both products is also very good.

The producers Hoechst Celanese and Amoco, commercially offer Xydar and Vectra respectively in different grades, filled and unfilled but not yet in the prepreg form. Typically, these LCPs are used in mechanical components of various electronic and audio-visual devices. Vectra has been used as strength members for fibre optic cabling [166]. Development and evaluation of these materials in missile and ballistic structural applications have been underway [166].

Experimental work with Vectra reinforced with continuous carbon fibre has been performed by Chung [15, 16]. Carbon reinforced LCP Vectra prepreg tape with a fibre volume fraction of 40-55%, a fair wet out and good fibre aligment has been produced by melt impregnation. Lay-up and moulding of prepreg into laminates have yielded composites of good quality with a void content lower than 0.8% by volume. Many mechanical properties such as tensile and flexural properties, open-hole tensile strength, $\pm 45^{\circ}$ tensile strength are comparable to those of commercial carbon fibre/epoxy composites at the same volume fraction. Impact resistance is superior to thermosets, however both shear and compression strengths are slightly inferior to those of epoxy/carbon fibre. Flexural modulus retention at elevated temperature is extremely good. However, flexural strength retention at 93° C is only fair (67%) and becomes poor at a temperature of 121° C. The poor retention may be due to the interface between fibre and matrix. Deficiencies in shear and compressive strength have also been attributed to the poor interfacial adhesion between fibre and matrix.

2.3.7 Polybenzimidazoles (PBI)

Many aromatic variants of polybenzimidazoles (PBI) have been prepared and investigated since their first synthesis in 1961, but the principal polymer used in all commercial and most developmental applications is poly[2,2'-(m-phenylene)-5,5'-bibenzimidazole] which is discussed here [17, 18, 24, 72, 167]. PBI is commercially available from Hoescht Celanese under the trade name Celazole. The polymer is almost completely amorphous; crystallinity can be induced only under specific conditions [24]. In almost all cases, it behaves as an amorphous polymer with very high Tg (430° C). The Tg can be increased to 500° C by annealing in nitrogen at 500° C for 200 min. [24].

PBI is a polymer with high temperature stability and high chemical resistance [17, 18, 24, 72, 167]. It is intrinsically non-flammable in air; the rate of gas evolution in air is low and the off-gases produced are relatively inert [24]. It is being used as a replacement for asbestos, in fire-blocking applications, thermal-protective clothing and numerous other high temperatureand chemical resistant applications [24]. PBI can be converted into fibre with excellent textile and tactile performance.

PBI exhibits the highest compressive strength (390 MPa) known for any available unfilled thermoplastic or thermoset resin [17, 18]. In addition, the tensile strength of PBI (160 MPa) is higher than most unfilled thermoplastics. Flexural strength and modulus are also very high. PBI has the greatest surface hardness of any known molded thermoplastic with Rockwell M values greater than 125 and it has also the highest heat deflection temperature value for any available thermoplastic resin. The coefficient of linear thermal expansion is lower than for any non-liquid crystalline thermoplastic resin. However, the notched Izod impact strength is relatively low.

PBI is the only polymeric matrix material capable of maintaining load bearing properties for short periods of time (3-5 min) at temperature up to 649° C [17]. Good tensile and compression strength retention (approximately 65% and 38% of the room temperature strength, respectively) is achieved at temperature of 300° C [17].

PBI exhibits excellent chemical resistance to most organic chemical systems [17, 167]. No effect on mechanical properties or dimensional stability was observed upon extended, hot exposure to aerospace related environments such as kerosene, Skydrol hydraulic fluid, engine oils or methylene chloride. When exposed to hot aqueous environments, weight gain was observed as well as loss of hardness, tensile and compressive strength and modulus. However, the original properties were restored after drying the specimens in a vacuum oven indicating that it is resistant to hydrolysis.

Prepregs of PBI reinforced with glass, carbon or quartz, either in the fabric or tape form, are produced by Y.L.A. Corp which buys the neat resin from Hoechst Celanese. The retention of mechanical properties at elevated temperature is excellent. But there are major disadvantages; its high cost, difficult processing conditions (high temperature, high pressure, evolution of volatiles), short-term shelf life and its unreprocessability [18, 167]. Although it is considered a thermoplastic, it cannot be really reprocessed. The chemistry of PBI polymerization results in the formation of large amounts of condensation by-products during cure [18, 167]. As a consequence carefully staged, high pressure curing conditions (9-10 MPa) are needed to minimize void formation. However, there is research work underway to optimize molding conditions and preliminary results have shown that a pressure as low than 1.4 MPa can lead to satisfactory PBI composites, but curing time is still very long (about 10 hours) [18]. Prepregs have to be stored tightly wrapped at freezer temperatures to prevent solvent evaporation, and as for epoxy, they have a short shelf life due to solvent evaporation and the occurrence of polymerization.

2.3.8 Polyphenylquinoxalines (PPQ)

Polyphenylquinoxalines are part of an important family of polymers, the polyquinoxalines, that offer high chemical and thermal stability coupled with high mechanical properties [14]. Although experimental work has been conducted to produce high quality reinforced PPQ laminates [19], PPQ is not expected to be available as a matrix for reinforced composite materials due to its high viscosity, low modulus and its high cost.

2.4 Summary

High-performance thermoplastic resins are newly introduced into the marketplace but already there is an interesting choice available for use as matrices for composites in aircraft structural applications; and others are expected to emerge very soon. Many of them, from different polymer families, have been presented in this chapter. The main advantages and disadvantages of these high performance thermoplastics as compared to thermosets are summarized in Table 16. They are characterized by outstanding toughness, high ductility as reflected by high tensile strain to failure and low moisture absorption. In general, they exhibit good temperature capability as they possess high glass transition temperature (Tg). However, the desired high Tg leads to high melt viscosities which render difficult the complete impregnation of continuous fibre bundles. High processing temperatures often close to the decomposition temperatures are needed to lower the melt viscosity. Polyimides for example exhibit very high Tg's but their melt processability is very poor. The development of very flowable high performance thermoplastics that possess enhanced elevated temperature performance is

TABLE 16.	Comparison	Between Neat	t Thermoset and	Thermopla	stic Resins
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Property	Thermosets	Thermoplastics
Melt viscosity	low	high
Fiber impregnation	easy	difficult
Processing cycle time	long	most of them short, except most
		polyimides and PBI
Processing temp. / press.	low to moderate	high
Mechanical properties	fair to good	fair to good
Toughness	low	high, except PPS
Moisture resistance	poor	excellent except polyamides
Creep behavior	generally good	unknown, but not expected to be
		as good as thermosets
Data base	large	small

highly desirable and should be investigated. In addition to this high melt viscosity disadvantage, the database for thermoplastic resins is not extensive as it is with thermosets; creep behavior of these new materials is not well known and needs to be more thoroughly assessed.

In general, mechanical properties of neat thermoplastic resins are comparable and often better than those of thermosets. They exhibit higher tensile strain to failure than thermosets. Thermoplastics can be used more efficiently with the newer high strain, high strength carbon fibres. Liquid crystalline polyesters are particularly low in compression strength, and polysulfones and polyphenylquinoxalines exhibit low tensile and flexural modulus, at least below the generally accepted value (3.1 GPa) to achieve reasonable composite compression strength.

Each thermoplastic resin has its own advantages and caveats; the final selection depends mainly on the application and the cost involved. For higher temperature applications such as supersonic aircraft, polyimides and polybenzimidazoles are the best choice, but there is a trade-off of difficult processing (high melt viscosity, long processing cycle times and evolution of volatiles). If moisture resistance is required, polyamides should be avoided. If exposure to aircraft fluids is likely to occur, then polysulfones should be eliminated. For very high toughness requirements, all thermoplastic resins are suitable except polyphenylene sulfide (PPS) which has G_{lc} toughness values similar to those of thermosets. Overall it seems that the polyketone family offers more balanced properties. The mechanical properties in general are not exceptional but they are at least comparable to conventional thermosets; they exhibit outstanding toughness and excellent solvent and moisture resistance and they have good melt processability. In addition, the latest polyketones exhibit higher Tg's than the well known polyetheretherketone PEEK.