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## 8.1 Introduction (ARH)

Chemically resistant organic polymeric fibres include those which are designed to resist chemical attack for acceptable periods during their service lives at both ambient and elevated temperatures. As a consequence of their generally inert structures they may also be flame resistant and so address markets where that property is also desirable.

Obviously, some members of this group will overlap with other fibres more often considered to be high-temperature resistant fibres, such as the aramids, arimids and others dealt with elsewhere in this text. Although primarily chosen for their strength and stiffness, many of the fibres described in Chapters 2 to 7 have good chemical resistance, albeit somewhat selectively. In this chapter, reference will be made only to applications and characteristics of these fibres which enable them to be used in environments where chemical resistance is the major priority.

Because chemical reactions have rates that increase with temperature, the main application areas will be those where the combined effects of heat and reactive chemical agencies operate, such as in wet and dry filtration. However, longer term durability to less corrosive environments is demanded in the geotextile and geomembrane sectors, where ambient conditions prevail. Protective clothing applications requiring specific chemical resistance will also seek to exploit members of this fibre group.

The essential chemical structural features of the members of this group will be general inertness as a consequence of the presence of strong chemical bonding systems within the polymeric backbone and/or the presence of no or unreactive side groups. In addition, because the presence of aliphatic chain hydrogen atoms increases the tendency of the polymer towards oxidation, their presence should be minimal. Consequently, fibres produced from poly(ethylene) and poly(propylene), while having acceptable resistance to many chemicals at ambient temperatures, are limited in resistance to temperatures much in excess of 50°C, especially if oxidising agents are

present. Fibres based on these polymers are excluded from this chapter. Furthermore, the polymer backbone should be free of hydrolysable functional groups such as ester and amide, and so fibres based on aliphatic polyamide and polyester structures lack sufficient chemical durability to be included. Aromatic analogues, however, show greater resistance and so the polyaramids, for example, may be considered to belong to this group as well as to the high-temperature resistant group.

Thus, the fibres discussed within this chapter do not belong to a single fibre genus and do not have a simple commonality of polymer backbone structure or a common set of chemical properties. However, they do present a most interesting and almost disparate group, linked together by the general property of chemical inertness extending over a range of temperatures. They tend also to see service in applications that are of a very similar character, differentiated only by the severity of thermal and chemical inertness demanded. For instance, hot gas and liquid filtration fabrics, braiding materials in chemical plant, gaskets, protective textiles, conveyor beltings and high performance sewing threads are typical end-uses.

## 8.2 Chlorinated fibres: PVDC (ARH)

The major fibres of importance here are those based on poly(vinylidene chloride) or PVDC. The chemical structure of the polymeric repeat unit  $-\text{CCl}_2\text{.CCl}_2-$  creates a polymer with a high degree of chemical resistance and a high degree of order. This latter makes the polymer difficult to process and so in commercially useful forms, copolymers with other vinyl and acrylic comonomers, such as vinyl chloride, acrylonitrile and methyl acrylate (usually present at <15% w/w), are utilised. Dow Chemical Company developed the *Saran* fibre based on this polymer in the 1940s and the name *Saran* is a registered trademark with respect to the polymer which is used in coatings, films, monofilaments and other extrusions. Currently, the resin *Saran 510* is that recommended for monofil applications and it is, in fact, a copolymer of vinylidene chloride and vinyl chloride. Fibres have been marketed under the names *Permalon* and *Velon*. Similar fibres, such as *Fugafil* produced in Germany by Saran GmbH, are also available.

The polymer melts over the range 160–170 °C and is melt spun at about 180 °C by conventional melt-spinning methods to yield both multi- and monofilaments. It softens over the range 115–160 °C, depending upon its copolymeric character and this limits its service temperature limit. The inherently golden-yellow coloured fibres have acceptably high tenacities, up to 0.25 N/tex, with breaking strains of 15–30%. The moderately low modulus (0.9N/tex) ensures that even the coarsest filaments have a high level of flexibility. With a moisture regain of less than 1%, tensile properties are main-

Table 8.1 Typical properties of PVDC fibres<sup>1</sup>

Property	Value
<i>Thermal:</i>	
Melting point, °C	171
Softening temperature, °C	115–160
Sticking temperature, °C	99–104
<i>Tensile:</i>	
Tenacity, N/tex	0.20
Tenacity (100°C), N/tex	0.13
Tenacity (loop), N/tex	0.06–0.10
Tenacity (knot), N/tex	0.09–0.15
Breaking strain, %	15–30
Elastic recovery at 3% strain, %	98.5
Elastic recovery at 10% strain, %	95
Modulus, N/tex	0.44–0.88
<i>General:</i>	
Specific gravity	1.6
Moisture regain, %	<1
Colour	Golden-yellow
Cross-section	Round
Limiting oxygen index, %	60

tained under wet conditions and permeation by chemicals is low. Table 8.1 summarises the main properties of these fibres.

Resistance to chemicals such as salts, acids, most alkalis, aliphatic hydrocarbons and alcohols is excellent at temperatures up to 100°C. However, resistance to aromatic and halogenated hydrocarbons, ketones, ethers and esters is less, with temperature playing an important part.

Coupled with its chemical resistance is an inherently low flammability and a limiting oxygen index value of 60%. When in a fire, however, it gives off hydrogen chloride, which is both toxic and corrosive.

Apart from some discoloration, PVDC fibres have excellent sunlight and weatherability resistance.

Main end-uses are those which demand a high level of chemical, and sometimes soil resistance and so car-seat covers, outside furniture, public vehicle upholstery and wet filtration are typical.

### 8.3 Fluorinated fibres: PTFE, PVF, PVDF and FEP (ARH)

While fluoropolymeric fibres tend to be very expensive, their extreme chemical inertness has ensured that a number of variants find use within filtration applications, where extreme chemical, and in some cases thermal

resistance are required. The most notable generic example is poly(tetrafluoroethylene) or PTFE, although other examples exist such as poly(vinyl fluoride), PVF, poly(vinylidene fluoride), PVDF and various fluorinated ethylene polymers or FEP types. Table 8.2 summarises the properties of a selection of these fibres which are often available as both continuous filament and staple forms.

While each fibre type in Table 8.2 is marketed essentially for a defined level of chemical resistance, the effect of temperature on chemical reactivity is also important and is quite different for each, although generally, these fibres are renowned for their excellent resistance to a variety of chemical environments at temperatures well in excess of 100 °C. Resistance to the combined effects of temperature and chemical action is a combination of the inherent stability and unreactivity of the polymer chain structure, coupled with the efficiency of intermolecular forces and chain order. These latter determine the magnitude of softening ( $T_s$ ) and melting ( $T_m$ ) temperatures, which determine the ease of accessibility to chemical agencies as well as the upper limits of the ability of respective fibres to remain as coherent, load-bearing structures. Not surprisingly, therefore, there is often a link between inherent unreactivity by virtue of a high degree of fluorine presence and hence polar C–F bond density in a polymer, the degree of chain order and the ability to withstand the combined agencies of temperature and chemical attack.




It is evident from Table 8.2 that PTFE fibres have the highest melting points. This, coupled with their insolubility, requires that conversion to fibres is via non-standard methods. The original DuPont *Teflon* filaments were, and still are, produced by the extrusion of fibrillar polymeric suspensions in a viscose (cellulose) dope followed by high temperature sintering to generate a coherent fibre structure.<sup>4</sup> This gives brown fibres because of the charred cellulose remnants present, so may be followed by a bleaching process if desired. This process, developed in the 1950s, generates fibres that are available in staple, continuous filament and flocced fibre forms, as Fig. 8.1 shows.

A recent review by Schick<sup>5</sup> contrasts this process with the so-called paste extrusion technology, used by companies such as W L Gore, and the split-peel process of Lenzing. In the paste-extrusion process, PTFE powder is mixed with a lubricant and preformed into a cylinder, which, after placing in an extruder, may be transformed into film or rod forms. The calendered film is slit, sintered and stretched to give high-tenacity fibres. This technology enables additives to be incorporated, such as graphite to improve internal lubrication properties in applications such as packings. The low density and open structure are ideal for medical applications including dental floss, as well as yielding lower thermal expansion coefficients ideal for high-temperature gland packings. The third method, split peel formation,

Table 8.2 Selected fluorine-containing, chemically resistant polymers<sup>2,3</sup>

Genus	Example	Manufacturer	Tenacity, N/tex	Breaking strain, %	$T_{m\prime}$ , °C	$T_s$ , °C	Max. temp. usage, °C	LOI, % O <sub>2</sub>
PTFE	<i>Teflon</i>	Du Pont	0.14	20	347	177	290	98
	PTFE	Lenzing	0.08-0.13	25	327	200	280	98
	PTFE	Albany	0.13	50	375	93	260	98
PVF			0.19-0.39	15-30	170	100	150	—
PVDF	<i>Kynar</i>	Albany	0.43	25	156	100	149	44
	<i>Solef</i>	Solvay	—	40	178	150	160	—
	<i>Trofil</i>	Dynamit	—	10-50	165	—	120	—
FEP	<i>Halar</i> -ECTFE	Albany	0.3	25	241	149	180	48
	<i>Teflon-FEP</i>	Du Pont	0.05	50-60	290	—	—	—
	<i>Tefzel</i> -ETFE	Albany	0.3	25	271	177	195	—

Notes:  $T_m$  is the melting temperature and  $T_s$  is the shrinkage temperature; LOI is the limiting oxygen index.

Form	Image	Characteristics and uses
<b>Continuous filament yarn</b>		<ul style="list-style-type: none"> <li>• Low coefficient of friction</li> <li>• High thermal and chemical resistance</li> <li>• Woven fabrics / tubes</li> <li>• Knitted fabrics / tubes</li> <li>• Combination with other yarns</li> </ul>
<b>Staple</b>		<ul style="list-style-type: none"> <li>• High thermal and chemical resistance</li> <li>• Low coefficient of friction</li> <li>• Used for needle-felting</li> <li>• Hot gas filtration</li> <li>• Low friction / high temperature resistant parts in office equipment</li> <li>• Performance enhancement in blends with other fibres</li> </ul>
<b>Floc</b>		<ul style="list-style-type: none"> <li>• Low coefficient of friction</li> <li>• Blends / compounds with other polymers for moulding</li> <li>• High chemical resistance for chlor-alkali electrolysis</li> </ul>

**8.1** Continuous filament, staple and floc forms of *Teflon*® PTFE. (*Teflon*® is a registered DuPont trademark; figure reproduced with permission of DuPont.)

involves the precision turning of a continuous outer film layer from a cylindrical PTFE billet, followed by slitting and sometimes coating with PTFE and/or graphite dispersions. This yields extremely regular filaments with good pressure and temperature resistance, although with poorer ability to withstand surface-dispersed additives.

All PTFE fibres and yarns show excellent thermal properties in terms of shrinkage, and maximum service exposure temperatures result from their wholly fluorinated ( $-\text{CF}_2\text{CF}_2-$ ) and extremely ordered polymer chains, which ensure maximum efficiency of the polar intermolecular chain forces of attraction present. This, coupled with the chemical inertness of the C–F chemical bond, enables these fibres to have some of the highest chemical resistances of all fibres, especially at high temperatures. They consequently find use in filtration, braiding, gaskets, packing and similar end-uses that demand this combination of resistances for long periods. They find particular use in chemical engineering applications where direct contact with and

resistance to corrosive chemicals at high temperatures are essential. For instance, braiding packings for pump shafts exposed to fuming (103%) nitric acid will last up to seven months and when used in pumps handling >50% caustic soda at 165 °C, will last several days.<sup>4</sup> Essentially, PTFE fabrics and yarns are attacked to any extent at ambient and moderate temperatures only by other fluorine-containing species, such as the element itself and chlorine trifluoride. Their high LOI value (Table 8.2) of 98% again demonstrates the almost complete flame resistance, and hence resistance to oxidation, of PTFE fibres and fabrics. One major drawback with all PTFE fibres is their high creep at elevated temperatures and, to overcome this, they may be combined with low creep fibres such as para-aramids and arimids, although these may reduce acid and/or alkali resistance. In addition, in composite yarn formation with a range of other fibres, where the PTFE provides the chemical resistance, a harder core enables varying yarn densities and hardnesses to be generated thereby modifying compressibility in packing applications.<sup>5</sup>

PVDF, PVF and FEP fibres have lower melting points and so lend themselves to melt extrusion with all the advantages of being able to produce monofilaments in addition to the more conventional continuous filament and staple forms. They also have lower LOI values and hence increased flammability, which reflects their reduced resistance to oxidation compared with PTFE. Unfortunately, very little is published about these fibres outside of the technical data sheets provided by manufacturers. However, PVF and PVDF in particular, because of their excellent tensile properties, are used where a combination of good tensile properties and chemical resistance is required. Both find particular use as monofilaments in filter media that combine these characteristics with excellent abrasion and fatigue resistances.<sup>6</sup>

FEP fibres have structures and properties which may vary from type to type because they include copolymers of tetrafluoroethylene ( $-\text{CF}_2\text{CF}_2-$ ) and hexafluoropropylene ( $-\text{CF}(\text{CF}_3)\text{CF}_2-$ ) [PTFE-FEP]; ethylene and chlorotrifluoroethylene ( $-\text{CFClCF}_2-$ ) [ECTFE];<sup>7</sup> and ethylene and trifluoroethylene ( $-\text{CHF}\text{CF}_2-$ ) [ETFE]. These copolymers have reduced crystallinity and hence easier processibility compared to their respective homopolymers, while retaining the chemical inertness of the fluorinated groups present. This is especially the case for *Teflon-FEP* in Table 8.2, where its melting point of 290 °C is less than that of homopolymeric PTFE or *Teflon*.

ECTFE and ETFE fibres (also sold in engineering polymer resin forms) have superior mechanical properties, similar to those of other synthetic fibres such as the polyamides. Because of their greater thermoplasticity than PTFE, however, they are unable to retain significant tensile strength much above 180 °C, which is similar to these same conventional synthetic fibres.

Table 8.3 Resistance of *Tefzel* ETFE fibres to selected chemicals after 7 days' exposure<sup>8</sup>

Chemical	Boiling pt., °C	Test temp., °C	Retained properties, %		
			Strength	Elongation	Mass gain
<i>Acids:</i>					
Acetic acid	118	118	82	80	3.4
Trichloroacetic acid	196	100	90	70	0
Hydrochloric acid (conc)	106	23	100	90	0
Hydrofluoric acid (conc)	—	23	97	95	0.1
Sulphuric acid (conc)	—	100	100	100	—
Nitric acid (70% conc)	120	120	0	0	—
Chromic acid	125	125	66	25	—
<i>Bases:</i>					
Aniline	185	180	95	90	—
<i>N</i> -butylamine	78	78	71	73	4.4
Pyridine	116	116	100	100	1.5
Ammonium hydroxide	—	66	97	97	0
Sodium hydroxide (50%)	—	120	94	80	0.2
<i>Halogens:</i>					
Bromine	59	23	90	90	1.2
Chlorine	—	120	85	84	7
<i>Solvents:</i>					
Carbon tetrachloride	78	78	90	80	4.5
Chloroform	62	61	85	100	4.0
Dichloromethane	40	40	85	85	0
Dimethylformamide	154	90	100	100	1.5
Dimethyl sulphoxide	189	90	95	95	1.5
Mineral oil	—	180	90	60	—
Benzene	80	80	100	100	0

Their chemical resistance is similar to that of *Teflon-FEP* and superior to PVDC, PVF and PVDF. These latter will degrade in 98% sulphuric acid, 70% nitric acid and 50% caustic soda solutions at elevated temperature, whereas ECTFE is resistant. The resistance of *Tefzel* ETFE to a number of organic and inorganic chemicals at temperatures upto 180°C in some cases has been well documented.<sup>8</sup> The selected examples of chemical resistance listed in Table 8.3 show behaviour considerably inferior to that expected of PTFE fibres but still superior to other chemically resistant fibres, including others within the fluorinated group.

Thus, both ETFE and ECTFE fibre types are ideal for use in filter screens and cloths, column packings, braided sleeveings, gaskets and conveyor belt-ings, for example, where extreme chemical resistance at temperatures as high as 150°C is required.

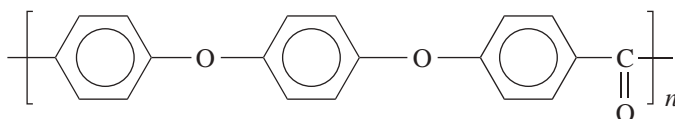


## 8.4 Poly(etheretherketones): PEEK (BM)

### 8.4.1 Polyetherketones

PEEK (polyetheretherketone) is the foremost member of a family of semi-crystalline aromatic thermoplastic polymers, the polyetherketones (PEKs). It is capable of being formed into an extensive range of monofilaments and fibres using high-temperature melt-spinning techniques. The glass–rubber transition temperature ( $T_g$ ) and the melting point ( $T_m$ ) are given for the principal members of the series in Table 8.4.

Chemically, PEEK has a polymer repeat unit of one ketone and two ether groups. This provides a linear, fully aromatic, highly stable structure containing only carbon, hydrogen and oxygen atoms:



Although some experimental work was carried out in the 1960s, PEEK polymer was first manufactured<sup>9</sup> and commercialised<sup>10</sup> by ICI Advanced Materials in the late 1970s and early 1980s under the brand name *Victrex PEEK*. The first emphasis was on injection moulding application, but work by ICI<sup>11</sup> and Leeds University<sup>12</sup> showed the polymer's potential for producing high-specification fibres.

Although other manufacturers introduced pilot plant developments of competitive polyetherketones through the 1980s, notably BASF with PEKEKK,<sup>13</sup> DuPont with PEKK<sup>14</sup> and Hoechst with PEEKK,<sup>15</sup> PEEK proved to be the only polymer to survive and prosper in an expanding range of applications through the 1990s. The technical difficulty of polymerising and the high cost of purifying polyetherketones to a quality suitable for processing into finer components has limited competition. PEEK is now

*Table 8.4* Thermal transitions of the various PEK polymers, where E signifies an ether and K a ketone segment

Polymer	$T_g$ , °C	$T_m$ , °C
PEEK	143	334
PEEKK	150	365
PEK	152	365
PEKEKK	170	381
PEKK	165	391

well established with a long development lead-time advantage over other polyetherketones. It is principally produced by Victrex Ltd – an independent company formed from the break-up of ICI Advanced Materials in 1993.

#### 8.4.2 PEEK fibre-performance factors

As an introduction to the general bulk properties of PEEK as a thermoplastic material, Table 8.5 will be a useful reference.

The general factors which characterised the acceptance and underpinned the successful growth of PEEK as a new thermoplastic material can be set out briefly as:

- *Temperature performance*: a continuous operating temperature for many applications of up to 260°C, with short excursions to 300°C being possible, and a non-brittle low temperature performance down to –60°C.
- *Chemical inertness*: it is unaffected by high-temperature steam and most fluids and chemical reagents. However, it is dissolved by concentrated sulphuric acid (>50%) and degraded by strong oxidising agents such as nitric acid.
- *Abrasion resistance*: it has a tough, low friction, low wear, cut-resistant surface and is particularly good at resisting abrasion at elevated temperatures and relatively high surface speeds.
- *Dimensional stability*: it exhibits low creep and low shrinkage, especially below its  $T_g$  (143°C). It has excellent dynamic recovery and flex fatigue performance.
- *Polymer purity*: fibres are exceptionally pure, without the need for stabilising additives, and they have EEC and FDA approval for medical

Table 8.5 Properties of PEEK

Property	Value/parameter
Colour	Beige (thick section) Golden (thin section)
Specific gravity	1.30
Melting point, $T_m$ , °C	334
Glass transition, $T_g$ , °C	143
Crystallinity, %	30–35
Moisture regain, 65% rh 20°C, %	0.1
Dielectric strength, kV/cm	190
Resistivity, ohm-cm	$5 \times 10^{16}$
Heat capacity, kJ/kg°C	1.34
Thermal conductivity, W/m°C	0.25

and food-contact use.<sup>16,17</sup> A good low surface energy self-cleaning characteristic minimises contamination in use.

- *Flammability*: fibres are self-extinguishing with an LOI of 35% while emitting one of the lowest levels of smoke and toxic gases.
- *Processability*: the room temperature physical properties of PEEK fibres are similar to those of both polyester and nylon, so textile processes such as weaving and braiding can be conveniently performed.
- *Sustainability*: recovery and recycling of PEEK as a material can be carried out under certain conditions with little loss of key physical properties.<sup>18</sup>

### 8.4.3 Fibre products

Starting in the early 1980s, a number of companies set out to produce PEEK fibres of various different types for commercial sale. Initially, circular cross-section monofilaments in the diameter range 0.4 to 1.0 mm were extruded at high temperature, cooled, drawn and relaxed to give low-shrinkage products with physical properties in the range 0.3 to 0.4 N/tex tenacity and 30 to 40% extension-to-break, with hot-air shrinkages below 2% at 180°C.

By the mid-1980s the polymer quality had improved sufficiently to allow multifilament products in the range 5 to 15 dtex per filament to be viably produced. These, depending on the process employed, could be spun with tenacities up to 0.65 N/tex at extensions below 25% and shrinkages below 1% at 180°C. Modulus values at about 4 to 5 N/tex are typically intermediate between similar polyester and polyamide products.

Finer and heavier monofilaments were also developed, with some specialist products in the 0.2 to 0.3 mm range having tenacities up to 0.60 N/tex at extensions below 20%, and some of the larger diameter products being made with higher shrinkages at about 10% so that they could be conveniently heat-set into spiral structures in subsequent processing.

The first crimped filament staple products with a fineness range from 3 to 25 dtex and staple lengths of 40 to 80 mm were also developed at this time. Finer individual monofilaments and progressively finer multifilament yarns down to 100 dtex and filament finenesses of 3 dtex (20 µm) have been refined through the 1990s, yielding further improvements in tenacity. Additionally, a wider range of cross-sectional types, including rectangular and hollow filaments and an increasing range of colour pigmented monofilaments, have become available for the main monofil diameters (0.20 to 1.50 mm).

The manufacturer with the most comprehensive range of PEEK fibre products through this period has been ZYEX Limited.<sup>19</sup> Other producers, such as Teijin, Kosa, Shakespeare, Luxilon and Albany International, have

at different times been active in different segments of the PEEK fibre business but none other than ZYEX has yet attempted to cover more than a small part of the potential product range.

#### 8.4.4 Fibre properties

The value of PEEK fibre products does not normally lie in their measured starting properties or with their short-term performance. As has been indicated, PEEK monofil, yarns and fibres are in fact similar to polyester or nylon products in these respects. It is rather PEEK's ability to retain useful properties at an extreme condition or throughout an extended working life that differentiates it from mainstream industrial fibres.

The thermal, chemical and abrasive endurance of PEEK sets it apart from comparable industrial fibres, as is indicated in the following tables. This is especially true in real industrial processing situations where a combination of these factors, rather than just one, may be causing standard materials to fail prematurely.

Table 8.6 shows the resistance to hot air exposure over a 28-day period, and Table 8.7 the ability of PEEK fibres to withstand steam for 7 days. Clearly, PEEK can perform well at temperatures up to 300°C in both dry air and steam, thus indicating its oxidation and hydrolysis resistance.

*Table 8.6* PEEK and other fibres exposed to elevated temperatures for 28 days in air

Fibre Temperature	% Strength retained			
	150 °C	200 °C	250 °C	300 °C
PEEK	100	100	95	90
m-aramid	100	95	75	0
PPS	100	90	0	melted
PET	90	30	0	melted

*Table 8.7* PEEK and other fibres exposed for 7 days in pressurised steam

Fibre Temperature	% Strength retained				
	100 °C	150 °C	200 °C	250 °C	300 °C
PEEK	100	100	100	95	80
PPS	100	100	90	0	disintegrated
m-aramid	100	90	0	0	0
PET	90	0	0	0	disintegrated

*Table 8.8* Cycles to failure for PEEK and other fibres as threads – thread on thread abrasion at 120°C loaded at 0.05 cN/tex

Fibre	Cycles to failure
PEEK	900
PA	600
PET	500
m-aramid	250
PPS	50

Its resistance to abrasion is also superior to many competing fibres, as Table 8.8 shows.

Table 8.9 ranks the chemical resistance of PEEK fibres at three different temperatures. Generally, the most common or the most potentially vulnerable situations have been covered. It is probable that a ‘no attack’ category is very likely for other chemical situations, but, if in doubt, the latest technical data should be consulted.<sup>20</sup>

#### 8.4.5 Fibre applications

Applications relate to industrial and technical end-uses where a combination of good physical properties and inertness to the environment are essential features:

- *Process conveyor belts:* The mainstream application for PEEK fibres is in industrial conveyor belts that carry product through aggressive processing stages effectively on a continuous basis, in particular, in the manufacture of paper or nonwoven fabric products where pressing, bonding or drying stages can involve temperatures up to 300°C at line speeds up to 300m/min. In some situations, significant flex and surface abrasion is also experienced by the conveyor belt as it passes around pulleys and drive rolls, or through nip restrictions. Here again, PEEK belts may well deliver cost-effective increases in life expectancy or process flexibility when compared with other high-tech fibre or steel belts.

Initially, PEEK was used in the most vulnerable part of such conveyor belts – at the joint or on the edges. Joints are often made using PEEK monofil, heat-set as interlocking spirals and joined by a larger diameter straightened PEEK ‘pintle pin’ monofil. Subsequently, PEEK has been used more as a substantial part of the belt, up to 100% of the construction, products normally being woven from monofil although some multifil yarns or needled staple felts are also used, especially in narrow

Table 8.9 The chemical resistance of PEEK fibres at various temperatures

Chemical	23 °C	100 °C	200 °C
Acetic acid, 10%	A	A	
Carbonic acid	A	A	
Citric acid	A	A	
Formic acid	B	B	
Hydrochloric acid, 10%	A	A	
Nitric acid	A	A	
Nitric acid, 30%	B		
Phosphoric acid, 50%	A	A	A
Sulphuric acid, <40%	B	B	B
Ethanol	A	A	A
Ethylene glycol	A	A	B
Ethylene glycol, 50%	A	A	A
Acetone	A	A	
Formaldehyde	A	A	
Methylethyl ketone (MEK)	A	B	C
Ammonia, aqueous	A	A	A
Sodium hydroxide, 50%	A	A	A
Aluminium chloride	A	A	
Carbon monoxide (gas)	A	A	A
Ferric chloride	B	B	
Hydrogen sulphide (gas)	A	A	A
Iodine	B		
Ozone	A	B	
Phosphorous pentoxide	A	A	
Potassium bromide	A	A	
Sulphur dioxide	A	A	A
Carbon tetrachloride	A	A	
Chloroform	A	A	
Trichlorethylene	A	A	
Aromatic solvents	A	A	
Benzene	A	A	
Brake fluid (mineral)	A	A	A
Dowtherm ht			B
Methane (gas)	A	A	A
Motor oil	A	A	A
Naphthalene	A	A	
Oils (petroleum)	A	A	
Dimethyl formamide	A	B	
Pyridine	A	A	
Dimethylsulphoxide (DMSO)	B	B	
Diphenylsulphone (DPS)	B	C	C

Note: A = no attack, B = slight attack, C = severe attack. Where no concentration is given for the chemical it may be assumed that 100% or a saturated solution was used.

woven tape belts. Complete belts of interlocking coils are also increasingly being specified where maximising open area is important. Other industries where PEEK conveyor belts are used include textile printing and heat setting, food drying and filtering and laundry ironing.

- *Press filters*: Fine woven screens of PEEK are used in frame filters, or slow-moving press filter applications for the production of board products or the dewatering of chemical powders. Dimensional stability and the ability to survive many more pressure cycles than equivalent metal screens are important here.
- *Protective braids*: PEEK braids, made mainly from coloured/pigmented monofilaments are increasingly important in aerospace, automotive and industrial applications. In particular, the additional chafe resistance and temperature stability delivered are ideal for electrical wiring looms associated with engine components in aircraft and motor vehicles. In addition, in any enclosed situations where toxic fumes from burning wiring could pose a threat to life, PEEK as a cable covering is ideal.

Industrial applications include the wiring for robotics in nuclear installations where high levels of gamma radiation would degrade conventional plastics, and hydraulic-pressure hosing reinforcement, where the monofilament diameters used are heavier.

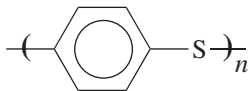
- *Reinforced rubber gaskets*: A multifilament PEEK scrim fabric is used to reinforce synthetic rubber gaskets and bellows. The fibre's unique combination of good flex fatigue performance and resistance to the chemical breakdown products of the rubber at high temperature greatly extends component lifetime in specialised applications.
- *Industrial bristles*: Brush bristles used for hot-cleaning extruders and injection moulds are sometimes preferred as PEEK monofilaments, rather than soft metal wires.
- *Protective clothing*: Multifilament PEEK sewing threads have found niche markets in industrial protective clothing, associated with their chemical inertness. Also, hook and loop fasteners utilising both monofilament and multifilament PEEK products are used in quick-release garments in high-temperature environments.
- *Sports strings*: The possibility of manufacturing fibres that exhibit deformation and rapid recovery from high stress rates has given rise to PEEK's use in up-market tennis, squash and racquet ball strings.<sup>21</sup>
- *Music strings*: The unique tonal quality and tension-holding that can be achieved from specified PEEK products have given rise to their adoption for guitar, violin and other stringed instruments.<sup>22</sup>
- *Thermoplastic composites*: PEEK fibres can also be used as a source of the matrix in composites. Intimately mixed with carbon fibres, PEEK fibres provide an ideal feedstock for the production of advanced thermoplastic composites. In the pressurised high-temperature moulding

stage, PEEK remelts and flows to encase and protect the carbon fibres, becoming the matrix phase of the composite. In addition to aerospace components, medical tools and bone replacements are being made to take advantage of PEEK's excellent biocompatibility and *in vitro* performance.

## 8.5 Poly(phenylene sulphide), PPS (ARH)

The presence of aromatic groups within the polymeric chains bonded together by relatively inert groups is not only a feature of PEEK, discussed above, but also of poly(phenylene oxide), PPO. PPO and its derivatives are mainly used as engineering plastics although some academic interest has been shown in wet-spun filaments.<sup>23</sup> Because of lack of commercial interest to date, they are not considered to be within the scope of this chapter. The related polymer, poly(phenylene sulphide), PPS, is more important as a fibre.

Developed in 1973, the first commercial fibres from PPS appeared in the early 1980s with the introduction of *Ryton* by Phillips Fibers Corp.,<sup>24</sup> and subsequently by other companies such as Bayer,<sup>25</sup> Teijin,<sup>26</sup> Toyobo as *Procon*, Toray as *Torcon*<sup>27,28</sup> and Celanese as *Fortron*.<sup>29</sup> Scruggs and Reed<sup>30</sup> reviewed this then new fibre in 1985 and described its chemistry of polymerisation, conversion into fibres, and their characteristic structure and properties. Its chemical structure is:



which, because of its aromatic backbone will anticipate challenges during the polymerisation and processing stages. Phillips Fibers pioneered the means of producing polymer with molecular weight high enough to enable fibres having tenacities as high as 0.35 N/tex to be melt spun above its melting transition of 278 °C. During drawing, the fibre melting temperature shifts to 285 °C, reflecting the effects of increasing orientation and crystallisation accompanying the process. This melting point, which is similar to those of the more conventional synthetic fibres, precludes the fibre from use in very high temperature-resistant applications. Its second order transition of about 93 °C also places a higher limit on useful service temperatures of this order when used under stressed conditions. Table 8.10 summarises the main physical properties of PPS fibres.

It is evident that PPS fibres have an acceptable balance of properties for many end-uses in terms of tensile properties under dry and wet conditions. The applications at high temperatures depend on the levels of applied stress during service; obviously for high stress end-uses, the second order



Table 8.10 Physical properties of PPS fibres<sup>28,30</sup>

Property	Staple	Monofilament
Tenacity, N/Tex	0.27–0.47	0.27–0.37
Tenacity retention, %:		
at 100 °C	70	
at 150 °C	58	
at 200 °C	52	
Tenacity (knot), N/tex		0.18–0.23
Breaking strain, %	25–35	12–16
Initial modulus, N/tex	2.7–3.7	4.1–5.0
Elastic recovery, %:		
at 2% strain,	100	
at 5% strain	96	
at 10% strain	86	
Boiling water shrinkage, %	0–5	
Moisture regain, %	0.6	
Specific gravity	1.37	1.37
Melting point, °C	285	285
Colour	Golden	Golden
Limiting oxygen index, %	34–35	
Autoignition temperature, °C	590	
Maximum service temperatures, °C	93 (high stress) 182–190 (low stress) 232 (surges)	93 (high stress) 182–190 (low stress)

transition temperature will define the upper useful limit, whereas in lower stressed applications, such as gas filtration bags, long-term exposures above 180 °C are possible. Exposure to sudden elevated temperature changes shows that these fibres can withstand up to 230 °C for very short periods. Experimental exposures to hot air show that PPS fibres retain 60% of their original strength after 1000 hours, at 260 °C and 90%, 70% and 60% retention after 2000, 5000 and 8000 hours, respectively at 204 °C.

The relatively high LOI of 34–35% (although LOI values as high as 39–41% have been claimed<sup>31</sup>) indicates an acceptable level of inherent flame resistance. However, the general ease of oxidation of the sulphur atom present in the polymer chain is indicated by this value being less than observed for PPO fibres (LOI = 68%) and the susceptibility of PPS fibres to oxidising agents.

During light exposure it is discoloured but compares favourably with poly (meta-aramid) fibres in terms of retention of tensile properties; in general, however, light resistance may be said to be poor.<sup>31</sup>

Table 8.11 Chemical and solvent resistance of PPS fibres<sup>30</sup>

Chemical	Temp., °C	Strength retained after one week's exposure, %
<i>Acids:</i>		
48% Sulphuric acid	93	100
10% Hydrochloric acid	93	100
conc. Hydrochloric acid	60	100
conc. Phosphoric acid	93	95
Acetic acid	93	100
Formic acid	93	100
<i>Alkalis:</i>		
10% Sodium hydroxide	93	100
30% Sodium hydroxide	93	100
<i>Oxidising agents:</i>		
10% Nitric acid	93	75
conc. Nitric acid	93	0
50% Chromic acid	93	0–10
5% Sodium hypochlorite	93	20
conc. Sulphuric acid	93	10
Bromine	93	0
<i>Organic solvents:</i>		
Acetone	B.Pt	100
Carbon tetrachloride	B.Pt	100
Chloroform	B.Pt	100
Ethylene dichloride	B.Pt	100
Perchloroethylene	B.Pt	100
Toluene	93	75–90
Xylene	B.Pt	100

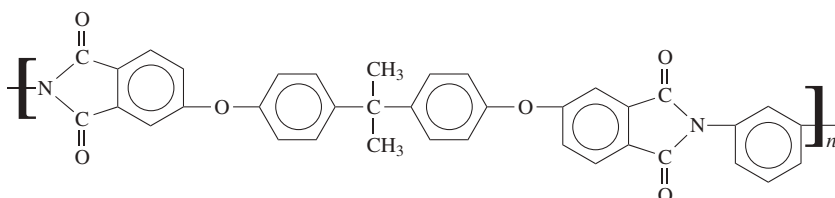
The excellent chemical resistance of these fibres is demonstrated in Table 8.11. Resistance to non-oxidising acids is excellent, as is that to hot alkalis, thereby showing that in spite of PPS being a condensed polymer, it has considerable resistance to hydrolysis. However, exposure to oxidising agents shows that its durability is reduced as a consequence of the vulnerability of the sulphur chain group. Organic solvent resistance is variable, although still high. When compared with conventional fibres such as polyester, acrylic and polypropylene, its resistance to both hot acid (50% sulphuric acid) and alkali is demonstrated even after only short exposures of 24 hours or so. After exposure periods of several days or so, its superiority to the aromatic heat-resistant fibres polyaramid and even poly(benzimidazole) becomes apparent.<sup>30</sup>

Applications for poly(phenylene sulphide) fibres lie primarily in the wet and dry filtration areas, where they have proved to be exceptionally durable

for coal-fired boiler gas filtration at temperatures in the region of 150–200°C, in the presence of ash and acidic, high-sulphur flue gases. During pulsed jet cleaning, needle-punched fabrics prove to be more efficient in not only their filtering capacity but also their resistance to wear during cleaning. In some cases, lifetimes of up to 3 years have been reported for bags under these conditions,<sup>32</sup> where they have proved to be superior to homopolymeric acrylic fibre-containing filter bags. Other uses include felts used in the drying operation of paper production, as well as for battery separators and filter cloths (as felts or woven constructions) for filtering hot, corrosive chemicals such as organic chemicals, acids and bases. Sewing threads for use in these products are also valid applications.

## 8.6 Poly(ether imide), PEI<sup>33,34</sup> (ARH)

Like PEEK, poly(ether imide) is really an engineering plastic which has found application as fibres in some applications where chemical and temperature resistance are required. Although its temperature resistance is slightly inferior to that of PEEK, PEI is a cheaper material. Currently, both Teijin and Acordis (formerly Akzo) have reported commercial fibres based on PEI. The chemical structures of both commercial forms are believed to be similar and as outlined below:<sup>33,34</sup>



With its less than ideally regular polymer chain structure, PEI is essentially an amorphous polymer which may be melt-spun to yield fibres having only moderate tenacities (0.25 N/Text) and breaking elongations of about 40%. Fibres can resist temperatures up to 190°C for long periods and also possess high LOI value of 45%, which is higher than the values for PEEK and PPS. A comparison of the properties of PPS, PEEK and PEI is presented in Table 8.12.

As for all these fibres, mono- and multifilament forms are preferred for PEI, although staple forms (e.g. 6 mm, 2.8 dtex; 60 mm, 8.3 tex) are available. Their high LOI value again represents a stability at high temperatures and resistance to oxidation and so they are used in hot gas filtration applications, especially where aggressive chemical environments are present. However, chemical resistance is specific rather than general and so fibres should be tested before use.

Table 8.12 Comparison of properties of PEI with PPS and PEEK fibres<sup>33,34</sup>

Fibre	$T_m$ , °C	$T_{max}$ , °C	LOI, %	Tensile strength, N/tex
PEI	215–225 (= $T_g$ )	170–190	44–45	0.19–27
PPS	285	190	34	0.45
PEEK	334	260–300	35	0.60–0.65

Note:  $T_{max}$  = maximum continuous-service life temperature.

Table 8.13 Chemical resistance of PEI fibres<sup>34</sup>

Chemical	Concentration	Strength retention after 1500 h at 20 °C, %
HCl	10%	101
HNO <sub>3</sub>	10%	99
H <sub>2</sub> SO <sub>4</sub>	10%	95
HF	10%	106
CH <sub>3</sub> COOH	10%	104
NaCl	Saturated	101
Mineral oil		104
Borax	pH 9	110
(NH <sub>4</sub> ) <sub>3</sub> PO <sub>4</sub>	pH 10	104
NH <sub>3</sub>	pH 11	96
Ca(OH) <sub>2</sub>	pH 12.5	107
NaOH	pH 13.5	84

Table 8.13 lists some chemical resistance data for these fibres, from which it is seen that these fibres have very good resistance to dilute acids and alkalis although resistance to concentrated acids is poor. Resistance to organic species is variable and may be poor for aromatic solvents and vapours.

## 8.7 Others (ARH)

Other fibres in this group include the polyaramids (both meta- [e.g. *Nomex*, DuPont] and para-derivatives [*Kevlar*, DuPont; *Twaron*, Acordis]), polyarimid [*P84*, Inspec Fibers], poly(aramid-imide) [*Kermel*, Rhodia], poly(benzimidazole) [*PBI*, Celanese] and the oxidised acrylics [*Panox*, RK Textiles/SGL UK]. Most of these are primarily marketed and used as high-temperature fibres and will be discussed in detail in the next chapter. However, primarily because of their oxidation resistance, they find application in

high-temperature gas filtration applications. Their resistance to chemicals such as acids and bases is often poor, however, because the majority are condensed polymers and so are susceptible to hydrolysis.

## References

- 1 Gordon Cook J, *Handbook of Textile Fibres, II Man-made Fibres*, London, Merrow, 1993.
- 2 Massue B N N, *Compilation of Fibre Data*, ATI Dissertation, Textile Institute, Manchester, 1984.
- 3 Ref.1, pp. 484–492.
- 4 Moncrieff R W, *Man-made Fibres*, 6th edition, London, Butterworths, 1975.
- 5 Schick W, 'Fluorocarbon-based fibres and yarns', *Textile Month*, 2000, August, 20–23.
- 6 Dohany J E and Humphrey J S, 'Vinylidene fluoride polymers', *Encyclopedia of Polymer Science and Technology*, 2nd edition, eds. J I Kroschwitz, H F Mark, N M Bikales, C G Overberger and G Menges, Vol. 17, London, John Wiley & Sons, 1989, pp. 532–543.
- 7 Robertson A B, 'Poly(ethylene-chlorofluoroethylene) fibers', *Appl. Polym. Symp.*, 1973, No.21, 89–100.
- 8 Gangal S V, 'Tetrafluoroethylene polymers', as ref.6, Vol. 16, 626–642.
- 9 Taylor I C, Production of aromatic ethers, *BPI569603*, September 1977.
- 10 Smith C P, 'Polyetheretherketone (PEEK). A new high performance fibre', *Swiss Plastics*, 1981, 3 (4), 37–44.
- 11 ICI Research Disclosure, 1981, No.202016, 10/2/81.
- 12 Ali F, *Formation of Fibre from an Aromatic Polyetheretherketone*, MSc thesis, University of Leeds (Dept. of Textiles), 1981.
- 13 Buchert H, Neuberg R, Matthias, H-G and Butzheiman K-A, 'Sewing threads of polyether ketone', *Europ. Pat. Appl. 90105692.9*, BASF, 30/3/89.
- 14 Gardner, K H, Hsiao S, Matheson R R and Wood B A, 'Structure, crystallisation and morphology of poly(aryletherketoneketone) polymer', *Polymer*, 1992, 33, No.12, pp. 2483–2495.
- 15 Heidel P, 'Fibres of aromatic polyetherketone – characteristics of new engineering material', *Internat. Man-Made Fibres Congress*, Dornbirn, Austria, No.556, September 1989.
- 16 *European Union Commission Directive 90/128/EEC*, 1990.
- 17 Anon, Poly(aryletheretherketone), *Federal Register FDA CFR 177.2415*.
- 18 Arzak A, Nazabal J and Eguiazabel J I, 'Effect of processing on the properties of polyetheretherketone', *Plastics, Rubber and Composites Processing and Applications*, 1990, Feb., 119–124.
- 19 [www.zyex.com](http://www.zyex.com).
- 20 [www.victrex.com](http://www.victrex.com).
- 21 Smith F S, McIntosh B M, Hayman N W and Davidson S, 'Sports racket strings', US Patent Office, *Patent No. 4,586,708*, March 1984.
- 22 McIntosh B M, Smith F S and Briscoe N A, 'Musical instrument strings', US Patent Office, *Patent No. 5,587,541*, October 1995.
- 23 Pechocova M, 'Fibres from poly(phenylene oxide)', *Chemicke Vlakna*, 1986, 36, No.3, 165–170; 1989, 39, No.1/2, 13–19.

- 24 Anon, 'PPS fibre for dry filtration', *High Perf Text.*, 1982, **3**, (5), 1–3.
- 25 Anon., 'Polyphenylene sulphide fibre from Bayer', *High Perf Text.*, 1989, **10**, (2), 6–7.
- 26 Anon, '3 new super fibres', *Jap. Text. News.*, 1988, No.405, 52.
- 27 Anon., 'New Torcon PPS fibre', *Man-made Fibres Yearbook*, 1998, **31**, 30.
- 28 Datasheets, *PPS Fibre Torcon*, Toray Industries, circa 1990.
- 29 Datasheets, *Fortron Staple Fibre*, Hoechst Celanese, 1994.
- 30 Scruggs J and Reed O, 'Polyphenylene sulfide fibers', in *Handbook of Fibre Science and Technology, Volume III, High Technology Fibres*, Part A, eds. M Lewin and J Preston, New York, Marcel Dekker, 1995, pp. 335–349.
- 31 Christoph G, *Chemiefasern/Textilindustrie*, 1989, **39/91**, (7/8), T182–T184, E98–99.
- 32 Datasheets, *Ryton Sulfur Fiber*, Phillips Fibers Corp., April 1991.
- 33 Heidel P, 'New opportunities with melt-spun aromatic polymer fibres', *Chemiefasern/Textilindustrie*, 1989, **39/91**, (7/8), T178–T181, E97–98.
- 34 Anon., *PEI High Performance Fibre*, Akzo Fibres and Polymers Division Data Sheet, 1990.