4 Product Forms

4.1 Standard Powders and Granules

Unfilled polyaryletherketones (PAEK) are typically supplied as powders or granules - typical properties are listed in **Chapter 3**. Compounds will have been through a melt-compounding process and will be granular in form. Granules are easier to feed in many processes such as injection moulding. Unfilled granules may have been filtered to reduce the level of gels and black speck present in the product.

PAEK are typically available in a range of viscosities. For example, Victrex polyaryletheretherketone (PEEK) is available as 450, 380, 150 and 90 grades. A lower number indicates a lower molecular weight and viscosity. It should be noted that short-term properties may not be the most sensitive indicator of molecular weight effects, and requirements such as long-term fatigue performance or complex environmental resistance should always be taken into account. In general the author believes that it is best to use the highest useable molecular weight. However, there are exceptions: it is not necessarily the case in processes that require high degrees of filler or fibre wetting, low degrees of fibre breakage or low process forces. It should also be noted that some granular grades are designed to be especially suitable for particular processes. For example, some Victrex grades (e.g., 380) are particularly suitable for extrusion processes in which very low levels of gels and black speck are required.

Standard particle size powders are typically used as a feedstock for processes such as extrusion and compression moulding. There are also fine powders which are used in products such as coatings which will be discussed later.

4.2 Compounds

PAEK compounds contain fibres, fillers and other effect additives. A range of compounds is available from PAEK producers and general compounders. There are also speciality products produced by a number of custom compounders - such as RTP and Lehman and Voss. Polymics produces compounds based on PEEK, PEKK and their new high temperature PAEKs. As true thermoplastics, PAEK can be compounded using conventional single-screw and twin-screw equipment. The normal effects of fillers and additives apply in PAEK as they do in other thermoplastics. However, temperature is an important limitation. Many fillers, additives, fibre treatments, etc., are too volatile or thermally unstable to be used at 400 °C. In some cases these problems could be overcome by redesign of the molecules, for example to reduce volatility, but the size of the PAEK market is relatively small and so relatively unattractive to additive developers.

Table 4.1 summarises some properties of compounds produced by Victrex plc. Glass and carbon fibres are the commonest reinforcements and are available in a range of base resin viscosities. The effects are exactly as expected. Carbon produces the highest strength and modulus with a relatively low density. Lower viscosity grades of PAEK allow for higher filler content with less fibre breakage and so the tensile strength and modulus of 90GL30 are somewhat higher than for 450GL30. However, longer term properties such as fatigue strength might benefit more from increased molecular weight. **Figures A1-A4** in **Appendix 1** show the fatigue performance, yield strength as a function of temperature, specific strength and coefficient of thermal expansion for a number of PAEK compounds and composites. Some of the standard ICI compounds have been extensively characterised in terms of their engineering design properties [1].

Table 4.1 Properties of some Victrex compounds

Material	Tensile strength (MPa)	Tensile elongation (%)	Flexural modulus (GPa)	Unnotched Izod (kJ/m^2)	Notched Izod (kJ/m^2)	HDT (°C)
PEEK 90GL30	190	2.3	12.0	40	8.5	335
PEEK 150GL30	190	2.5	12.0	50	9.0	335
PEEK 450GL30	180	2.7	11.3	60	10	328
PEEK 90 GL60	220	1.4	23	45	9.5	343
PEEK 150CA30	240	1.5	23	40	6.5	339
PEEK 450CA30	240	1.7	23	45	8.0	336
PEEK 450CA40	250	1.6	28	40	8.5	–
PEEK HMF 40	350	1.3	36	-	-	349
PEK22 GL30	200	2.9	11	70	11	360
PEK 22 CA30	250	2.2	22	45	8.0	368
PEKEKK 45GL30	200	2.5	11.0	70	11	380

GL = glass fibre; CA = carbon fibre. Number after CA or GL = fibre content (%). PEEK molecular weight: 450 > 150 > 90 (150 and 90 are easy-flow grades). HMF grades combine high-flow resins with special compounding technology to achieve increased strength, stiffness and fatigue performance. Note that the grade codes are trademarks of Victrex plc.

Long-fibre-reinforced compounds are available from organisations such as RTP. These materials are tough and yet lightweight and are particularly suitable for metal replacement. Long-fibre compounds might be expected to offer improved impact resistance, better creep and modulus retention at high temperature, improved dimensional stability and improved resistance to warpage as a result of reduced shrinkage. RTP and Oxford Performance Polymers offer compounds of polyaryletherketoneketone (PEKK). Glass bubbles can be used to reduce weight but there are also high specific gravity grades. Other fillers such a talc and mica reduce shrinkage and coefficients of expansion which can be useful in low-warpage grades. Fillers can be used to reduce the coefficient of thermal expansion such that it is comparable to that of metals. This can help with the direct replacement of metal components.

Special wear grades are available. These are typically reinforced with carbon fibre and contain lubricants such as graphite and polytetrafluoroethylene (PTFE). Recently Victrex has introduced PTFE free wear grades. Various studies have related the wear of PEEK compounds to mechanical properties [2]. Aramid fibres are sometimes used to reduce counterface wear and fluoropolymer synthetic oils are also used. The processing temperatures of PAEK can push the thermal stability limits of fluoropolymers and suitable ventilation is required. PTFE is effective as an internal lubricant since it coats the wear surfaces and dramatically reduces the coefficient of friction. Graphite is often used in the presence of an external lubricant. A typical generic wear grade of PAEK might contain 10-15% of each of carbon fibre, graphite and PTFE (e.g., 15% carbon fibre and 15% PTFE). Some suppliers of such compounds quote a single wear factor for a given product of pressure and velocity. However, the failure mechanism depends on the combination of pressure and velocity. It has been shown that under high-pressure, low-velocity conditions, wear is predominantly cohesive. Under conditions of low pressure and high velocity (but the same overall pressure × velocity) the specific wear rate is much lower and this is due to an interfacial wear mechanism with polymeric film transfer [3]. Comparisons have been made using pressure and velocity conditions relevant to real applications - such as automotive powertrains. Materials such as Victrex PEEK 450FC30 compare well with competing products [4]. Analysis of wear debris can show evidence of thermal oxidative degradation of PAEK under failure conditions [5]. The wear performance of PAEK compounds can be further improved by blending with polybenzimidazole; this blend is described later.

Conductive compounds are very important in electronic applications. Many silicon chip and wafer handling processes require well-controlled static dissipation. This can be achieved using a variety of conductive fillers including milled carbon fibre, carbon black, metal fibres, indium tin oxide-coated glass and carbon nanotubes [6-10]. In general conductive compounds fall into three resistivity ranges. Definitions vary but, in general, 10^9-10^{11} ohm/sq is said to be 'antistatic', 10^7-10^9 ohm/sq is 'dissipative' and less than 10^6 ohm/sq is conductive. Often a particular resistivity range is required for the application. This can be difficult to achieve since resistivity changes rapidly as the filler concentration approaches the percolation threshold (roughly the point at which each fibre touches at least one other fibre to form a continuous conducting network). Various strategies have been developed to reduce this effect but it is often found that the precise resistivity also depends on the moulding conditions and the level, dispersion and distribution of the filler at the point in the moulding actually being measured. Nevertheless statically dissipative PAEK are a very important class of compounds. There are a number of manufacturers of conductive PEEK compounds. Victrex produces materials in the antistatic and dissipative ranges including a non-carbon-based, low out-gassing dissipative material. RTP manufactures a range of glass-reinforced and high-purity carbon nanotube compounds which are controlled to within narrow ranges of resistivity.

Coloured materials and masterbatches can be obtained from a variety of compounders including RTP and Colorant Chromatics. Other speciality PAEK compounds include radio opaque, antimicrobial, magnetic, laser markable and authentication grades.

4.3 Composites

The term PAEK composite generally means a continuous fibre reinforced material and mostly refers to continuous carbon fibre reinforced products. These can come as unidirectional tape or woven cloth which is then used to form melt-processed components.

Whereas compounds can be produced using standard twin-screw extrusion technology, the production of PAEK composites usually involves a proprietary process. Some processes do little more than bring the PAEK into contact with the fibre and leave the final forming process to individually wet the carbon fibres with polymer. Such products are relatively low cost and simple to produce but it can be difficult to make void-free, high-quality parts. The more advanced processes use a variety of techniques to produce low-void products in which there is a strong interface between the polymer and the fibre and a high degree of fibre distribution and wetting. It is possible to crudely assess the quality of the product by snapping a piece of tape and looking for loose fibre and evidence of fibre pull-out. Higher quality tapes will tend to break cleanly and show little evidence of unwetted fibres. More sophisticated tests involve polishing sections and microscopic examination. It is important to realise that mechanical properties in the fibre direction will be dominated by the fibre and may not be very sensitive to the quality of the impregnation. Accordingly it is useful to measure transverse properties such as transverse flexural and transverse tensile strength as a method of assessing the quality of pre-impregnated tape. Other key tests include damage tolerance measurements such as damage area and compression after impact.

Impregnation methods include:

- direct melt impregnation [11];
- processes assisted with volatile plasticisers [12];

- powder impregnation, either electrostatic or aqueous dispersion [13–17]; and
- fibre co-mingling [18, 19].

The early technology (known as APC2) was pioneered by ICI and is now owned by Cytec. Cytec also acquired the DuPont technology and now offers a product range that includes both PEEK and PEKK. Other suppliers include Tencate (which acquired Phoenix TPC), Suprem (formerly Gurit and before that Sulzer), Schappe (co-mingled products), Toho Tenax and Ticona. Typically uniaxial pre-impregnated sheet is around 120 to 100 µm thick. Recently Mitsuya has produced a 40 µm product using PEEK film which allows even more design flexibility.

The benefits of thermoplastic composites include:

- high-volume, low-cost manufacturing processes;
- ease of recycling;
- high thermoplastic toughness and damage tolerance;
- no shelf life issues;
- no chemistry occurring during part fabrication, no volatile organic compounds; and
- welding, fusion bonding and repair.

Table 4.2 summarises some basic properties of PEEK-based APC2 thermoplastic composites from Cytec. The properties of finished components can be tailored by controlling fibre orientation during the layup process. Full characterisation of a thermoplastic composite will include measurement of in-plane shear properties, open hole tensile and compressive failure, interlaminar fracture toughness and compression after impact. Cytec also produces TPC based on PEKK [20].

Table 4.2 Properties of PEEK thermoplastic composites		
	In fibre direction	**In transverse direction**
AS4 carbon fibre		
Tensile strength (MPa)	2070	86
Failure strain	1.45	0.88
Tensile modulus (GPa)	138	10.2
IM7 carbon fibre		
Tensile strength (MPa)	2900	60
Failure strain	1.5	–
Tensile modulus (GPa)	172	10

In spite of their advantages PAEK thermoplastic composites have made relatively slow progress since their invention in the 1980s. In many cases this has been due to a lack of fabrication technology and competition from newer toughened thermosets. PAEK also face competition from polyphenylene sulfide (PPS) composites which are much less expensive but have some limitations in terms of T_g and toughness. PPS composite parts have found a large number of aerospace applications – including the leading edges of Airbus wings. There are also industrial and oilfield applications which will be discussed later in this review.

High-volume fabrication should be a key advantage for thermoplastic composites over thermosets. Conventional techniques include press lamination, autoclave lamination and thermoforming. Thermoforming can convert flat consolidated sheets into complex shapes. Autoclave lamination requires the use of expensive bagging materials (such as Kapton polyimide), lengthy heating and cooling cycles and expensive autoclaves. Accordingly a number of automated processes have been developed which do not need autoclaves.

In fibre placement with *in situ* consolidation, a robot lays down tape onto a tool as it is heated with hot gas, infrared radiation or lasers and is consolidated *in situ*. This process is operated by companies such as Automated Dynamics and Accudyne. Much effort has been put into perfecting the consolidation process which requires relatively void-free and smooth tapes [21-24]. Other processes use automated layup (e.g., the FibreForge Relay Station) followed by press consolidation and thermoforming. Xperion Aerospace has created a continuous compression moulding process which can be used to make rails, beams and profiles. Icotec has developed a 'composite flow moulding' process [25] which allows the moulding of pultruded rods into articles such as screws, fasteners and bone plates while maintaining fibre length and orientation.

4.4 Films

Film can be produced using a conventional single-screw extruder and coathanger die, preferably with closed loop control of thickness. The crystallinity of the film is controlled using the temperature of the casting rolls.

PEEK films were first marketed by the ICI Stabar films group. Thicknesses were available down to about 25 μm, and a variety of processing techniques such as thermoforming were developed. More recently films have been produced by Ajedium, Lipp Terler and Sumitomo. In 2003 Ajedium launched a 6 μm film product. In 2007 Victrex started to produce Aptiv PEEK film in a range of thicknesses from 6 to 750 μm. The film is also available as tape coated with silicone or acrylic adhesives. Thicker sheet products are available from suppliers such as Ensinger and RTP. In June 2009 Oxford Performance Materials introduced OXPEKK Permetta film at thicknesses down to 25 μm in both amorphous and crystalline forms.

PEEK film competes with polyimide and PTFE. In comparison to PTFE it offers much higher strength, modulus, abrasion and creep resistance and lower density. The comparison with polyimide is more complex. PEEK has similar electrical, physical and thermal ageing performance. It offers lower moisture absorption which allows more stable properties and improves resistance to thermal shock. Hydrolysis resistance and resistance to strong alkalis are further advantages. PEEK films are available in very low thicknesses. The permeability of PEEK film to gases such as carbon dioxide, helium, hydrogen, nitrogen, oxygen and water vapour is also relatively low.

Amorphous film can be thermoformed by heating to a temperature close to or above T_g for a few seconds. If the process is quick enough and if the tool temperature is below T_g then amorphous mouldings can be produced. However, longer heating times and higher tool temperatures will produce crystalline parts. The thermoforming of crystalline films requires temperatures close to the melting point and higher powered heaters.

Adhesion to the film can be enhanced by surface treatment. The conventional method is corona discharge but more recently atmospheric pressure oxygen plasma treatments have been developed. The film can also be vacuum metallised to improve barrier performance, coated with copper for surface conductivity or with more advanced coatings such as sapphire. Mineral fillers can be used to provide higher modulus and to the control coefficient of thermal expansion in relation to particular coatings or specific applications.

4.5 Fibres

Fibres were originally developed by ICI Fibres and the technology is now owned by Zyex Ltd in the UK. Zyex produce a wide range of monofilament, multifilament and staple fibres and can make hollow monofilaments and tubes. PEEK is the most common material but PEK and PEKK can also be used. The fibres are manufactured by extrusion and orientation and have good mechanical properties with high strengths. They compete with fibres such as Kevlar, Vectran, polybenzimidazole (PBI) and PBO. Kevlar, PBO and PBI are non-melting materials and offer obvious advantages in protective, fire-resistant clothing. Kevlar and Vectran offer high orientation and very high strength due to their rigid rod character. However, PEEK fibres can have advantages in terms of chemical resistance (especially to hydrolysis and alkalis), flexural fatigue and abrasion resistance.

4.6 Fine Powders and Coatings

Large particle size powders are used for processes such as compression moulding, but PAEK can also be obtained in a range of sizes down to about 10 μm [26] from suppliers such as Evonik and Victrex. These can be used for powder and dispersion coating and carbon composite impregnation. Victrex produces Vicote coatings for both powder and aqueous dispersion applications [27]. The coatings offer all the properties expected of PAEK. Abrasion and wear resistance can be exceptional – far superior to that of fluoropolymer coatings. Special wear-resistant [28] and electrostatic dissipative grades have been developed and there is a product line based on PEK [29]. Recently it has been claimed that coating performance in terms of adhesion, cracking and processability onto concave surfaces can be improved by using a base layer of amorphous PEKK [30]. A wide range of coating techniques can be used with fairly standard equipment. These include conventional electrostatic powder and dispersion spraying techniques and also flame spraying. Flame spraying is a one-step process in which the powder passes through a flame that melts the polymer particles before they are deposited on the substrate surface. This removes the size and location restrictions imposed by the use of ovens and offers much greater design freedom. Both Victrex and Evonik offer flame spray technology and collaborate with suppliers of flame spray equipment. A key requirement of PAEK coating is to avoid contamination with other materials since these can degrade at process temperatures and lead to defects in the coatings.

4.7 Stock Shapes

Stock shapes can be made by extrusion or by compression moulding – although some smaller shapes are injection moulded. They can be used for prototyping, small production runs and even quite large-volume applications if the machining costs are acceptable. Companies such as Ensinger, Quadrant, Advanced Polymer Technologies, Vertec and Gehr produce a range of PEEK polymer and compound stock shapes. A wide range of sizes is available.

4.8 Foams

Zotefoams and Victrex have collaborated to produce PEEK foams. The process uses Zotefoam's nitrogen saturation technology to impregnate granules which are then used in conventional injection moulding equipment or in extrusion to produce foamed components [31]. According to the 2008 MuCell applications guidelines from Trexel, PEEK foams well with Mucell supercritical gas foaming technology.

References

1. D. Moore, J. Smith and S. Turner, *Plastics, Rubber and Composites Processing and Applications*, 1994, **21**, 1, 19.

2. Z. Zhang, C. Breidt, L. Chang and K. Friedrich, *Tribology International*, 2004, **37**, 3, 271.

3. I. Griffiths, D. Kemmish, P. Tweedale, M. Morgan and R. Weidig in Proceedings of the *SAE International Congress*, Detroit, MI, USA, 1997, 970658.

4. I. Griffiths, D. Kemmish and M. Morgan in Proceedings of the *SAE International Congress*, Detroit, MI, USA, 1998, 980716.

5. M. Zhang, Z. Lu and K. Friedrich, *Tribology International*, 1997, **30**, 2, 103.

6. J. Sandler, P. Werner, M. Shaffer, V. Demchuk, V. Altstadt and A. Windle, *Composites: Applied Science and Manufacturing*, 2002, **33**, 8, 1033.

7. J. Sandler, P. Werner, M. Shaffer, R. Jaskulka, O. Jacobs, V. Altstadt and A. Windle, *Wear*, 2004, **257**, 9, 1006.

8. J. Sandler, P. Werner, M. Shaffer, R. Verdejo, F. Wollecke and V. Alstadt, *Advanced Materials*, 2005, **17**, 23, 2864.

9. J. Sandler, A. Windle, P. Werner, V. Alstadt and M. Shaffer, *Journal of Materials Science*, 2003, **38**, 10, 2135.

10. D. Bangarusampath, H. Ruckdaschel, V. Altstadt, J. Sandler, D. Garray and M. Shaffer, *Polymer,* 2009, **50**, 5803

11. F. Cogswell and D. Hezzell, inventors; ICI, assignee; US4549920, 1982.

12. F. Cogswell and U. Measuria, inventors; ICI, assignee; US4624886, 1985.

13. S. Mills, inventor; Philips Petroleum, assignee; US4900499; 1988.

14. J. O'Connor, J. Geibel and W. Beever, inventors; Philips Petroleum, assignee; US4792481, 1986.

15. D. Soules, inventor; Philips Petroleum, assignee; US5019427, filed 1989.

16. A. Vodermayer, J. Karger and H. Erlach, inventors; Sulzer, assignee; US6277238, 1999.

17. A. Vodermayer, J. Karger, H. Erlach and S. Kaufmann, inventors; Sulzer, assignee; US6372294, filed 1999.

18. P. McMahon and T. Chung, inventors; Hoechst Celanese, assignee; US4799985, 1986.

19. P. McMahon, T. Chung and L. Ying, inventors; Hoechst Celanese, assignee; US4818318, 1986.

20. J. Pratte, J. Bai and D. Leach in *Proceedings of the 37th SAMPE Technical Conference*, Seattle, WA, USA, 2005.

21. M. Lamontia and M. Gruber in *Proceedings of 2007 SAMPE Conference*, Baltimore, MD, USA, 2007.

22. M. Lamontia, M. Gruber, J. Tierney, J. Gillespie, B. Jensen and R. Cano in *Proceedings of 2009 SAMPE Europe Conference*, Paris, France, 2009.

23. A. Wood, D. Padey, J. Walling, R. Lenferink, S. Wijskamp, R. Day and J. Benn, *SAMPE 2008*, Long Beach, CA, USA, 2008.

24. R. Becker, A. Nettles, R. Bucinell, R. Langone and J. Mondo, *SAMPE 2001*, Long Beach, CA, USA, 2001.

25. U. Loher, J. Mayer, P. Tognini, T. Wegener and E. Wintermantel, inventors; Amsler Peter, assignee; WO96/19336, 1995.

26. A. Lucke and D. Steidl, inventors; Hoechst, assignee; US5247052, 1992.

27. I. Beckwith and J. Robinson, inventors; Victrex, assignee; WO2005/023893A2, 2004.

28. J. Robinson, inventor; Victrex, assignee; GB2437830, 2007.

29. B. Wilson and J. Robinson, inventors; Victrex, assignee; GB2425495, 2006.

30. T. Hsu, D. Berry and G. Butler, inventors; Polymics, assignee; WO2009/058362A1, 2008.

31. N. Witten and I. Tollett, inventors; Zotefoams, assignee; WO2006/100517A1, 2006.