TECHNICAL WHITEPAPER

Focus on: PEEK

Introduction

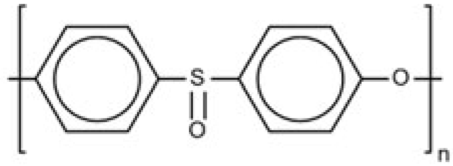
In past Newsletters we have often referred to the relationship between molecular structure and how it influences the properties of the polymer. The development of plastics has sometimes been one of accidents and fortuitous mistakes. Fawcett and Gibson at Imperial Chemicals Industries (ICI) Australia discovered polyethylene in 1931 after they noticed a small amount of a waxy solid produced during their high-pressure gas experiments with ethylene. This substance was later isolated to produce polyethylene and one of the great commodity polymers was “invented”. Similarly, PTFE was discovered by mistake in 1938 when Roy Plunkett at DuPont noticed that a supposedly full cylinder of tetrafluoroethylene appeared to have nothing in it. When the cylinder was cut open, a white residue (polytetrafluoroethylene) was found on the inside of the cylinder and PTFE was born.

Given the number of possible combinations of atoms and the ways they can be dimensionally arranged there appears to be an almost infinite number of ways to form polymers, but there are additional difficulties because the arrangement must yield a useful product. In a way, this is similar to the problem of “How many ways are there to knot a tie?”. Two mathematical physicists at Cambridge (UK) used topological (and geometric) knot theory and statistical mechanics to find that there are in fact 85 ways to knot a tie. Their research found all the knots currently in use and also discovered another nine new knots that matched the aesthetic criteria[1]. We have been wearing ties for hundreds of years and yet this vital piece of research was only conducted in 1999.

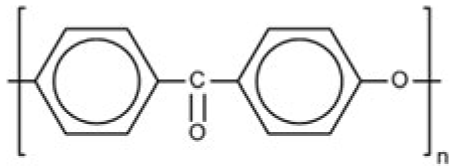
The polymer chemists were a little faster in attempting to develop useful polymers from the basic structure, and Carothers carried out some of the first work in the development of nylon in the 1930s. This basic research continued, and in the 1970s, Rose and his team at ICI began constructing polymers almost from the first reported principles. Their work was based on previously successful materials such as the polysulfones, and one of their first products was the aromatic polyether ketone family.

The preparation of these materials used a similar polyetherification process to the one that they had already developed for the polysulfones, and the structure of the resulting polymer was also very similar. The structure of the repeated unit of the polysulfones and the polyether ketones is shown below:

[1] The 85 Ways to Tie a Tie: The Science and Aesthetics of Tie Knots by Thomas Fink and Yong Mao.



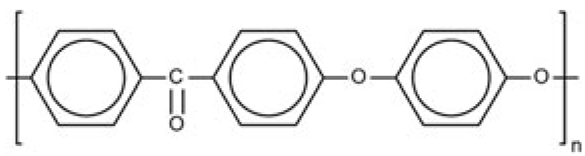
The general structure of the polysilfones



The general structure of the polyether ketones

The linear aromatic polyether ketone family consists of several variations on the theme of repeated monomers of ether and ketone. The first one produced in the laboratory in 1977 was the polymer polyether ether ketone B (now simply known as PEEK) and can claim to be one of the first designer polymers.

The structure of PEEK is shown below:



The structure of polyether ether ketone B (PEEK)

The diagrammatic representation of PEEK may appear daunting at first but this is nothing compared to the word description where the repeat unit can be described as:

[-oxy-1,4-phenylene-oxy-1,4-phenylene-carbonyl-1,4-phenylene-]

Is it any wonder that the material became known as PEEK?
ICI realized the potential for the outstanding properties of PEEK and test marketing was conducted in 1978, only one year after the first preparation of the material. ICI sold the PEEK business in 1993, via a management buyout, to Victrex plc (the original brand name for the PEEK product), and for many years Victrex remained the only commercial manufacturer and supplier of PEEK.

The annual production capacity of Victrex® PEEK is approximately 2800 tonnes (6.2 million lbs.) but demand is rising rapidly as applications increase. This means that not only is Victrex installing more capacity but also other manufacturers are starting production of PEEK to meet the market needs.

PEEK Grades

PEEK is available in a variety of grades for specific applications, and the main grades available are the following:

- **Standard unfilled:**

  This is a general-purpose grade, which has the highest elongation at break and also the lowest general mechanical properties (tensile strength, flexural strength and flexural modulus) at a given temperature. Unfilled PEEK also has the best impact properties of the PEEK range. Unfilled PEEK is compliant with FDA 21CFR 177.2145 for use in food contact applications.

- **30% glass filled:**

  The addition of glass fiber reinforcement greatly increases the general mechanical properties at a given temperature (tensile strength, flexural strength and flexural modulus), and reduces the elongation at break and impact strength at low temperatures. Glass fiber filled grades of PEEK also show reduced thermal expansion rates and are ideal for high temperature structural applications.

- **30% carbon filled:**

  The addition of 30% carbon fiber reinforcement further increases the general mechanical properties at a given temperature (tensile strength, flexural strength and flexural modulus), and further reduces the elongation at break and impact strength at low temperatures. Carbon fiber filled grades of PEEK also have much reduced thermal expansion rates and greatly improved thermal conductivity.

- **Lubricated:**

  The addition of 30% carbon/PTFE improves the tribological properties (friction and wear) of PEEK. The additives also improve the machinability and make this grade ideal for machined bearing parts.

Properties

There are many superlatives that can be used to describe the properties of PEEK, and it is regarded by many as the best performing thermoplastic. For heat resistance PEEK has the reputation of providing the ultimate performance in a commercially available melt-processable thermoplastic.

PEEK is a semi-crystalline material (typically 35%) and many of the properties derive from this degree of crystallinity in the final product. Degree of crystallinity is affected by the processing parameters, and therefore the properties quoted here should be regarded as being indicative only.

Physical and Mechanical

PEEK has greater strength and rigidity than many of the other engineering thermoplastics, making it tough over a wide range of temperatures.

It has good mechanical properties, including impact resistance, low wear rate, and a low coefficient of friction, but more importantly, these properties are also retained over a wide temperature range.

Property	Approximate Value		
	Unfilled	30% Glass Fiber	30% Carbon Fiber
Tensile strength (@23°C)	**100 MPa**	**150 MPa**	**215 MPa**
Tensile Modulus (@ 1% strain @ 23°C)	**3.5 GPa**	**11.4 GPa**	**22.3 GPa**
Elongation at Break (@23°C)	**34%**	**2%**	**1.8%**
Flexural Strength (@23°C)	**163 MPa**	**212 MPa**	**298 MPa**
Notched Impact Strength (@23°C)	**7.5 kJ/m^2**	**10.3 kJ/m^2**	**5.4 kJ/m^2**
Specific Heat (Melt)	**2.16 kJ/kg°C**	**1.7 kJ/kg°C**	**1.8 kJ/kg°C**
Glass Transition Temperature	**143°C**	**143°C**	**143°C**
Heat Deflection Temperature	**152°C**	**315°C**	**315°C**
Coefficient of Thermal Expansion	**< Tg 4.7 x 10^{-5}/°C > Tg 10.8 x 10^{-5}/°C**	**< Tg 2.2 x 10^{-5}/°C**	**< Tg 1.5 x 10^{-5}/°C**
Long Term Service Temperature (Electrical)	**260°C**	**240°C**	**N/A**
Long Term Service Temperature (Mechanical - no impact)	**240°C**	**240°C**	**240°C**
Long Term Service Temperature (Mechanical - impact)	**180°C**	**220°C**	**200°C**
Specific Gravity	**1.30**	**1.51**	**1.40**
Water Absorption	**0.50% (50% rh)**	**0.11% (50% rh)**	**0.06% (50% rh)**
Transparency	**Opaque (grey/brown)**	**Opaque (brown)**	**Opaque (black)**

Thermal

The thermal oxidative stability of PEEK is excellent and the material has an UL-rated continuous operating temperature of around 250°C (depending on the grade used).

PEEK has excellent resistance to burning and very low flame spread being rated as UL 94 V-0 for thicknesses down to 2 mm. The LOI (Limiting Oxygen Index) is 35% (depending on grade) and even when burning the material has one of the lowest smoke generation characteristics of the engineering thermoplastics.

Electrical

PEEK has good dielectric properties, with high volume and surface resistivities and good dielectric strength. These properties are retained at temperatures as high as 200°C.

Chemical resistance

PEEK has outstanding chemical resistance and is extremely resistant to most organic and inorganic chemicals. It is dissolved or decomposed only by concentrated anhydrous or strong oxidizing agents.

The material has exceptionally good resistance to hydrolysis in hot water and remains unaffected after several thousand hours at more than 250°C in pressurized water.

PEEK is not greatly resistant to UV radiation but has good resistance to beta and X-rays, as well as exceptional resistance to gamma rays (more than 1000 Mrad without significant loss in mechanical properties). These properties allow for ease of sterilization, and coupled with good biocompatibility (USP Class VI), PEEK makes a strong candidate for medical applications.

Advantages and Limitations

Advantages	Limitations
Excellent high temperature performance for all mechanical properties	**Extremely high cost but the properties can justify this when it becomes almost the only polymer capable of being used**
Excellent electrical performance at high temperatures	**Limited supplier base**
Excellent wear and abrasion resistance at high temperatures	**Limited range of colors**
Excellent chemical resistance at high temperatures	
Excellent gamma radiation resistance	

Excellent hydrolysis resistance at high temperatures	

Processing

Despite the exceptional properties of PEEK, it can be processed by many of the traditional plastics processing methods and is manufactured in formats to suit these conventional processes. For injection molding, it is sometimes possible to use existing tooling if the tooling has suitable cavities and cores that will withstand the higher processing temperatures.

Processing Method	Applicable
Injection Molding	**Yes**
Extrusion (profiles, sheet and monofilament)	**Yes**
Compression Molding	**Yes**
Powder Coating	**Yes**

Finishing

Although PEEK can be produced in finished parts by conventional processing methods, it is also possible to machine parts for prototype evaluation or small run production. The material machines easily and accurately using conventional machine tools with carbide or diamond-tipped tooling. If large amounts of machining are being used, the material should be annealed first.

PEEK can be joined using most common thermoplastic welding techniques or a range of suitable adhesives such as epoxies, cyanoacrylates, polyurethanes, or silicones.

While the color range available with PEEK is limited due to the inherent color of the material, it is possible to color it using conventional masterbatch colors and to post-finish using conventional printing, hot foiling, or other common finishing methods.

Range of Products

Ascribable to PEEK's multiple processing and finishing methods, a wide range of forms can be made from the resin. PEEK products include various configurations of tubing, such as multi-lumen, corrugated, convoluted, Lay-Flat®, Sub-Lite-Wall®, flared, and flanged. The newest product to debut is PEEKShrink™, a heat-shrink product with all of the unsurpassed properties of PEEK. It is designed to form a highly protective, shrink-to-fit shield against extreme temperatures, high pressure, caustic fluids, and dielectric interference. Currently Zeus is the only manufacturer capable of producing it.

Typical Applications

The outstanding mechanical properties of PEEK at high temperatures make it suitable for the most demanding applications, but the high cost sometimes limits applications to those where the properties are very necessary. Typical applications are the following:

Automotive: Piston components and bearing linings. These applications are particularly suitable for the carbon fiber reinforced grades where the improved thermal conductivity means that heat is dissipated very quickly.

Electrical engineering: Wire insulation for extremely high temperature applications, cable couplings, and connectors. In some of these applications, PEEK is even better than PTFE or other fluoropolymers because it has a greater resistance to cut-through by sharp edges.

Appliances: Handles and cooking equipment.

Medicine: Prosthetics, instruments, and diagnostics.

Others: Aircraft parts and wire insulation, pump casings and impellers, monofilament for production of woven products for filters, belting, and meshes.

Summary

PEEK is one of the few polymers that can be considered for use as a true metal replacement for high temperature applications. As one of the first designer polymers, the superb range of properties has opened up new and highly demanding markets for plastics. Initially, PEEK was considered an exotic material, but now it is an essential tool in the materials engineer's armory for applications when no other material can meet the requirements. For more information on PEEK as a metal substitute, see Zeus' previous Whitepaper "PEEK vs. Metal: Why Plastic is Better" at **http://www.zeusinc.com/pdf/Zeus_PEEK.pdf**

How Zeus Can Help

With a technical inside and outside sales force backed up with engineering and polymer experts, Zeus is prepared to assist in material selection and can provide product samples for evaluation. A dedicated R&D department staffed with PHD Polymer chemists and backed with the support of a world-class analytical lab allows Zeus an unparalleled position in polymer development and customization.

Since 1966 Zeus has been built upon the core technology of precision extrusion of high temperature plastics. Today, with a broad portfolio of engineered resins and secondary operations, Zeus can provide turnkey solutions for development and high-volume supply requirements.

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