

PERP Program – Crystalline High Temperature Polymers New Report Alert

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Nexant's *ChemSystems* Process Evaluation/Research Planning (PERP) program has published a new report, *Crystalline High Temperature Polymers (04/05S3)*. To view the table of contents or order this report, please click on the link below:

http://www.nexant.com/products/csreports/index.asp?body=http://www.chemsystems.com/reports/show_cat.cfm?catID=2

Chemistry

Polyetheretherketone ("PEEK") shares many properties and characteristics with polyethersulfone ("PES"), from which its basic process was adapted. Both of these materials are wholly aromatic polymers that can be used at prolonged high temperatures and can be processed on conventional thermoplastic process equipment.

PES is an amorphous material. In contrast, the partially crystalline nature of PEEK endows it with a high crystalline melting point (circa 335°C) and a very broad range of chemical resistance, derived from its high degree of oxidative stability.

PEEK is a linear aromatic polymer, and the basic monomer unit is shown in Figure 1.



The process for the production of PEEK is primarily operated by Victrex plc, the world's leading producer. Victrex has sufficient capacity (around 2,800 tons per year to meet the bulk of world demand (currently around 1,800 tons per year). However, the newly announced venture in China (Degussa/Jida) will have a capacity of 500 tons per year (plus 300 tons per year PES). Gharda in India has a further 80 tons per year of PEEK capacity.

The initial chemistry for PEEK synthesis was developed by ICI in the late 1970s, based on its PES process. In the 1960s/1970s, ICI was developing a family of high temperature plastics of which the



first was PES - a higher-temperature competitor for Union Carbide's UDEL[®] polysulfone. This was followed by polyetherketone (PEK) which processes at a temperature about 30° above that of PEEK. Raychem was awarded patents on PEK, and at that time it was used almost exclusively for wire coating in the aerospace industry.

The basic chemistry is a nucleophilic substitution involving a fluorine-based para-aromatic dihalide and a bisphenol.



The solvent for the reaction is diphenylsulfone ("DPS"), and it is carried out at a high temperature of $>200^{\circ}$ C. Note that DPS is a solid at room temperature.

The reaction involves converting the "bisphenol", usually hydroquinone, to the corresponding alkali (phenolate) using potassium hydroxide. The subsequent reaction of phenolate and dihalide species in the same autoclave results in PEEK and substantial quantities of potassium fluoride, which has to be leached out.

For this leaching to be effective, it is necessary to reduce the particle size of the post-reactor "toffee" to increase the surface area/volume ratio. The leaching agent to remove the contained potassium fluoride is water. In addition to leaching the KF, residual solvent DPS must be removed using acetone which is subsequently recovered.

Economics

The cost of production for PEEK by the Victrex process route is provided in the report based on its feedstock DFBP at cash cost transfer from a diazotization unit. The report also includes a cost of production analysis for the DFBD step.

The cost analysis shows that PEEK is more costly to make than its immediate competitors polysulfone (PSU), polyether sulfone (ES), and polyether imide (PEI). However, its performance bracket also places it into a higher margin structure than these competitors enjoy.



Commercial Analysis

PEEK is a linear thermoplastic which can be melt processed in the range of 350°C-420°C. Corrosive gases are not liberated during processing; consequently, corrosion-resistant materials of construction are unnecessary for PEEK equipment. PEEK is a particularly versatile material and a variety of processing techniques can be used to produce a range of products. These include:

- Molding
 - Injection molding
 - Compression molding
- Extrusion
 - Shapes
 - Film
 - Cast
 - Oriented
 - Monofilament
 - Wire covering
- Coating
 - Development status
- Composites
 - Matrix for high-strength
 - Continuous fibers

Despite its high-temperature performance, PEEK can be processed on standard equipment. Drying for three hours at 150° is recommended. Failure to dry results in bubbling and surface streaking but no degradation and consequently the scrap can be re-used.

A summary of the main properties of PEEK is given in Table 1.

Figure 2 illustrates the segments of the overall PEEK market.

Instigation of production capacity in Asia – Gharda entered in 2001 and Degussa has just established a position in China - will encourage Asian demand. It will also impact the global inter-regional trade pattern. Regional demand and trade patterns for Nafta, Europe, and Asia are projected through 2010 in the report.



Table 1PEEK Key Properties

Mechanical	Tough, ductile, abrasion resistant
	Excellent fatigue characteristics
	Load bearing at high temperature
Thermal	High melting point
	High continuous service temperature
Flammability	Low flammability, fire, smoke properties
Chemical	Essentially inert to organics
	High degree of acid and alkali resistance
	Particularly resistant to high temperature
	water/steam
Hard radiation	No significant degradation below 1,100 Mrad
Processing	Easily processed on conventional equipment





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