RESINATE

SPECIAL EDITION

October 2018

RESINATE

Your quarterly newsletter keeping you informed about trusted products, smart solutions, and valuable updates.

NEW FOCUS ON PEEK

REVISED and EDITED BY:
KEVIN J. BIGHAM, PhD.

ZEUS®

INTRODUCTION

Polyether ether ketone, or PEEK, is a high-performance and highly popular engineered thermoplastic. PEEK is a member of the polyaryletherketone (PAEK) family which includes other familiar semi-crystalline polymers such as polyetherketone (PEK), polyetherketoneketone (PEKK), and polyetherether-ketoneketone (PEEKK). This family of polymers is known for such performance characteristics as excellent mechanical properties and chemical resistance. PAEK family polymers retain these attributes even at high temperatures, and thus their thermal stability has become one of their hallmarks. Although relatively new to the commercial synthetic polymer market (ca. 1978), PEEK has now found its way into such diverse applications as tubing, molded parts ranging from bearings to plates to gears, insulation such as motors parts and coating for wires, to prosthetics and implantables for use within the human body. For performance plastics, PEEK is often compared to fluoropolymers because it shares several high-performing and beneficial features with several of the best-performing fluoropolymers – including a service temperature up to 260 °C (500 °F). PEEK, however, provides more diversity options to attain properties that may be out of reach for some fluoropolymers. Today, PEEK is the most widely commercialized PAEK family polymer, and new uses continue to come to the fore.

SYNTHESIS AND STRUCTURE

PEEK was first synthesized in 1977 and was industrialized in 1981 [1, 2]. PEEK is produced most immediately from difluorobenzophenone and disodium hydroquinone **(Fig. 1)**. Often viewed in a class with fluoropolymers such as PTFE or PFA, PEEK polymer, however, does not contain fluorine. Initial synthesis of PEEK was difficult due to its insolubility in most organic solvents [2, 3]. Early synthesis methods produced shorter chain length PEEK molecules which precipitated prematurely and were entirely amorphous [3]. The breakthrough came when high boiling point solvents were used resulting in much longer-chain PEEK molecules [2, 3]. PEEK chain length can be influenced during synthesis allowing some control over certain properties such as glass transition temperature (T_g) and tensile strength. Typical PEEK is not an elastomer (or *rubber*), and non-crosslinked and straight-chain PEEK synthesized by today's means is a semi-crystalline hard plastic.

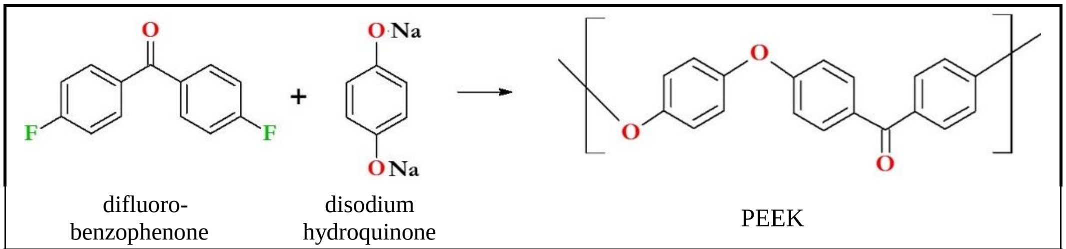

Figure 1: PEEK synthesis and immediate precursors. PEEK is synthesized most immediately from difluorobenzophenone and disodium hydroquinone. Note that PEEK does not contain fluorine and therefore is not a fluoropolymer.

PEEK is composed of consecutive ether and ketone linkages **(Fig. 2)**. These linkages give PEEK a degree of flexibility, though PEEK generally is considered a rigid molecule. PEEK's ether and ketone linkages prevent it from adopting a fully planar conformation, but stacking interactions among the aryl moieties support increased crystallinity of PEEK. The ether linkages also aid in bringing PEEK into the melt-processable realm for extrusion. These minor yet highly significant additions to the aryl chain moieties have made PEEK an extremely versatile, consistent, and very high-performing polymer.

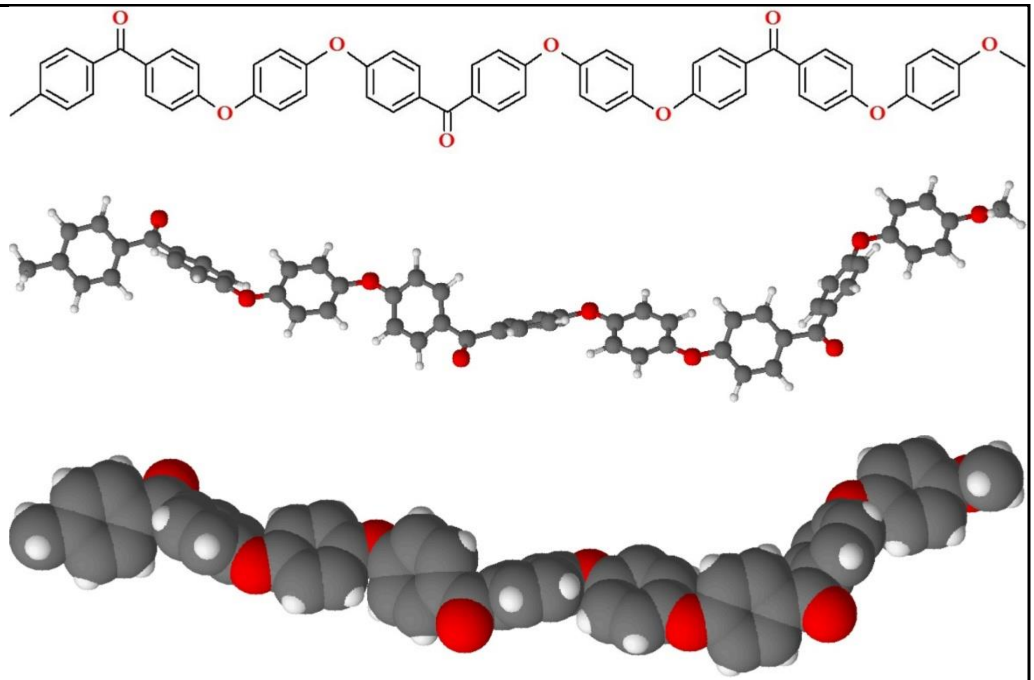

Figure 2: Structure of PEEK. A) Stereo bond-line drawing, **B)** ball-and-stick model, and **C)** space-filling model of PEEK. (Conformations of PEEK are variable during melt and amorphous phases).

PROCESSING

As a thermoplastic, PEEK is melt-processable. PEEK is comparatively more expensive to process, however, because of its high melting temperature (343 °C / 649 °F). The fluidic melt-state PEEK is stable and can be processed using most common and industry-standard equipment at temperatures between 360 °C to 400 °C (680 °F to 752 °F) **(Table 1)** [4]. Under such heat, however, no corrosive gases are produced by PEEK causing no undue hardship to processing equipment. Cooling greatly influences crystallinity of PEEK and thus its mechanical behavior. Rapid cooling produces less crystallinity and greater amorphous character and a more transparent PEEK.

Conversely, slower cooling yields high crystallinity and a more opaque PEEK material. Raw PEEK material should also be thoroughly dried before processing to avoid porosity or bubbles in molded PEEK parts [4].

Processing Method	Suitability
Injection molding	**Yes**
Extrusion (profiles, films, sheet, tubing, heat shrink tubing, and cable coating)	**Yes**
Blow molding	**No**
Compression molding (overmolding, etc.)	**Yes**
Impregnation and coating	**Yes** (as coating)

Table 1: PEEK processing suitability. PEEK can be processed by several means but is generally is not suitable for blow molding.

PEEK PROPERTIES

PHYSICAL AND MECHANICAL

PEEK has gained popular use due largely to its good mix of mechanical properties such as toughness, strength, stiffness, and creep [5-7]. Like most semi-crystalline polymers, PEEK's properties are greatly affected by crystallinity. As an example, PEEK's elastic modulus is close to that of human bones increasing its use as an implantable device [8, 9]. PEEK has a higher working temperature than most commercial plastics including some fluoropolymers. Conversely, PEEK's density is less than most high performing polymers except for most polyethylenes and nylons. This low density of PEEK translates to lighter-weight PEEK parts. PEEK also exhibits broad chemical resistance supporting its use not only in harsh industrial applications but also within the body. In this latter context, PEEK tolerates sterilization protocols such as autoclave, gamma irradiation, or ethylene oxide (ETO) [10, 11]. PEEK's mechanical and physical benefits combined with its comparative low weight give PEEK an advantage over many other commercial plastics **(Table 2)**.

Property	ASTM	Value (natural polymer)
Appearance	–	**Opaque; light tan or brown**
Density (g/cm^3)	D792	**1.3**
Specific Gravity (23 °C)	D792	**1.3**
Water Absorption (50% rh; %)	D570 / ISO 62-1	**0.07* – 0.45***
Refraction Index	D542	**1.67**
Limiting Oxygen Index (LOI) 3.2 mm thickness	D2863	**35**
Biocompatible	USP Class VI	**Yes**
Chemical Resistance	–	**Excellent**
Sterilization	–	**Autoclave, Gamma, ETO**

Table 2: PEEK typical physical properties. PEEK's physical properties support its use in areas ranging from harsh chemical environments to medical applications. (Methods are ASTM test standards except where indicated or by *).

PEEK mechanical properties place it in a small group of very high performing thermoplastics. PEEK retains many of its critical properties such as tensile, flexural, and impact strength at temperatures near or even above its normal maximum working temperature **(Table 3)** [7]. PEEK exhibits good wear traits for parts that may be subject to surface interaction and friction with other parts. In line with PEEK's biocompatibility, PEEK tolerates high levels of gamma radiation and can withstand multiple sterilization cycles [7]. PEEK, however, performs poorer under UV exposure making it less amenable to outdoor use [12]. The result of prolonged exposure can be seen as embrittlement associated with exterior environmental use [13, 14]. In these scenarios, carbon is routinely added as a filler to improve PEEK UV resistance.

Property	ASTM	Value (natural polymer)
Tensile Strength (MPa)	D638	**99**
Elongation at Break (%)	D638	**40 – 45**
Modulus of Elasticity (GPa)	D638	**3.7 – 4.0**
Flexural Modulus (GPa)	D790	**3.8 – 4.2**
Flexural Strength (MPa)	ISO 178 / D790	**125 – 165**
Hardness (Shore D)	D2240	**84.5**
Impact Strength (23 °C; kJ/m)		
notched	ISO 180	**8.0**
unnotched		**No Break**
Coefficient of Friction	D1894	**0.58**

Table 3: Typical PEEK mechanical properties. PEEK exhibits exceptional mechanical properties as a thermoplastic. Several PEEK properties are retained at temperatures above PEEK's typical maximum service temperature.

THERMAL

PEEK demonstrates very good thermal stability **(Table 4)**. PEEK outgassing and degradation begin only at temperatures far exceeding its melt temperature [7]. PEEK's thermal stability also facilitates its processability supporting its viscous flow at melt temperatures. Similarly, PEEK's comparatively low coefficient of thermal expansion translates to PEEK parts with good dimensional stability through large temperature changes. PEEK's low service temperature extends down to at least −70 °C (−94 °F) [15, 16]. Like most plastics, at extremely low temperatures, PEEK exhibits increased brittleness.

Property	Method	Value (natural polymer)
Thermal Conductivity (W/m-K)	D433 / ISO 22007-4 / C-177	**0.29 – 0.32**
Maximum Service Temperature (°C)	UL 746	**260**
Minimum Service Temperature (°C)	UL 746	**-70**
Melting Point (°C)	D4591 / D3418/ ISO 12086 / DOW Method	**343**
Glass Transition Temperature (°C)	E1356 (DSC) or E1545 (mechanical)	**143**
Decomposition Temperature (°C)	E1131	**541**
Coefficient of Thermal Expansion, Linear (µm/m-°C)	D696	**45**
Flammability Rating (UL 94)	D2863	**V-0**

Table 4: PEEK thermal properties. PEEK exhibits a large operating temperature window and resists burning and outgassing. (Methods are ASTM test standards except where indicated).

ELECTRICAL

PEEK shows very good insulating properties **(Table 5)**. PEEK's all-covalent bonding and no mobile electrons support its polarizability in an electric field. This trait along with its zero halogen structure support PEEK's ability to store electrical energy and function as a dielectric. The voltage at which the PEEK material will fail and no longer function as an insulator is its breakdown voltage, or dielectric strength. Thus, the greater the dielectric strength of material, the better is its insulating ability. As a dielectric and combined with its other properties such as strength and high temperature tolerance, PEEK has gained widespread use in an exceedingly large range of electrical applications.

Property	ASTM	Value (natural polymer)
Dielectric Constant (1 MHz)	D150	**2.2 – 2.8**
Dielectric Strength (V/mil)	D149 / IEC 60243-1	**584.2**
Volume Resistivity (Ω–cm)	D257 / IEC 60096	**4.9×10^{16}**

Table 5: PEEK electrical properties. PEEK's covalent bonding and aryl moieties allow it to function as a dielectric (insulator) and store electrical energy. (Methods are ASTM except where indicated).

FINISHING

PEEK parts can be produced in many different variations and forms. From piping and tubing to films to monofilament fiber and sheets, PEEK can be fashioned to almost any design that metal parts can be made into. PEEK can be machined by conventional equipment and methods, and vendors frequently offer guidelines to assist in this endeavor. Polymer materials, including PEEK, can suffer stresses during machining. Thus, it is not uncommon to include one or more annealing steps to relieve such stresses as part of the overall PEEK machining process. Additionally, care must be taken not to warp or otherwise deform the PEEK material either from physical force or from heat build-up during machining [4]. On the whole, however, PEEK can readily be transformed into unique shapes and configurations to suit a comprehensive range of specialized and common applications.

APPLICATIONS

PEEK engineered extrusions are among the highest performing thermoplastics matching even some fluoropolymers. PEEK's processability sets it apart, however, from many of its competing plastics allowing it to reach a very broad scope of application niches **(Table 6)**. As tubing, PEEK's excellent chemical resistance allows it to be used in a variety of fluid management systems insuring that the tubing will not react with or contaminate the fluid contained within it. PEEK's zero halogen nature has made it a preferred material for dielectric applications. PEEK insulated wire, PEEK slot liners, and PEEK phase insulation have been shown to improve motor performance when used together [17]. As a spray coating, PEEK can be used in aqueous environments for dielectric as well as corrosion protection applications [18]. PEEK can also be produced in a heat shrinkable form such as Zeus' own PEEKshrink® to protect wiring, splices, and connectors. PEEK's insulating ability is also utilized in a variety of switches and surface mounted potentiometers. PEEK dielectric properties are likewise especially beneficial in electrical circuitry involving low-intensity signals or output. PEEK drawn fiber can be used as braiding reinforcement for hoses and catheters. As a coating for optical fibers, PEEK's thermal stability enhances fiber optic sensing functions [19]. Secondarily, PEEK's low outgassing means that chemical or thermal sensors utilizing PEEK protection are much less likely to be affected by chemical traces emanating from PEEK. Whether in electrical, chemical, or temperature extremes, a PEEK product likely already exists to match these and more ever-expanding new demands.

Application or Industry	Key Benefits
Oil and gas	Chemical, heat resistance
Fiber optics	Thermally stability, data transfer integrity
Fluid management	Chemical resistance
Wire and cable insulation	Abrasion resistance, dielectrics
General industrial	Toughness, machinable
Heat shrink	Encapsulation, connector protection
Replacement for metal	Weight savings
Braiding • hoses • catheters	Strength reinforcement

Table 6: Survey of PEEK applications. With its retention of several key properties at temperature extremes, its chemical resistance, and heat shrinkable options, PEEK is one of the most widely utilized commercial plastics.

SUMMARY

PEEK polymer is now used all over the world in industries ranging from aerospace, automotive, oil and gas, alternative energy, fiber optics, to medical. Considered one of the highest performing materials, this relative newcomer to the thermoplastics industry can be extruded, injection molded, or used as a coating. PEEK's aryl and ketone moieties support its thermal stability during both the melt processing stage and as finished parts. Electrical industries prefer PEEK because of these same features resulting in high dielectric strength and insulating capabilities. Aside from its ability to tolerate harsh industrial chemical environments, PEEK's chemical resistance also means that it does not react when used within the body. Furthermore, PEEK exhibits many similar mechanical attributes to bone. As a final benefit of PEEK, its rugged mechanical attributes and machinability allow it to replace heavier metal parts in many applications where weight savings is vital. In its relatively short commercial lifetime, PEEK has proven to be a highly valuable material from the toughest to the most sensitive environments **(Table 7)**.

Advantages / Benefits (+)	Limitations (–)
• High temperature tolerance (260 °C / 500 °F) • Excellent chemical resistance • Retention of mechanical attributes • High dielectric strength *Zero halogen structure* • Can replace some metals; comparatively light-weight • Melt processable	• Requires high processing temperatures • Low impact strength • Low UV resistance • Cost

Table 7: PEEK advantages and limitations. PEEK offers many mechanical benefits including strength even at elevated temperatures. PEEK's chemical resistance and bone-like traits make it especially adapted to medical uses and prosthetics.

ABOUT ZEUS

Zeus is the world's leader in polymer extrusion technologies. For over 50 years, Zeus has been serving the medical, aerospace, energy exploration, automotive, and fiber optics industries. Headquartered in Orangeburg, South Carolina, Zeus employs approximately 1,500 people worldwide and operates multiple facilities in North America and internationally. You can find us at www.zeusinc.com.

CONTACT US

More information regarding the material discussed here is available by contacting one of Zeus' technical account managers. They can be reached in the US toll-free at **1-800-526-3842** or internationally at **+1-803-268-9500**. You can also email us at editor@zeusinc.com.

Zeus Industrial Products, Inc.
3737 Industrial Blvd.
Orangeburg, SC 29118
USA

Zeus Ireland - Tel +353-(0)74-9109700
Zeus China - 电话 +(86)20-38791260

RESINATE SPECIAL EDITIONS

As part of our efforts to provide you with relevant, useful, and timely information, we regularly review our content available through our multiple outlets. Our review also includes previous publications which we have retained in our library. *RESINATE Special Editions* are our updated and revised versions of some of these previously issued yet valuable learning tools we wish to continue to provide to our customers.

REFERENCES:

1. Yao F, Zheng J, Qi M, Wang W, Qi Z: **The thermal decomposition kinetics of poly(ether-ether-ketone) (PEEK) and its carbon fiber composite**. *Thermochimica Acta* 1991, **183**:91-97.
2. Rose JB: **Production of aromatic polyketones**. In: *US Patent US4396755 (A).* C08G61/00; C08G61/12; C08G65/00; C08G67/00; (IPC1-7): C08G67/00 edn. United States: Imperial Chemical Industries Ltd.; 1983.

3. Mullins MJ, Woo EP: **The Synthesis and Properties of Poly(Aromatic Ketones)**. *Journal of Macromolecular Science, Part C* 1987, **27**(2):313-341.
4. **PEEK Processing Guide**. In.: Victrex; 2004.
5. Lu S, Cebe P, Capel M: **Thermal stability and thermal expansion studies of PEEK and related polyimides**, vol. 37; 1996.
6. Jenkins MJ: **Relaxation behaviour in blends of PEEK and PEI**, vol. 41; 2000.
7. **PEEK Materials Properties Guide**. In.: Victrex; 2012.
8. Kurtz SM: **Chapter 1 - An Overview of PEEK Biomaterials**. In: *PEEK Biomaterials Handbook*. Edited by Kurtz SM. Oxford: William Andrew Publishing; 2012: 1-7.
9. Garcia-Gonzalez D, Jayamohan J, Sotiropoulos SN, Yoon SH, Cook J, Siviour CR, Arias A, Jerusalem A: **On the mechanical behaviour of PEEK and HA cranial implants under impact loading**. *Journal of the mechanical behavior of biomedical materials* 2017, **69**:342-354.
10. Monich PR, Berti FV, Porto LM, Henriques B, Novaes de Oliveira AP, Fredel MC, Souza JCM: **Physicochemical and biological assessment of PEEK composites embedding natural amorphous silica fibers for biomedical applications**. *Materials science & engineering C, Materials for biological applications* 2017, **79**:354-362.
11. Sheiko N, Kékicheff P, Marie P, Schmutz M, Jacomine L, Perrin-Schmitt F: **PEEK (polyether-ether-ketone)-coated nitinol wire: Film stability for biocompatibility applications**. *Applied Surface Science* 2016, **389**:651-665.
12. Page D: **Neutron and Gamma Radiation Effects On The Viscoelastic Behavior Of Poly(aryl ether ether ketone)**. Kingston, Ontario: Royal Military College of Canada; 1997.
13. Mylläri V, Ruoko T-P, Järvelä P: **The effects of UV irradiation to polyetheretherketone fibres – Characterization by different techniques**. *Polymer Degradation and Stability* 2014, **109**:278-284.
14. Nakamura H, Nakamura T, Noguchi T, Imagawa K: **Photodegradation of PEEK sheets under tensile stress**. *Polymer Degradation and Stability* 2006, **91**(4):740-746.
15. AZoM: **Supplier Data - Polyetheretherketone (PEEK)**. In.: Goodfellow; 2003.
16. **PEEK - Polyetheretherketone**. In.: DesignerData (Promolding BV).
17. Bigham KJ: **Test Report: Impact On Low Voltage Motor Performance**. In. https://www.zeusinc.com/; 2016: 8.
18. Normand B, Takenouti H, Keddam M, Liao H, Monteil G, Coddet C: **Electrochemical impedance spectroscopy and dielectric properties of polymer: application to PEEK thermally sprayed coating**. *Electrochimica Acta* 2004, **49**(17):2981-2986.
19. Davis M, Fant J: **Test Report: PEEK Coated Optical Fiber Evaluation**. In. Edited by Bigham KJ. https://www.zeusinc.com/; 2016: 10.

