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A Review on the Tribological behaviour of Polyether ether Ketone (PEEK)

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Abstract
Poly ether ether ketone (PEEK), a colourless high performance organic thermoplastic polymer is employed in a diverse range of engineering applications. Due to PEEK's outstanding property profile, ceramic and metal tribo-components are being replaced with PEEK. However, in environments with high temperature, the tribological properties of the polymer deteriorate. Hence, suitable polymers are blended with PEEK to improve its wear and friction properties. The anti-wear feature of PEEK is enhanced by improving the wear resistance with reinforcements like Zirconium dioxide (ZrO_2), Tungsten disulfide (WS_2), Silicon carbide (SiC), Aluminium oxide (Al_2O_3), and so on. The tribological behaviour of PEEK carbon fibre can be further improved by treating it with plasma. PEEK and its compounds are deliberated extensively in this paper based on their tribological behaviour in dry and wet conditions. The thermal, chemical, wear and biocompatibility of PEEK, reinforced grades, applications and processing conditions are discussed in detail. Tribology of PEEK blends with liquid crystalline polymers (LCPs), polytetrafluoroethylene (PTFE) and polyether imide (PEI) along with the recent research trends are also studied in this purpose.

Keywords: Tribological Behaviour, Polymers, Composites, poly ether ether ketone, PEEK, Fibres;

1. Introduction

Alloys and steel used in the components and devices of industrial application involve operation in environments that are exposed to moisture thereby leading to corrosion [1], [2], [3]. However, to overcome such issues, various alternative materials like polymers and ceramics are considered. Addition of lubricants and reinforcements to polymers and polymer composites provide enhanced tribological properties that are best suited for industrial applications. Development of polymer– matrix composites that are of light weight and resistant to corrosion in damp conditions replacing metals are considered as a significant solution to the existing industrial challenges. Cohesive strength, excellent wear resistance, superior mechanical properties, enhanced chemical resistance and high service temperature are the essential properties for a tribological matrix. The profile property of Poly ether ether ketone (PEEK) thermoplastic is exceptional [4]. In 1962, W.H.Bonner first synthesized the high performance PEEK polymer. Ever since, various researches are performed on PEEK to improve its performance as a tribological material replacing alloys and metals while overcoming its drawbacks and understanding its nature. PEEK is the derivative of poly aryl ether ketones (PAEK) which are used for replacing alloys and metals in biomedical, automotive and aerospace applications [5]-[6].

High glass transition temperature, high melting point, high continuous service temperature and high toughness are some of the key features of PEEK. The inert chemical nature and stability of PEEK offers high resistance to bases, acids and organic solvents enabling easy processing of the material through injection moulding. At certain acute energy dissipation rates or interface temperatures, the PEEK metal contacts may experience mechanical or chemical damages due to the exceedingly rapid

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surge in friction [7]. This friction can be attenuated by using internal phase lubrication while preserving the significant mechanical characteristics of the material. Appropriate fillers can also be added to improve the tribological characteristics and mechanical features of the material. Traditionally, several approaches are undertaken for strengthening PEEK through incorporation of filler particles and fibers realizing the high-performance characteristics of PEEK that may not be accomplished due to scuffing and abrasion of PEEK-metal contacts in specific tribo-systems. Especially in damp environments, PEEK and its compounds are often used as a prominent tribological replacement [8].

2. Characteristics and Composites of PEEK

2.1. Properties of Polyetheretherketone

Outstanding thermal properties- The melting point of PEEK is over 650 ˚Fahrenheit providing exceptional heat resistance and high material strength. In applications with long term heat exposure, PEEK is capable of handling around 500 ˚F and much higher temperature during short term exposure. This temperature is far beyond the capability of most polymers. The softening or glass transition temperature of PEEK is around 300 ˚F [9]. Modification of the chemistry and reinforcement of the material can be done for compensating this inherent characteristic of PEEK.

Extensive chemical resistance- In comparison to polytetrafluoroethylene (PTFE), the chemical resistance of unfilled PEEK is higher. This makes PEEK the most preferred material for processing chemicals in several industries[10]. PEEK can resist several chemicals inclusive of toluene, sodium hydroxide, sodium carbonate, pentane, ozone, methylene chloride, MEK, methane, hydrogen sulfide, hydrogen peroxide, glycerin, fuels like gasoline, formaldehyde, ethylene oxide, chlorine, benzene, ammonia, alcohol and acetone with an exception of hydrobromic and hydrofluoric acid. This extensive resistance to chemicals makes PEEK the most preferred choice in various applications[11].

Superior wear resistance – The balanced wear resistance of PEEK can be matched by very few polymers. The irregularities of the counter surface leads to abrasive wear during cutting, while repeated stress and pressure causes deformation of material leading to fatigue wear. The resisting force in contradiction to the motion is termed as friction. The negative effects of fatigue and abrasive wear as well as friction are overcome by the properties of PEEK by its resistive nature and low friction coefficient. In abrasive and high PV conditions, reinforced PEEK with carbon fiber and PTFE graphite offers low wear rates. At low velocity and maximum stress levels, the wear resistance and fatigue resistance of unfilled PEEK is exceptional. Better wear rate and lesser friction coefficient are provided by 20% PTFE filled PEEK material [12].

Enhanced Processing – In voluminous commercial applications, PEEK is used widely due to its processing simplicity. From a thin film or strip stock, the PEEK components can be machined or stamped and injection molded or extruded into stock shapes. Hot runner system enabled high volume tooling equipment is used for injection molding purposes [13]. In manufacture of high performance thermoplastics, limited availability of required shapes lead to an increase in the manufacturing costs and time. Extrusion of PEEK is much efficient due to its melt stability and high molecular weight. The material is also available as tubes, plates and rods of various sizes. Extensive machining for creation of complex geometrical components is simplified when high performance thermoplastic material like PEEK is used. This opens the possibility of utilization of this material in a diverse range of applications.

Biocompatibility – The immune system of the human body rejects various polymers that may be used as biomaterials leading to serious and intimidating complications [14]. The intense friction of the body

may lead to abrasive wear causing internal injuries or disruption in the biological function of the body. PEEK is a favorable material in several bio-medical applications due to its mechanical properties like high modulus and strength. Some of the common applications include cartilage and bone replacement, skull reconstruction and spinal implants. During surgical procedure or chemical analysis, the biocompatibility of PEEK allows smooth contact with bio fluids. PEEK can be customized using a 3D printing process to improve its usability in various medical applications [15]-[16].

2.2 Reinforced PEEK grades

High temperature, bearing grade or graphite filled, 20% PTFE, 30% carbon-filled, 30% glass-filled and unfilled are some of the significant grades of PEEK. These materials can be synthesized into custom shapes for application in medical components, gears, hex nuts, flat washers, screws, bearing, fasteners and other components [17]. The properties of each PEEK grade and their applications are discussed.

High-Temperature PEEK, Polyetherketone (PEK) and Polyether ketone ether ketone ketone (PEKEKK) have slight variations in the chemistry and provide extreme softening temperatures. Even at high temperatures up-to 50°F, the stiffness and strength of the material can be retained enabling application of the material in downhole electric connectors for insulation [18]-[19]. The material also offers improved resistance to hydrolysis, low smoke emission, low flammability and improved compressive strength.

Bearing Grade PEEK – Best machinability, least friction coefficient, minimal wear rates are the benefits of bearing grade PEEK which incorporates PTFE, graphite and carbon fiber. In extreme wear applications, the low mating part wear and high pressure-velocity (PV) performance makes it an ideal choice. Remarkable heat dissipation, high ductility and abrasion resistance are some of the significant properties of this material. It is commonly used in consumable parts and aggressive service bearings [20].

30% Carbon-Filled PEEK – Reinforcement of carbon-fiber offers excellent load-carrying capability, outstanding wear resistance, high stiffness, rigidity and creep strength to the PEEK material. The capability and life of the bearing is improved allowing faster heat dissipation from the bearing surface. [21] The thermal conductivity is 3.5 times greater when compared to unfilled PEEK. In comparison to glass-filled PEEK, it is 7% less dense and consists of more reinforcements per unit volume. Inherent flame impeding, superheated steam and hydrolysis resistance, high energy radiation resistance and excessive dimensional stability are the other significant features of this material.

30% Glass-Fiber filled PEEK – The bending resistance or flexural modulus of the material is increased while the expansion rate is reduced and the stiffness and high strength of material is maintained in glass-fiber PEEK. The thermal and electrical insulation characteristics of this material are high, making it an optimal choice in high load parts and several structural applications. Some significant features of this material include easy fabrication, excellent flame retardance, low emission of toxic gas and smoke, low absorption of moisture, and high temperature performance [22].

Unfilled PEEK – Highest toughness and elongation is offered by general-purpose, unreinforced grade PEEK material. In applications requiring ductility and inertness, this material offers excellent steam and water resistance [23]. It emits minimal toxic gases and smoke and is resistant to environments with

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harsh chemicals. The maximum operating temperature of this material is around 480 °F. Even at extremely high temperatures, the physical properties and shape of the material is retained.

The table below (Table 1) provides a comparative study between 30% glass fiber, 30% carbon fiber and unfilled.

Property	**30% glass fiber**	**30% carbon fiber**	**Unfilled**
Toughness (Notched Izod Impact at Room Temperature) (J/m)	95 - 130	85 - 120	80 - 94
Density (g/cm3)	1.49 - 1.54	1.4 - 1.44	1.26 - 1.32
Thermal Insulation (Thermal Conductivity) (W/m.K)	0.43	0.9 - 0.95	0.25
Young Modulus (GPa)	9 - 11.4	13 - 22.3	3.5 - 3.9
Flexibility (Flexural Modulus) (GPa)	9 - 10	13 - 19	3.7 - 4
Elongation at Break (%)	2 - 3	1 - 3	30 - 150
Volume Resistivity (x 1015 Ohm.cm)	15 - 16	1 - 8	16 - 17
Dielectric Strength (kV/mm)	15 - 24	18.5 - 19	20
Dielectric Constant	3.3 - 4.2	3.2 - 3.4	3.2

When compared with fluoropolymers, there are many mechanical properties that prove PEEK to be superior such as toxic gas emission, processing, bonding, operating temperature and HDT. However, in terms of UV weathering, toughness, cost and chemical resistance, PEEK is found to be inferior. PEEK shows higher characteristics of flashing, toughness and superior thermal resistance when compared with PPS [24]. Similarly PEEK will also have higher fatigue performance, chemicals resistance, wear resistance and temperature performance in comparison to PES. It is also worth noting that blending of PEEK with other polymers is not done in a normal manner. Rather, they form miscible blends with PEI as well as an array of poly ketones. Both PEI and PEEK are said to have higher glass transition temperature and can blend with PES and PPS with high compatibility.

2.3 Applications of PEEK

PEEK is widely used in a wide range of applications such as medical, electrical, automotive, aerospace etc. This material is also used in the fabrication of specific products like cable insulation, compressor plate valves, HPLC columns, pumps, piston parts, bearings etc due to its robust property. When compared to filled PEEK, unfilled PEEK is in more demand and is used in many products [25]. Its processability, availability and durability make PEEK one of the best option of material when in need of material that exhibits excellent inertness and high strength at elevated industry temperatures. The application of PEEK keeps increasing and expanding due to its exuberant properties. Some of the prominent uses of the polymer are mentioned below:

Semiconductors and electronics –The property of PEEK to withstand its strength at high temperature apart from its characteristics of purity makes it the apt polymer to be used in electronics and semiconductor manufacturing to withstand the use of chemicals. In chemical washing process, the PEEK polymer can also be used in building hardware and wafer handling machinery. On the other hand,

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during the chip production process, chemical etching and mechanical planarization, unfilled PEEK [26] is being usrf. An excellent example of this would be the use of PEEK film in chips that are embedded in the cell phones.

Gas and Oil – The glass-filled PEEK and unfilled PEEK are used as electrical connectors and seals. In this field they are also used as isolators and insulators and as reinforcements in order to create materials that are softer in nature. Because of its ability to withstand steam as well as its sustainability to harsh chemicals, PEEK serves as a good choice in gas and oil applications. In the downstream, PEEK value seals and seats are used to handle petrochemical liquids and gases without the risk of chemical degradation.

Aerospace –In military as well as commercial aircraft, materials which are durable and reliable are used and PEEK is one of the optimum choices of materials utilized. PEEK's high thermal resistance and low smoke generation make it an apt fit in aerospace engineering. Moreover, it is observed that PEEK is highly resistant to fire and heat that it is said to self-extinguish itself when need arises. The electronics in aerospace are usually thermal isolators and are highly stressed, requiring them to handle extremely cold and heat conditions and PEEK falls under this category [27]. KT820CF30 and 450CA30 are some of the carbon fibre reinforced PEEK materials that have high stiffness and strength properties.

Medical – PEEK plays a crucial role in making implants such as dental implants and spinal implants because of its biocompatibility. In fact, the carbon fiber reinforced PEEK is so stable and inert that they outlive the patients who have been implanted. Moreover, the stability and inertness of PEEK make it the right choice for making reusable medical instruments. PEEK also has radiolucency property which makes it invisible during MRI and CT scanning. This property is also useful in studying growth of tissues as it will not be easy to screen the tissues surrounding the implant.

Food and packaging – In the food and packaging industry, there is a need for food-grade materials that can be used and unfilled PEEK satisfies these conditions, making it possible to integrate it into appliances that require physical contact with food particles. Some of the components in which unfilled PEEK is used include valve, bushings, bearings, mixing paddles and nozzles that are used in hot filling machines and citrus fruit processing. Moreover, Clean in Place (CIP) solutions are built with the use of unfilled PEEK.

These applications are but just a drop in the ocean outlining the uses of PEEK and its compositions. As there is progress and advancement in technology, the number of companies that are turning to PEEK are high, primarily because of its cost effectiveness. PEEK is one of the most versatile and easily available polymers which offers high performance in the market [28].

2.4 PEEK Polymers- Processing Conditions

Conventional methodologies such as compression molding, extrusion, injection molding etc can be used to process PEEK. There is a possibility that crystallinity might occur when PEEK mold is made in the processing conditions. Between the temperature of 370°C and 420°C, PEEK is melt processed as a linear thermoplastic. Initially PEEK is to be dried at 180°C for 2 hours or 150°C for 3 hours before being processed and during processing, corrosive gases shouldn't be liberated. Detailed below are the three common ways in which Polyether ether ketone is processed.

Injection Molding

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In order to minimize warping as well as to get the right crystallization, a mold temperature of 165°C to 195 is prescribed. After it attains 200°C, there is a possibility of post crystallization which is however not the best choice in places which need a higher rate of dimensional stability. The PEEK polymer has been identified to be best suited to be used on miniscule parts that require high dimensional tolerance such that the environmental conditions are maintained at 70-140 Mpa of injection pressure and a mold shrinkage filled (0.1-1.1%) and unfilled (1.2-2.4%) [29].

Extrusion

The performance of the polymers as well as their crystallinity is greatly affected by the cooling temperature. At 50°C the cooling cylinders can be used for sheet and film extrusion to attain a transparent amorphous material. At an increased temperature of 170°C, a highly crystalline and opaque material is formed. Moreover, using an extrusion process, it is possible to produce a bio-oriented or oriented film.

3D printing

The unique properties of PEEK make 3D printing of very complicated design geometry possible to be constructed while it can't be done so with other technologies. Fused Filament Fabrication and Fused deposition modeling are some of the methods using which PEEK filaments can be used for 3D printing. Using a heated bed at 120°C and maintaining the nozzle temperature between 360°C and 400°C is the apt candidate for FFD as it will ensure that the rate of moisture absorption is maintained at a low rate. This is especially considered to be an advantage since other used materials like Acrylonitrile Butadiene Styrene (FFT material) will not be able to sustain in the aforesaid conditions [30].

2.5 PEEK blends

Poly (ether imide)/Poly(ether ether ketone) blends- It has been observed that PEEK and PEI are miscible at different compositions. Similar to PEEK, PEI also shows thermoplastic performance to be as high as expected. Though PEI is said to hold a low coefficient of friction, this does not reflect in its wear and tear properties and is said to have a negative impact on its usage. Thus the best of both worlds are combined in PEEK resulting in acceptable tribological properties. At a glass transition temperature of 145°C, PEEK will attain an amorphous state while PEI will reach this state only at 215°C. Hence a blend of PEI and PEEK is said to be an interesting take that will result in combining the characteristics of both the polymers. This blend is also intriguing as PEEK can be built with PEI as the joining agent.

Poly tetra fluoro ethylene/ Poly (ether ether ketone) blends- This polymer is said to be highly resistant to chemical attacks as well as atmospheric degradation. When used with PEEK at varying composition, it will result in creating an immiscible blend. On the other hand, is said to have the best blend as it portrays high wear rate which is required apart from its friction properties.

Liquid crystalline polymer blends/ Poly (ether ether ketone)- During recent times, a number of novel techniques have been introduced to blend engineering thermoplastics and thermo tropic LCPs. These types of polymers will prove to be a good methodology to improve the characteristic properties of thermoplastics which will have a meso-phase. Moreover, these LCPs when cooled will result in solidifying with fibrous structures that are highly oriented. Thermal stability, improved tensile strength and low melt viscosities are some of the mechanical characteristics that result from these properties.

3. Research Focus

Replacing the use of aluminum, PEEK polymers and its composites can be used in a number of aircraft parts. Moreover, it will also be useful in building cost-effective and highly tolerant components in large volume without the need for modification or assembly. As far as the aerospace market is concerned, PEEK is used especially in building parts of the engine that is required to withstand high temperature as well the wear due to contact between lubricated and dry material. In recent days, there is much concentration on the development of nanocomposites and PEEK nanocomposites are not an exception. These composites are preferred because of their viability at extreme conditions such as cryogenic, hydrogen and vacuum [31]. Studies are also being made on hybrid soft-hard nano-fillers for PEEK to observe if there is any significant advancement in its tribological properties. Similarly, the application of modified PEEK in applications of biomedical field is observed in terms of prosthesis, dentistry and medical [32] with varying environmental conditions and a comparative study is also made accordingly to observe changes and improvements, if any. Similarly, in [33] there is focus on aqueous environment and how PEEK will display different characteristics like reduced water lubrication and wear resistance. However, it has also been seen that PEEK matrix will display a higher resistance to wear in aqueous environment when compared to its other compositions. This has encouraged a number of research works on the development of nano-fillers which can help to enhance PEEK's mechanical tribological properties in order to enable it to be used in important parts of sub-marines and ships like propeller shaft bearings. This is owing to PEEK's low water absorption, good chemical stability and excellent corrosion resistance.

4. Conclusion

This paper outlines an extensive review of the mechanical behaviour of PEEK composites and the various fields of its application. Surface modification and composite preparation are the two important methods that are used to enhance wear behaviour of PEEK polymer. Based on the review, the following conclusions are drawn.

- Examinations indicate that composite preparation or surface modification using inorganic reinforcements will enhance wear resistance, micro hardness, stiffness, strength of the PEEK matrix. Moreover, it will also improve the binding between inorganic content and PEEK, resulting in improved matrix composition of PEEK. Similarly, the synergetic attraction between the PEEK matrix fill will play a crucial part in building the composites' mechanical strength.
- It is also to be noted that when compared to PEEK, carbon fiber-filled PEEK composites will display higher mechanical strength.
- When reinforcing with chemical properties, microstructure and composition, it will have a high impact on the wear properties of PEEK composites.

Based on our review, we have identified that in order to improve the wear behaviour of PEEK matrix and polymer composites, a potential reinforcement is to be prepared. One recommended solution is to incorporate fillers into PEEK matrix which will thereby improve its wear characteristics.

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