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Review of Tribological characteristics of Modified PEEK Composites

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Abstract: *The behavior of and structure with use of polyetheretherketone (PEEK) composites are summarized here in details. The research progress of friction and wear resistance properties as a tribological charaterstics of PEEK composites with modified by carbon fiber, other nano scale and micro-scales particles, are also summarized scopes for further future research ahead are put forward.*

Keywords - *Wear property, Carbon fiber, Polyetheretherketone, Tribological*

I. INTRODUCTION

PEEK is a thermoplastic that has excellent thermal, mechanical, as well as chemical resistance properties, and it is widely used for composite materials. Adding fiber to this thermoplastic resin enhances these properties further. Carbon fiber (CF) is one of the most widely used fibers with PEEK.

PEEK has a low vapor pressure and exhibits good resistance to combustion when burnt and it produces less amount of gas in comparison to other thermo plastic plastics. PEEK has good resistance when exposed to beta, gamma and X- rays but it has only moderator poor resistance when exposed to UV radiation. Polyetheretherketone (PEEK) polymer is typically prepared by the reaction of difluorobenzophenone with the disodium salt of hydroquinone, which is conducted in-situ by deprotonating with sodium carbonate. The rigid benzene ring, flexible ether bone, and carbonyl group which can improve the intermolecular attraction, form the regular structure of PEEK. With higher strength than most metals, PEEK is suitable for wide range of commercial and industrial applications, especially for the aerospace industry, energy and electronic field. PEEK retains high wear resistance and low friction coefficient and bears continuous service temperature up to 250℃. The friction property can be further improved when PEEK is modified by reinforced and blended[.This paper introduce the research progress of friction property, tribological behavior of PEEK composites, reinforced by micrometer and nanometer particles, especially by carbon fiber(CF), and composites blended with other fillings.

The melt process ability is also enhanced due to the ether linkage and because of this reason it is possible to adopt the following manufacturing methods such as injection molding, compression molding and extrusion. PEEK and it’s composites are used for fabricating Bio medical components, subsea equipment, and valve components because of the excellent resistance against various chemicals and sea water. PEEK is also used for manufacturing high speed rotors, pistons, gears, O – rings, piston rings and valve plates.

1.1. PEEK – Carbon fiber composites

When exposed to the UV radiation, during the first 240 h the elastic modulus and hardness increased by 11.6% and 48% respectively and the improvement in properties has been attributed to chain scission and cross linking. After 1560 h the elastic modulus and hardness decreased by 38% and 61% respectively and this is attributed to the formation of micro holes and micro cracks and this is confirmed by SEM micrographs. It has been reported that by adopting thermal ageing treatment for the PEEK – Carbon fiber composite, the hardness increased by 10% and also the specific wear rate decreased by about 33%. Due to the thermal ageing treatment, crystallization occurred at the interface between carbon fiber and the PEEK matrix. The crystallized region improved the adhesion between the matrix and carbon fiber and due to this reason the wear resistance increased.

Dynamic mechanical analysis results indicated that the Tan d value of thermally aged samples were much less than that of the aged samples. An environmental friendly surface treatment method for carbon fibers has been developed by Martin A et al. and Pitch based carbon fibers have been used for this investigation. These authors reported that the crystallinity increased by 25% for the PEEK carbon fiber composite in comparison to the neat PEEK. The transverse tensile strength of the surface treated composite increased by 17%. The surface treatments on the carbon fibers play an important role in improving the inter laminar shear strength and flexural strength , these aspects were investigated by Lei Pan et al. The surface of the carbon fibers were modified by two different methods i.e., by treating with oxidizing chemicals (piranha and chromate solutions) and silicone based compatibilizers. By using Silikophen P 80, as a compatibilizer it is reported that about 27% increase in flexural strength and 37% increase in Inter laminar shear strength can be achieved in comparison to the PEEK composite reinforced with untreated carbon fiber. Commercial carbon fibers have sizing, a coating which is used to prevent the breakage of individual fibers and also improve the compatibility with the matrix. The chemicals used for sizing can be harmful to the human beings if Bio medical components are fabricated using carbon fibers having sizing. Yun- Hae Kim et al. carried out investigation regarding the effect of sizing removal by heat treatment at 300 C and 400 C on the mechanical properties of PEEK – carbon fiber composites. The authors reported that sizing removal that sizing removal did not affect the tensile strength, compressive strength and short beam strength. Three different ply orientations were used. The orientation resulted in the highest tensile, compressive and short beam strength values. An improved method of joining two different PEEK – Carbon fiber composite parts has been reported i.e., tape performs and or gano sheets were joined using a novel stamping method. It is reported that Inter laminar fracture toughness improved by 30% and this novel method can be used for manufacturing integral structures.

II. MATERIALS AND METHODS

2.1 Material

Commercially available PAN-based short carbon fibers (Toray T300) manufactured by Toray Industries Inc. have 4900 MPa tensile strength, 235 GPa tensile modulus with a density of 1.82 g/cm3, 7 μm average diameter, and 5 cm average length. PEEK powder was supplied by Jilin University, China, and has 343 °C of melting point, 143 °C glass transition temperature, and 1.32 g/cm3 density. There were two different high temperature resistance polymers coatings (polysiloxane-based) utilized for coating of short CFs.Methyl silicone resin (Silres K) was obtained from Wacker Chemicals (China) Co., and phenyl methyl polysiloxane resin (Silikopen P 80/MPA) was obtained from Evonik Degussa (China) Co., Ltd. Ethyl acetate, 30% hydrogen peroxide solution, sulfuric acid and potassium dichromate were supplied by Nanjing Chemical Reagent industry Co., Ltd in China. Chemical treatment Piranha solution was prepared by the direct addition of hydrogen peroxide into concentrated sulfuric acid while cooling in order to dissipate heat during reaction. H_2SO_4 þ H_2O_2 ! H_2SO_5 þ H_2O The equilibrium composition of the mixture depends on the concentrations and mole ratio of the reactants.[13] There was another possible reaction occurring during preparation of the piranha solution. H_2SO_4 þ H_2O_2 _! H_3Oþþ HSO_ 4 þ O Reaction produces highly reactive oxygen species and helps to dissolve elemental carbon. It is extremely difficult to attack on the carbon allotropes because of typically strong graphite-like hybridized bonds. Treating with piranha solution can disturb stable carbon–carbon surface bonds.
Polymer coating- Siloxane-based polymers (Silikophen P 80/MPA and Silres K) were used for the coating of CFs. Table 2 shows the formulations that were used for coating. Homogeneous solution was produced by appropriate stirring, and then, fibers were dipped into solution and pulled. Coated CFs were put into the oven to remove excess ethyl acetate. Temperatures were varied for different coating polymers because the recommended curing temperature of each polymer is not the same. During drying, formation of (–Si–O–Si–) film by crosslinking occurred on the surface of the CF. the mechanism of the coating can be seen in Figure 1. Coating amounts are determined by measuring CFs before and after coating. PEEK retains high wear resistance and low friction coefficient and bears continuous service temperature up to 250℃[18-19]. The friction property can be further improved when PEEK is modified by reinforced and blended[20-25].This paper introduce the research progress of friction property, tribological behavior of PEEK composites, reinforced by micrometer and nanometer particles, especially by carbon fiber(CF), and composites blended with other fillings. The tribological behaviors of PEEK/CF under sea water lubrication were comparatively investigated by Beibei Chen[29]. The results show that the CF greatly improve the friction and wear properties in sea water, because exposed CF shares the main load between the contact surfaces, better lubricating effect of sea water protecting the matrix from severe wear. PEEK – CNT composites
PEEK composites are used for fabricating air craft, space craft and satellite components and also can be used for shielding against electromagnetic interference. PEEK – CNT composite plates were etched using an environmental friendly method and then metalized by electro less plating method [10]. Ekataterial Pavelenkoet al. [11] reported that the addition of carbon nano tube did not affect the crystallinity of PEEK, however the failure strain decreased significantly from 28% for pure PEEK to 5% for PEEK –0.5% CNT composite.

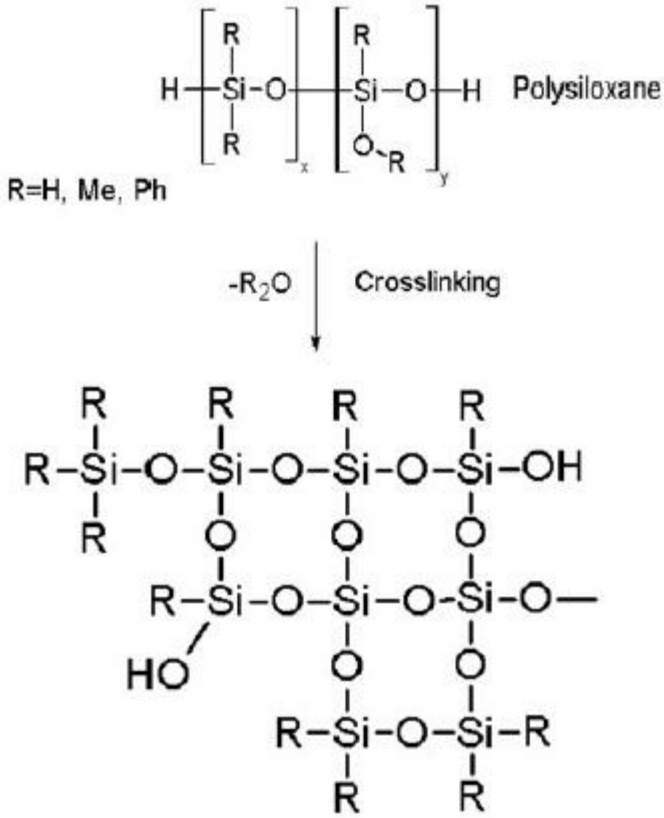

Fig 1. Common mechanism of coating with polysiloxane resin polymers

PEEK – Other reinforcements and hybrid composites Hamid Tournai [2] reported the effect of short carbon nano Fibers (SCF) and the nano Si O2 particles on the mechanical and biological properties. Nano indentation tests were carried out, PEEK with 20 vol% SCF, 2% nano Si O2 exhibited the highest elastic modulus Pa and a hardness of 0.7 G Pa. By adding the nano Si O2 the elastic modulus increased by 142% and the hardness by 700%. During the nano indentation studies for neat PEEK, the load – displacement curves were uniform for neat PEEK but for PEEK – carbon fiber composites these were inconsistent and addition of Nano ZrO2 particles to this composite increased the young's modulus and tensile strength [23]. PEEK – Nano diamond composite containing1–3% surface modified diamond has been evaluated [24] for various properties such as thermal conductivity, electrical conductivity and dielectric permittivity. Authors reported that sonication during the grafting of PPA improved the dispersion of nano diamond and the thermal conductivity increased by 38% in comparison to pure PEEK.

PEEK composites for tribological applications. The effect of addition of graphite to PEEK on mechanical and tribological properties has been investigated by Ying Shang et al. Composites were made with various sizes of graphite i.e., 10 lm,50 lm and 150 lm and the graphite content was also varied i.e.,2%, 5%, 10%, 15%, 20% and 30%, beyond 25% graphite there was no significant reduction in the co efficient of friction and wear rate.
By increasing the graphite content the co efficient of friction, wear rate, tensile strength, strain at failure and flexural strength decreased but the flexural modulus increased. For the composite containing 10 lm graphite particle the lowest co efficient of friction, wear rate and the highest, tensile strength, strain at failure flexural strength and flexural modulus were reported. Hybrid PEEK composites containing SCF, PTFE and grapheme were developed for the possible applications in harsh environment i.e., at 150. The presence of grapheme improved the thermal conductivity. Composites containing 10% short carbon fiber, 10%PTFE and 2% grapheme exhibited the lowest co efficient of friction and wear rate. Thermal conductivity of this composite was0.56 W/mK. Porous PEEK composite containing an ionic liquid 1- butyl – 3methylimida sodium tetra fluoridate were developed and evaluated for tribological properties [27]. This particular type of composite exhibited a very low co efficient of friction i.e., 0.035under a normal load of 200 N and a sliding speed of 1.4 m/s. The typical contact temperature for PEEK / PTFE /CF/IL, i.e., during ring on disc test was reported to be 150 C whereas for the PEEK/PTFE/CF composite it was 300 C. Another interesting aspect is that the wear loss occurred mostly during

the initial period of the test and the wear loss is negligible after this period. Juan Juan Zhu et al. [48] have evaluated various PEEK composite materials reinforced with carbon fiber, glass fiber containing PTFE as bearing bushes on a custom made wear testing rig. It was found that the following composite i.e., PEEK / 10% CF/ 10% Graphite /10%PTFE exhibited the best performance in terms of co-efficient of friction, wear loss and the lowest the rise in temperature on the contact surface and this particular material may be used for fabricating bushes. A composite film of PEEK – PTFE reinforced with nanoAl2O3 has been evaluated for the tribological performance by Banganet al. [28]. A ring on disc was carried out according to ASTMD3702-94 and it was found that wear rate and co efficient of friction of PTFE/10% PEEK / 5% Nano Al2O3 were the lowest in comparison to all the other compositions tested. The wear surface was relatively smooth for this composition compared to other compositions. In the case of composites with 3% Nano alumina scratched were deep and wide and in the case of 7% Nano alumina there were cavities on the surface.2.2. PEEK based materials as dental implants and bone substitute materials Various aspects related to PEEK dental implants has been reviewed by Andreas Schwitalla and Wolf – Dieter Muller [29]and the following important conclusions were made1. Titanium coating on PEEK improved osseo integration i.e., high degree of formation of bone cells2. Long term investigations of PEEK implants in vitro and in vivo are necessary3. Studies related stress distribution in the surrounding areas of implant are to be carried out PEEK based materials are used for bone implants because these materials have good bio compatibility and the mechanical properties are similar to those of bone but the bio activity of PEEK implants are very low. In order to improve the suitability of PEEK as a bone substitute PEEK –Nano calcium silicate composites were evaluated
Flexural test

A three-point bending test was performed to measure the flexural mechanical properties of the composites according to the process of ASTM D-790. Specimens (dimensions 80 × 6.5 × 3 mm) were tested at constant span at 16/1 at 10 mm/min crosshead speed and values were reported. The fracture surfaces of the samples were examined by SEM.

TABLE 2.1

Table 1
Effect of surface treatment on the reinforcement on the properties of the composite.

Type of Composite	Surface Modification	Effect	Result
MWCNT / PEEK	MWCNT functionalized with aminated poly ether sulfone (PES)/ethanolamine	Very good adherence between fiber and matrix	Increase in Tensile strength, Impact strength. Decrease in strain at failure and co efficient of friction – low specific wear rate
Graphene / PEEK	Thermally reduced graphene modified with PES	Homogeneous dispersion of graphene	Improved thermal and electrical conductivity
MWCNT/ PEEK	ethanolamine	CNT can be dispersed easily	-
PAN based carbon fiber/ PEEK	Silicone based coating, oxidative and non oxidative treatment	Improved adhesion of the fiber to the matrix	Increase in inter laminar shear strength and flexural strength
Nano diamond particle/ PEEK	Phenylphosphonate (PPA)	Sonication during grafting	Increase in thermal conductivity
Pitch based carbon fiber/ PEEK	Polyethleneimine	Environmentally friendly method	Increase in PEEK crystallinity at the interface

Table 2
PEEK composite manufacturing methods.

Type of composite	Method of manufacturing
MWCNT / PEEK	Melt blending
MWCNT / PEEK	Functionalization (PES)
	Sonication
	Compression moulding
MWCNT / PEEK	Polymer solution casting – solvent used – Dimethyl formamide
MWCNT / PEEK composite film	Polymer solution method composite film formed on a glass plate
Graphene / PEEK film	Sonication of powder dispersed in ethanol, evaporation of the solvent, doctor blade method
Graphene/ PEEK nano composite	Dry blending – injection moulding – machine with a novel screw design
Modified graphene oxide /PEEK	Ultrasonication of powder dispersed in ethanol – dried – melt blending using a twin extruder
Carbon fiber ply / PEEK	Vacuum bag process
MWCNT / PEEK	Melt blending using twin extruder
Nano diamond / PEEK	Mixing in a jar and melt blending in twin extruder
Carbon fiber / PEEK	Thermal aging
Glass fiber / PEEK	

III. CONCLUSION

Summary. The fine friction and wear resistance of CF counteract the thermal softening of PEEK and form strong protection transfer films, which lead to lower friction coefficient and specific wear rate of PEEK/CF compared with pure PEEK. The improvement of wear property of PEEK filled by CF is 5 times more than that of by GF. CF greatly improves the friction and wear properties in sea water because of better lubricating effect.

The stainless steel and CF increase the stability of the friction coefficients of the PEEK matrix. The transfer layer is formed on the worn surface. The interfacial adhesion between CF and PEEK matrix is effectively promoted after the CF were treated by ozone, cold oxygen and nitrogen plasma, which improved the wear resistance of PEEK/CF composites. The nanometer SiO2 treated SCF reduces the friction coefficient of PEEK/SCF/SiO2, and the wear rate increases strongly dependent on the temperature. The effect of fiber orientation closely related with the nominal pressure. Under most conditions, lower friction coefficients observed when the fibers were orientated at the anti-parallel rather than the parallel. The inclusion of PTFE reduces the friction resistance of PEEK-PTFE blends. The higher molecular PEEK has better wear resistance. The friction and wear performance are strongly dependent on the size and hardness.

The wear resistance of pressed PEEK membrane, filled with nanometer SiC, was ere greatly improved while wetting by distilled water and on dry slide. The PEEK composite filled with Si3N4, ZrO2, and Al2O3, show better tribological behavior than that of neat PEEK. The wear property of a new invented titanium-based whisker reinforced PEEK composite is 10 times more than that of PEEK/CF. the developed composite can be applied in special environment such as high temperature, vacuum, radiation and corrosion Suggestions. The PEEK, with regular structure composed of rigid benzene ring, flexible ether bone, and carbonyl group, has excellent thermal, mechanical, electrical properties. The remarkable strength, wear-resistance performance, and thermal properties of PEEK are suitable for wide range of commercial and industrial applications, especially for wear-resistance application to the aerospace industry and the extremely high temperature demanding environment. Reviewing the literatures, the effect of the following factors and conditions on the friction properties, wear resistance, and mechanism of PEEK composites deserved to be further researched: Corrosive influence of PEEK composites by sea water, chemicals, etc.; Properties of PEEK composites under different temperature, humidity, pressure; Behavior of PEEK composites under severe environment such as high-altitude radiation; Properties of PEEK composites modified by different nanometer particles, whiskers; Compatibilities between reinforcement materials and PEEK; Modification of PEEK composites made from different mediums and techniques etc.

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