Research Article

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Biological tribology properties of the modified polyether ether ketone composite materials

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Abstract: Modification of poly-ether-ether-ketone (PEEK) to adapt to the biological properties of materials is currently the key point in the research of medical materials. The tribological properties and biocompatibility of the PEEK composites modified by carbon fiber (CF), potassium titanate whisker (PTW) and nano-particles were discussed in this paper. The results show the modified PEEK composites by a certain length to diameter ratio of CF show the best using effect in vivo experiments in good blood compatibility, which is suitable for orthopaedic implant materials. A large number of experiments show that the PEEK composites would be modified with a certain ratio of CF (about 30%wt.), whisker (about 15%wt.) and HA (about 5%wt.) particle with better biological tribological properties, more important value in medical research.

Keywords: modified PEEK composites, biological tribology properties, carbon fiber

1 Introduction

Although the traditional biomedical titanium alloy has good tribological properties and compatibility in vivo circumstances, there were some obvious problems such as insufficient strength and rigidity, and the wear debris side effects in applications [1–7]. In the development of bone repair biomaterials, poly-ether-ether-ketone (PEEK) modified reinforced composites have been developed by leaps and bounds [5, 6]. PEEK is a new type of semi-crystalline thermoplastic polymer, which has the advantages of elastic modulus closing to cortical bone, good biocompatibility,

constant physical and chemical properties and mechanical properties, and no artifacts in magnetic resonance imaging (MRI) scanning. It is considered as an ideal biological implant material [8–11], with the better protein synthesis of osteoblasts, and no obvious cytotoxic effect. For the implantation of heterogeneous materials in vivo, it is necessary to reduce the wear resistance of implant materials. One of the ways to reduce the wear rate of materials is to promote the formation of effective transferring film, so that the relative sliding is carried out between the implant and the friction surface to effectively improve the in vivo adaptability [12–15]. The characteristics comparison of PEEK material with other biomaterials is as shown in Table 1. The application of PEEK composites materials is relatively in a wide range. All kinds of orthopedic implants made with PEEK in clinic, and the prepared CF reinforced composites that have been implanted in vivo experiments show that, the CF composite materials with a certain length diameter ratio have the best fusion effect with body fluid and cortex, and a good blood compatibility in vivo [12]. In view of the development of implantology and the growing demand for new biomaterials, increasing biocompatibility and improving osseointegration are becoming the primary goals of PEEK surface modifications. Flejszar and Chmielarz [16] summarized the use of polymerization methods and various monomers applied for surface modification of PEEK to increase its bioactivity, which is a critical factor for successful applications of biomedical materials. In order to further improve the biological adaptability and physical and chemical properties of bionic bone repair PEEK composite material, and expand the research scope of medical materials, the authors make a comparative analysis of the biological tribological properties of PEEK composite materials modified and reinforced by CF, potassium titanate whisker and hydroxyapatite particles, with the better reinforcement effect and clinical effect in recent years. The results show that a certain ratio of CF, PTW and HA particle reinforced PEEK composite represents a suitable orthopedic implant material.

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Table 1: Characteristics of biomaterials

Material	Advantages	Disadvantages	Application
Stainless steel	Very strong Very stiff	Corrosion Relatively poor biocompatibility	Scoliosis correction (rods) Formerly used in screws; now mostly replaced by titanium
Titanium	Easily doped/alloyed to be stronger Inexpensive Lightweight Strong Flexible Biocompatible Easily doped/alloyed to be stronger	High artifacts in imaging Relatively Expensive Some artifacts during imaging	Screws Rods Plates Cages
PEEK	Lightweight Flexible Relatively Inexpensive	Low Young's modulus Some grafting issues, but improved with coatings	Rods Cages Disc replacement Spine femur
CoCr	Biocompatible Easily doped/coated for improved grafting Low artifacts on imaging Strong	Relatively expensive	Adolescent scoliosis correction (rods) to provide a more flexible buttress for the spine to curve about.
Ceramic	Flexible Biocompatible Relatively inexpensive Biocompatible	High artifacts on imaging Brittle Grafting issues, but can be improved with coating/doping	Used in cage biomaterials Doped with A/W
Nitinol	Ware resistant Easily doped Strong	Relatively expensive	Not frequently used, but can be implemented for young scoliosis correctional surgery.
	“Memory metal” (shape recovery)	Sometimes not stiff enough for proper correction	

PEEK, polyetheretherketone; CoCr, cobalt-chromium alloys; A/W, Apatite-Wollastonite

2 Modification to Enhance the Tribological Properties of PEEK

2.1 PEEK Composite Reinforced with CF

Many scholars have studied the biological tribological properties of CF reinforced PEEK composites [17, 18]. The results of literatures [19–27] show that the lower friction and wear properties of CF, graphite and polytetrafluoroethylene reinforced PEEK composite have little relationship with the increase of the CF content under water lubrication. The wear mechanism mainly presented the fatigue wear characteristics under the lower load, and mainly presented the micro cutting wear characteristics under the higher load [19]. Monich *et al.* [21] discussed the influ-

ence of sliding speed and contact pressure on the friction and wear of zirconia ceramics and CF reinforced PEEK (CFR/PEEK) matching materials under water lubrication. The experiments results show that the friction coefficient decreased with the increase of speed, and there was a running in process when the speed was low, but obscure relationships between the speed with the friction coefficient and the wear rate. The pressure affects obviously on the friction coefficient and the wear rate. The wear failure is mainly due to the adhesive wear caused by high temperature of friction [21].

The analysis software was used to simulate the influence of surface roughness, sliding speed, contact stress and other parameters of friction pair (stainless steel) on the tribological properties of PEEK composite with CF enhanced according to the movement of hip joint during

walking [22, 23]. The results show that the surface roughness of the friction pair was the most important factor affecting on the tribological properties of the composites. The friction coefficient and wear rate of PEEK/CF composite were lower than that of the smooth surface of the two pair slides. When the composites were used as joint cup and various joint head matching materials, the tribological experiments results show that the wear rate of 20% and 30% PAN in PEEK/CF composite was one order of magnitude lower than that of UHMWPE, while pure PEEK was 9 times higher than that of UHMWPE. With the increase of CF content, the wear rate of PEEK composite decreased sharply. The wear rate of 30% PAN reinforced with CF or resin PEEK composite with Co-Cr is much higher than that with Al_2O_3 or Zr_2O_3 . Compared with Al_2O_3 or Zr_2O_3 ceramics, the wear rate of PAN-PEEK composite reinforced with CF is higher than that of resin-PEEK composite reinforced with CF. The wear rate of PEEK composite reinforced with CF to Zr_2O_3 ceramic was the lowest [22–26]. The literatures results show that the volume wear rate of PEEK/CF composite is 1/50 and 1/20 of Ti and Co-Cr-Mo respectively [20, 26], which is 1/2 of UHMWPE, and the interface bonding strength of PEEK/CF bone is obviously better than that of traditional artificial joint materials. Histological images show that there was a good biological fixation between the PEEK/CF composites with the bone. Rahmizadeh *et al.* [18], Scholes and Unsworth [26], and Schwitala *et al.* [27] used PEEK/CF composite as the acetabulum cup and alumina ceramic as the joint head to simulate the friction and wear experiment of hip joint by the measured and calculated volume friction rate. The experimental results show that the volume wear rate of PEEK/CF composite was lower, the wear surface of PEEK/CF composite and ceramic was smooth the wear marks were small, and the CF was well combined in the matrix without fiber extraction under the lubricant condition. There were deep and wide wear marks in the wear surface of UHMWPE with a lot of wear debris. Many experiments show that PEEK/CF composite is superior to UHMWPE in friction and wear resistance, and the interface bonding strength between resin matrix and CF is much higher than that between resin matrix and UHMWPE. Overall, the mechanical properties of compared biomaterials was shown in Figure 1, we can find that the result of Young's modulus of PEEK is according with cancellous bone. Therefore, PEEK/CF composite is widely used in medicine, which will further improve the medical value of PEEK composite.

Pace *et al.* [28] analyzed the technique and histology properties of PEEK/CF composite as the acetabulum cup and alumina ceramic as the femoral head implanted into the human body 28 months after total hip replacement,

Figure 1: Young's modulus of common biomaterials

and discussed the clinical application of PEEK/CF composite as the hip joint material. The investigation results show that the maximum wear depth of PEEK/CF pad was 0.130 mm (0.057 mm/y), and only a small amount of PEEK/CF wear particles entered the tissues around the prosthesis of patients after 28 months. All these research prove that the PEEK materials have a good wear resistance and biocompatibility with human body under the condition of humoral environment, and it is more suitable for making artificial joints than other polymer, metal and ceramic materials.

2.2 PEEK Composite Reinforced with Whisker

The addition of the whiskers can reinforce the modified polymer rigidity, toughness, wear resistance, corrosion resistance and other properties of the products, and reduce the cost of materials. The mechanical and tribological properties of PEEK/CF/PTW composite prepared by melt blending have been investigated in water lubrication conditions [29–32]. Experimental results show that the hybrid reinforced composite has good mechanical properties. Under the condition of water lubrication, the friction coefficient has no obvious change while the specific wear rate decreases with the external force increase. The main wear mechanism of the material in water lubrication conditions is approximate to slight abrasive wear. The addition of whiskers can reduce the stress concentration on the interface between CF and matrix, and effectively restrain the damage of CF during the friction process. The

Figure 2: Comparison of contact area and contact pressure of CFR/PEEK, PEEK and UHMWPE

Figure 3: Effects of whisker content on tribological properties of composites

PEEK composite reinforced with the constitution of CF and whiskers has more excellent wear resistance than single fiber reinforcement. The experimental results show that the PEEK/PTW/CF composite had strong load resistance, the carrying capacity of CF in the composite can resist the external forces, and the specific wear rate of the composite was low under the water lubrication condition [30]. These results proved that the tribological properties of PEEK composite were improved and the synergistic reaction of the dispersed PTW and CF can protect and reduce the wear degree of matrix PEEK. Boudeau *et al.* [31] also proved that the PEEK/CF composite has a good biocompatibility compared with traditional metal bone as implant materials. It can be inferred that the synergistic effect of whisker and CF improved the mechanical properties of PEEK composite, reduced the contact stress at the contact interface and the wear rate of the composite, and improved the tribological properties of the composite. The contact pressure of PEEK/CFR composite compared with pure PEEK and

UHMWPE is shown in Figure 2. We can find that the contact area of CFR/PEEK is relatively large than others with its contact pressure. The author studied the tribological properties of CaCO_3 whisker reinforced PEEK composites. The results of Figure 3 show that the variation of friction coefficient and specific wear rate of PEEK/ CaCO_3 composite with whisker content under normal saline lubrication, load of 20 kg and rotating speed of 200 r/min. As can be seen from the figure, when the content of CaCO_3 whisker added to the composite material is less than 15% under the lubrication condition of normal saline, the friction coefficient of PEEK composite material decreases continuously and the specific wear rate decreases gradually with the increase of the content of whisker. When the content of whisker is 15%, the friction coefficient of the composite material reaches the lowest value of 0.231, and the specific wear rate is only 27.5% of pure PEEK. When the whisker content exceeds 15%, the friction coefficient and the specific wear rate increase with the increase of whisker content. This shows that the addition of a certain amount of CaCO_3 whiskers can significantly improve the wear resistance of PEEK composites.

2.3 PEEK Composite modified with Nano-Particles

Hydroxyapatite (HA) is the main inorganic component in human bone with a good biological activity and biocompatibility [18, 20]. The addition of HA into PEEK can improve the elastic modulus of PEEK, and the mechanical properties of the composite should be modified with other substances to meet the mechanical requirements of replacing the inheritance forcing bones. Bonnheim *et al.* [32] discussed the mechanical properties and biocompatibility of the PEEK/CF/HA composite in vivo circumstances.

The experimental results proved that the surface modification of CF can improve the mechanical strength of the PEEK/CF/HA composite with the better physical and mechanical properties. And the friction fusion of the modified PEEK composite had a better biocompatibility in vivo circumstance.

The hardness, wettability and crystallinity properties of PEEK composite modified with proper amount of nanoparticles by molding method were improved [33–39]. The effects of different types of nano-particles, particle size, friction pairs and lubrication conditions of distilled water, normal saline and calf serum on the friction and wear properties of PEEK composites as artificial joint materials were investigated in the literature [36]. The experimental results show that the friction coefficient of PEEK was reduced, and its wear resistance was improved by the reinforced of nano- Al_2O_3 . With Si_3N_4 ceramic ring as friction pair, the wear rate of PEEK composite filled with nano- $\alpha\text{Al}_2\text{O}_3$ was 63%, 88% and 50% lower than that of pure PEEK under the lubrication of distilled water, normal saline and calf serum. The friction coefficient of PEEK with CoCrMo was 70% lower than that of pure PEEK under distilled water lubrication. Among the three-lubricating media, the distilled water has the best effect on reducing the friction coefficient, while serum lubrication can significantly improve the wear resistance of the composite. Under the same conditions, the wear resistance of PEEK composite with Si_3N_4 ceramic matching pair was 9 times higher than that of CoCrMo alloy ring matching pair at most. The results show that the wear resistance of PEEK/ Al_2O_3 (5%wt.) composite with Si_3N_4 ceramic ring is the best, and the wear rate is $0.72 \times 10^{-6} \text{ mm}^3 (\text{n}\cdot\text{m})^{-1}$. There were almost no spots formed by adhesion and ploughing on the worn surface, only micro cutting traces, mainly slight abrasive wear. The tribological properties of PEEK/CF/ ZrO_2 prepared by melt blending in water lubrication conditions were discussed by literatures [38, 39]. The experimental results proved the addition of ZrO_2 particles can effectively inhibit the damage and fall off of CF during the friction process. However, too many particles will aggravate the fatigue wear and reduce the wear resistance of the material.

3 Conclusion

As an important orthopedic implant material, PEEK and its composites have been expected to be widely used in spine, joints, trauma and tissue engineering scaffolds and other fields. The bioactivity, mechanical properties, porous capillary and biocompatibility of PEEK and its composites are

constantly improved. Compared with the tribological properties of the above-mentioned modified and reinforced PEEK composites, the PEEK composite reinforced with the constitution of CF (about 30%), whiskers (about 15%) and HA particles (about 5%) has more excellent wear resistance than single phase reinforcement. As the addition of whiskers can protect the wear degree of the matrix PEEK, and improve the tribological properties of PEEK composites, and the introduction of hydroxyapatite (HA) particles can significantly improve the bioactivity and biocompatibility of the composite. The PEEK/CF/whiskers/HA composite can meet the requirements of replacing the traditional titanium alloy to make internal fixation apparatus. If we combine the three factors and control the proportion of the modified materials, the current bio-tribological properties of PEEK composite will be effectively improved in the medical application.

Conflict of Interests: The authors declare that they have no conflicts of interest.

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