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RESEARCH ARTICLE

Influence of molecular weight of modified ultrahigh-molecular-weight polyethylene with Cu(II) chelate of bissalicylaldehyde-ethylenediamine on wear-resistant materials

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Abstract: Reciprocating friction and wear performances of pure ultrahigh-molecular-weight polyethylenes (UHMWPEs) with molecular weights (MWs) of 2, 3, 5, and 9 million and their modified UHMWPEs with 15 wt.% Cu(II) chelate of bissalicylaldehyde-ethylenediamine (add1) against titanium alloy (Ti6Al4V) were investigated under boundary lubrication with 25 vol.% calf serum deionized water solution. Differential scanning calorimetry (DSC) of purchased UHMWPE powders was performed. The enthalpy changed with an increase in MW. UH300 had the lowest temperature of an extrapolated peak and the best peak symmetry in DSC analysis. The friction coefficient curves of molded pure and modified UHMWPEs/Ti6Al4V were compared, and the volume loss by the wear of polymers was measured. 3D topographies of the worn surfaces of polymers and images of the worn surfaces of polymers and titanium alloy against polymers were analyzed by confocal white light microscopy and scanning electron microscopy, respectively. Results showed that the influence of MW of UHMWPE was obvious on the friction and wear characteristics of pure UHMWPEs and 15% add1 UHMWPEs. An MW of 3 million was the best to reduce the friction of rubbing pairs, enhance the wear resistance of pure UHMWPEs and 15% add1-UHMWPEs, and improve the mating properties of Ti6Al4V.

Keywords: ultrahigh-molecular-weight polyethylene; reciprocating friction and wear; boundary lubrication; molecular weight; Cu(II) chelate of bissalicylaldehyde-ethylenediamine

1 Introduction

Ultrahigh-molecular-weight polyethylene (UHMWPE) exhibits excellent performance because its molecular weight (MW) is more than 1 million [1]. Changes in its MW may affect its physical chemistry, mechanical properties, and tribological performance. The wear resistance of UHMWPE does not change with an increase in MW as it reaches the point of transition [2]. The MW of UHMWPE is not a decisive factor of wear performance, but it influences the erosion behavior of UHMWPE. Brach-Prever et al. [3] discussed "historical" issues such as oxidation, sterilization, and storage associated with UHMWPE ($MW = 2 \times 10^6$) for arthroplasty as well as "new" topics such as crosslinking and stabilization. Wu et al. [4] found that the friction coefficient of a UHMWPE sample ($MW = 3.3 \times 10^6$) significantly depends on load and sliding speed. The wear of polyethylene (PE) causes the loosening of joint prostheses because of the particle-mediated activity of the host tissue. Particle suspensions of six PE materials (crosslinked and conventional UHMWPEs with $MW = 3 \times 10^6 - 4 \times 10^6$ and $5 \times 10^6 - 6 \times 10^6$, respectively) were injected into the knee joints of Balb/c mice. After 1 week, intravital microscopic, histological, and immunohistochemical evaluations were conducted in this study; the data of this study support the use of crosslinked PE in total knee arthroplasty [5]. To enhance creep resistance, high crystallinity appeared

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to be more critical than a high degree of crosslinking when UHMWPE samples (MW = 5 × 10^6) were prepared by gamma irradiation and post-irradiation annealing at a low temperature [6]. In the present study, UHMWPE tibial inserts were made suitable for femoral components and tibial tray by enlarging the designed size by 10.5% in the X and Y directions and 6.5% in the Z direction. This study demonstrated that the new manufacturing capabilities for UHMWPE (MW = 7 × 10^6) tibial insert will be developed further [7]. Studies on the relationship between four different molecular weights (MWs) and tribological performance under similar conditions are rare.

A Schiff base is an organic compound with imine groups, and it is usually synthesized by the condensation of an amine and a carbonyl compound [8]. Schiff base copper complex compounds have good thermal stability with decomposition temperatures above 200 °C, and they are biologically active materials that exhibit anti-tumor, antiviral, and antibacterial properties [9]. Hence, such compounds have been used in the field of tribology, typically as nano-Schiff base copper complexes for the formation of self-assembled monolayers on mechanical mating pairs to improve tribological behavior [10]. The present study investigated the relationship between the physical characteristics and tribological performance of UHMWPE of different MWs modified with 15 wt.% Cu(II) chelate of bissalicylaldehyde-ethylenediamine (add1). This chelate is a Schiff base copper complex with special tribological characteristics and wear resistance. This study will allow the development of wear-resistant materials of modified UHMWPE for engineering applications.

2 Methods

2.1 Differential scanning calorimetry test

Code names, nominal MWs, particle diameters, manufacturers, and models of the purchased UHMWPE powders for tests are listed in Table 1. For the differential scanning calorimetry (DSC) of UHMWPE powders, a DSC 822e thermal analyzer by METTLER TOLEDO Corporation was used.

Table 1 UHMWPE powders for tests.

Code name	Nominal MW	Particle diameter (μm)	Manufacturer	Model
UH200	2 × 10^6	100–200	China Beijing No.2 Additives Factory	M II
UH300	3 × 10^6	100–200	China Beijing Eastern Petrochemical Co., Ltd	MIII
UH500	5 × 10^6	100–200	America TICONA	GUR®
UH900	9 × 10^6	100–200	America TICONA	GUR®

2.2 Preparation of specimens and lubricant

The Cu(II) chelate of add1 is a kind of Schiff base copper complex used as an additive for modifying UHMWPE. Methods for preparing and molding pure UHMWPE and modified UHMWPE with 15 wt.% add1 were conducted as previously described [11]. First, 85 wt.% UHMWPE powder was evenly mixed with 15 wt.% Cu(II) chelate of add1 and silane coupling agent, WD-60. The well-blended mixtures were fed into a blinded hollow cylindrical mold that was coated with silicon oil mold release agent on the inner surface of the mold cavity and mounted on a 45-ton compressive molding machine. Both the female and male mold halves were then successively closed and opened three times under a pressure equal to 45% of the molding pressure. The mold was then closed. It was heated and maintained at 195 °C for 90 min. The mold was subsequently compacted by 45-MPa molding pressure for at least 40 min, cooled naturally to room temperature, and removed. Molded pure UHMWPE and modified UHMWPE were machined into polymer rings as the upper specimens, which had an outer diameter and thickness of Φ 30 mm × 6 mm. The specimens were machined with a surface roughness of Ra = 1.6 μm. Titanium alloy (Ti6Al4V) was machined into a disc as the lower specimen and had a diameter and thickness of Φ 50 mm × 6 mm. The two titanium head faces were polished to a surface roughness of Ra = 0.06 ± 0.005 μm. Each specimen was carefully rinsed and washed for 5 min in an acetone bath. A deionized water solution with 25 vol.% calf serum was prepared according to ISO 14242-1:2002.

2.3 Method of reciprocating sliding friction and wear tests

Tribological performances of the modified UHMWPE/Ti6Al4V pairs were tested with a reciprocating tribometer (manufactured by Wuhan Research Institute of Material Protection) [12] for comparison with that of the pure UHMWPE/Ti6Al4V pair. The contact between the polymer ring outside the circumference and the titanium alloy disc head face exhibited a line surface mode with a contact length of 6 mm. The lower specimen was mobile and moved with a slide at a reciprocating frequency of 1 Hz and a stroke of ±5 mm, resulting in an average sliding velocity of 0.02 m/s. The upper specimen (polymers) was motionless and fixed on a platform by a securing nut. The test environment was controlled to maintain a temperature of 37 °C and a relative humidity of about 80%. The tests were carried out under conditions of boundary lubrication with 0.2 mL of deionized water solution with 25 vol.% calf serum and a normal load of 50 N.

The method for measuring volume loss of wear of the upper specimen was described previously [6]. Worn surface topographies were observed with a JSM26300 scanning electron microscope (SEM), whereas 3D topographies of the worn surfaces were observed with a Micromeasure 2 confocal white light microscope (CWLM).

3 Results and discussion

3.1 DSC analysis of UHMWPE

UHMWPE in melting state is a viscoelastic medium such as rubber with high viscosity and poor flowability. Enthalpy is a melting peak of a polymer corresponding to heat release of solidifying reaction. Lee and Lee [13] showed that the enthalpy and MW of a polymer usually demonstrate a negative exponential relationship. Onset temperature represents the initial temperature of melting reaction, peak temperature is the temperature at which heat absorption/release reaches peaks, and endset temperature suggests an end of the melting reaction. Table 2 shows that the enthalpy changed and the peak width increased with the increase in MW. The temperature of extrapolated peak was the melting point of UHMWPE, and the smallest value was obtained by UH300 at 140.11 °C. A similar relationship was found between the peak temperature and MW. Ratios of left area to right area of UH200, UH300, UH500, and UH900 were 1.97/1, 1.43/1, 2.53/1, and 2.07/1, respectively. Thus, the peak symmetry of UH300 was the best as UH300 had the smallest ratio.

Table 2 DSC parameters of UHMWPE powders with 4 different molecular weight.

Data	Nominal molecular weight			
	2 million	3 million	5 million	9 million
Normalized enthalpy (J·g^{-1})	–455.70	–412.91	–391.84	–389.45
Onset (°C)	132.02	132.17	129.11	129.08
Peak height (mW)	36.52	52.01	34.62	49.45
Peak (°C)	140.88	139.69	140.36	140.96
Extrapolated peak (°C)	141.24	140.11	141.03	141.62
Endset (°C)	146.79	147.67	146.02	148.44
Peak width (°C)	8.35	8.92	10.28	11.50
Left limit (°C)	117.55	117.45	115.49	117.64
Right limit (°C)	151.07	152.12	151.87	154.60
Left area (%)	66.38	58.91	71.67	67.38
Right area (%)	33.62	41.09	28.33	32.62
Heating rate (°C·min^{-1})	10.00	10.00	10.00	10.00
Baseline type	Line	Line	Line	Line

3.2 Analysis of friction coefficient

Reciprocating friction and wear tests were carried out to investigate the influence of UHMWPE's MW on the tribological behavior of pure UHMWPE/Ti6Al4V and 15% add1-UHMWPE/Ti6Al4V under the condition of boundary lubrication with 25 vol.% calf serum deionized water solution. Figure 1 describes the friction coefficient–time curves, including eight rubbing pairs, which were (i) pure UHMWPE against Ti6Al4V and (ii) modified UHMWPE against Ti6Al4V with different MWs. Their code names were UH200, UH300, UH500, UH900, UH200+15% add1, UH300+15% add1, UH500+15% add1, and UH900+15% add1.

Figure 1 shows that the minimum friction coefficient of UH300 was the smallest among the four pure UHMWPE/Ti6Al4V at 0.065. Those of UH500 and UH900 were 0.074 and 0.072, respectively. The minimum

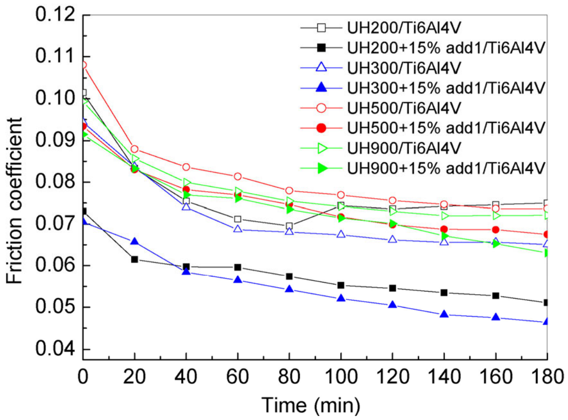


Fig. 1 Comparison of friction coefficient as a function of running time of UHMWPE and modified UHMWPE with different molecular weight.

friction coefficient of modified UHMWPE/Ti6Al4V was obviously much lower than that of pure UHMWPE/Ti6Al4V. The minimum friction coefficient of UH300+15% add1 was the smallest at 0.046, followed by that of UH200+15% add1 (0.051), UH900+15% add1 (0.068), and UH500+15% add1 (0.063). Moreover, the friction coefficient curves of the four modified UHMWPE/Ti6Al4V were lower than those of four corresponding pure UHMWPE/Ti6Al4V over the complete test duration. The minimum friction coefficient of UH300+15% add1 was the lowest among them, which almost reduced by 29% compared with that of UH300.

3.3 Topographies of worn surfaces of polymer upper specimens

After reciprocating friction and wear tests, the 3D CWLM images, microlocation SEM images, and profiles (X=0 section) of worn surfaces of pure and modified UHMWPE are shown in Fig. 2.

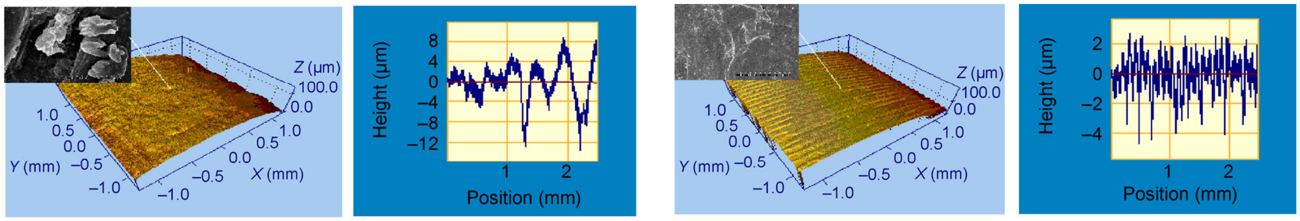
CWLM images showed that the worn surface of the pure UH200 surface appeared with numerous pits because of spalling of wear debris, and its surface was completely disfeatured. By contrast, the surface of UH200+15% add1 exhibited a nearly homogenous original machined texture with minimal abrasion topography. The wear of UH300 was not serious, but a few small pits formed from dislodged small debris. The surface of UH300+15% add1 exhibited only minimal abrasion topography. The wear of UH500 was very serious with many grooves and debris. The wear of UH500+15% add1 was lighter than that of UH500, but a deep furrow and a small amount of wear debris were still observed. The worn surface of UH900 was blurred by the adherence effect, and many pits formed by debris shedding; its wear was also very serious. The wear of UH900+15% add1 was minimal, and only some small pits were noted.

The attached SEM images showing the microlocation of worn surfaces, which were at the left upper corner of CWLM images, illustrated the following: (i) some furrows and tiny shorn off fragments were scattered in the microlocation of UH300, but only some slight friction scratches appeared in the microlocation of UH300+15% add1; (ii) many chippings to be pulled from furrows and cavities were observed, and the wear debris on the microlocation of UH500 suggested the occurrence of severe wear; (iii) the comparatively smaller cavities and lesser amount of wear debris on the microlocation of UH500+15% add1 obviously implied its mild wear compared with UH500; and (iv) some debris and a pothole were found in UH900, and no debris but some parallel strip friction scratches were observed in UH900+15% add1.

The profiles of worn surfaces of the upper specimens of UH300, UH500, UH900, UH300+15% add1, UH500+15% add1, and UH900+15% add1 are also shown in Fig. 2. The profile along the $X = 0$ section allowed the depth of scratch across the reciprocating slid path. The profile curve from the worn surface of UH200 in Fig. 2(a) slightly fluctuated, whereas that of UH200+15% add1 shown in Fig. 2(b) became less fluctuant with a maximum pit depth of −4.8 μm and a maximum bulge height of 2.8 μm. The profile curves from the worn surface of UH300 and UH300+ 15% in Figs. 2(c) and 2(d) also showed less fluctuations. Those of UH500 and UH500+15% add1 in Figs. 2(e) and 2(f) were rather fluctuant, but those of UH900 and UH900+ 15% add1 in Figs. 2(g) and 2(h) largely fluctuated with maximum pit depths of −116 and −130 μm, respectively, and maximum bulge heights of 108 and 22 μm, respectively.

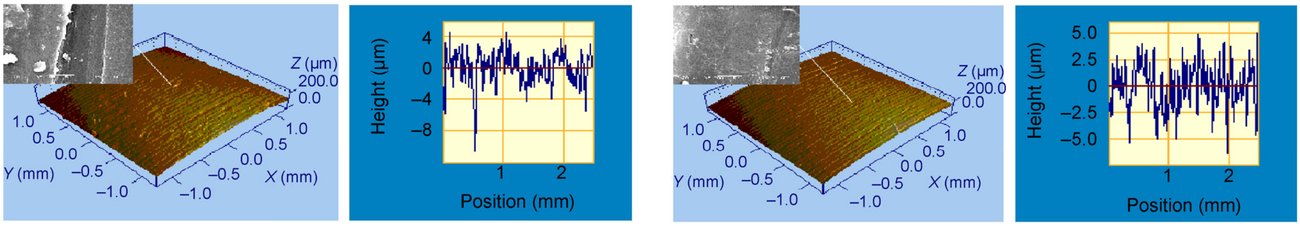
3.4 Volume loss of wear of pure and modified UHMWPE

Volume loss of wear of pure and modified UHMWPE is shown in Fig. 3. The results suggested that the



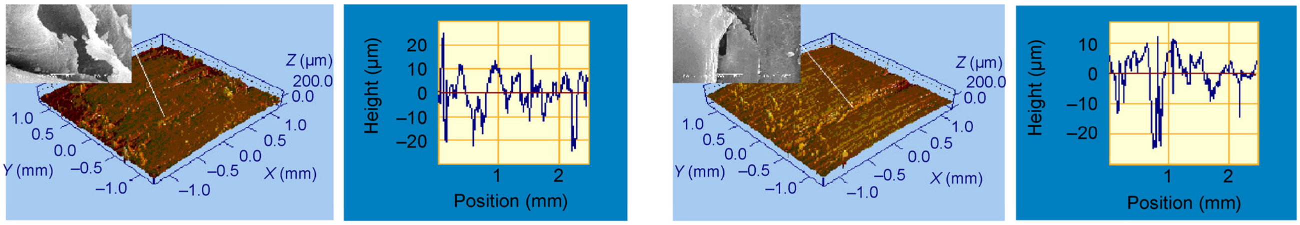
(a) UH200

(b) UH200+15% add1



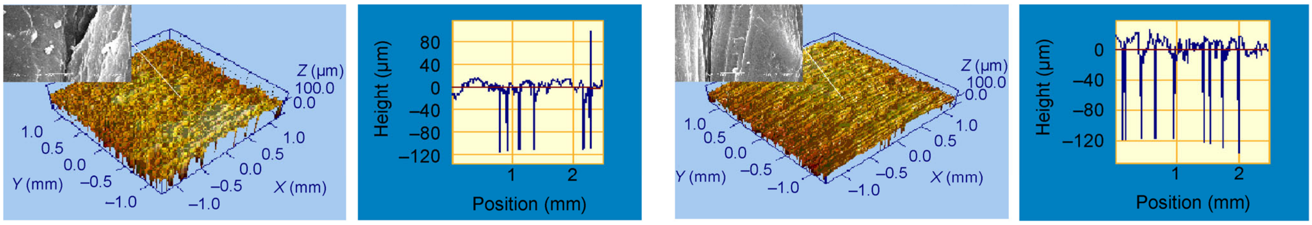
(c) UH300

(d) UH300+15% add1



(e) UH500

(f) UH500+15% add1



(g) UH900

(h) UH900+15% add1

Fig. 2 3-D CWLM images, their micro-location SEM images and profiles (X = 0 section) of worn surfaces of pure and modified UHMWPE.

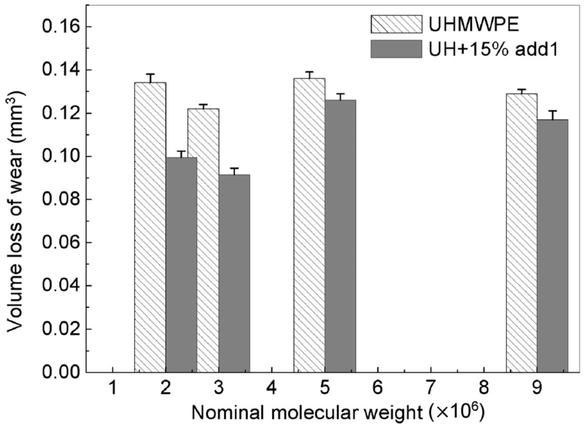
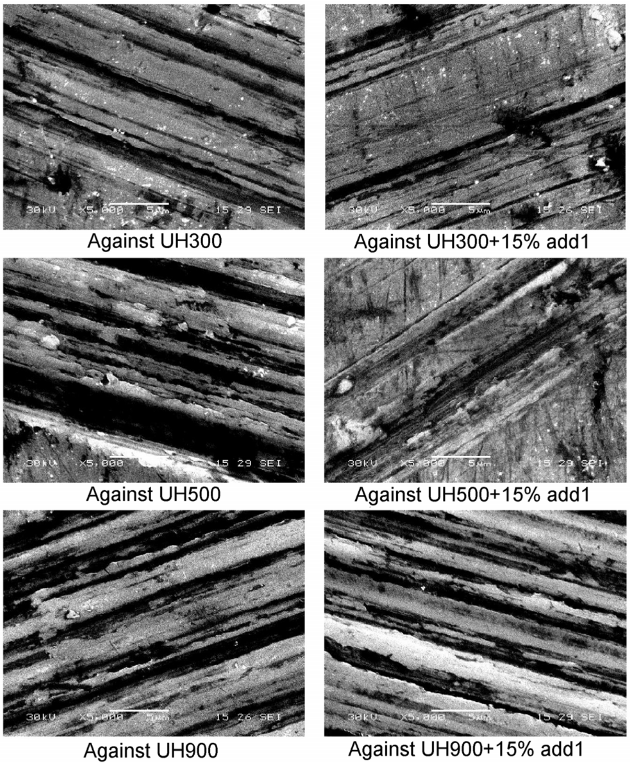


Fig. 3 Volume loss of wear varied with molecular weight of UHMWPE.

volume loss of wear varied with the MW of UHMWPE. The volume loss of wear of modified UHMWPE was lower than that of corresponding pure UHMWPE, and that of UH300 +15% add1 was the least at only 75% of UH300 and reduced by 8% of UH200+15% add1.

3.5 Topographies of the worn surface of titanium alloy lower specimens

SEM images of the worn surfaces of Ti6Al4V against UHMWPE and modified UHMWPE with different MWs are shown in Fig. 4. Comparison of these images with the SEM images of worn surfaces of Ti6Al4V against UH200 and UH200+15% add1 [8] showed: (i) deep and dense parallel furrows with many small debris on the worn surfaces of Ti6Al4V against UH300 but shallow and smooth furrows on the worn surfaces of Ti6Al4V against UH300+15% add1, (ii) the appearance of deeper and dense parallel furrows with



Against UH300
Against UH300+15% add1
Against UH500
Against UH500+15% add1
Against UH900
Against UH900+15% add1

Fig. 4 SEM images of the worn surfaces of Ti6Al4V.

many large debris on the worn surfaces of Ti6Al4V against UH500 but a decrease in furrow density and a few large debris on the worn surfaces of Ti6Al4V against UH500+15% add1, (iii) similar topographies on the worn surfaces of Ti6Al4V against UH900 and UH900+15% add1 to those of Ti6Al4V against UH500 and UH500+15% add1, and (iv) the lightest wear of the surface of Ti6Al4V against UH300+15% add1.

3.6 Wear mechanism analysis

UH300 had the lowest temperature of extrapolated peak and the best peak symmetry in DSC analysis. Simultaneously, UH300 showed the best tribological performance. The low temperature of extrapolated peak and high peak symmetry of DSC suggested good tribological performance of UHMWPE.

Abrasive materials were aggregated by numerous wear debris because of the local rising temperature and friction chemical reaction during repeated friction and wear. Thus, the friction and wear of friction pairs, including pure and modified UHMWPE/Ti6Al4V, were mainly controlled by a three-body abrasive wear mechanism.

Groups constantly transferred from the lubricant calf serum to the worn surface because the contact between the friction surface and air was cut off when a deionized water solution with 25 vol.% calf serum was added between the two contact surfaces of the friction pair. The service life of synovial fluid was cut down, and invalidation was accelerated as the main composition of calf serum changed. The tribological performances of modified UHMWPE with 15 wt.% Cu(II) chelate of add1 were obviously better than those of corresponding pure UHMWPE. Sufficient Cu(II) chelate of add1 may restrain the migration of groups from the lubricant calf serum to the worn surface and reduce friction and wear.

4 Summary

The reciprocating friction and wear performances of pure UHMWPE (MWs = 2, 3, 5, and 9 million) and modified UHMWPE with 15 wt.% Cu(II) chelate of add1 against Ti6Al4V, with 25 vol.% calf serum deionized water solution under boundary lubrication, revealed the following conclusions.

(a) The enthalpy changed with the increase in MW. UH300 had the lowest temperature of extrapolated peak and the best peak symmetry in DSC analysis. Low temperature of extrapolated peak and high peak symmetry of DSC suggested good tribological performance of UHMWPE.

(b) The friction coefficient of pure UHMWPE (MW = 3 million) was the lowest among four UHMPWEs with different MWs. The friction coefficients of modified UHMWPE with 15 wt.% Cu(II) chelate of add1 were obviously lower than those of corresponding pure UHMWPE. The minimum friction coefficient of UHMWPE (MW = 3 million) modified with 15 wt.% Cu(II) chelate of add1 against Ti6Al4V decreased by 29% of that of pure UHMWPE (MW = 3 million) against Ti6Al4V, and its friction coefficient was the least among them.

(c) The wear resistance of pure UHMWPE (MW = 3 million) was the best among the four pure UHMWPEs. The worn topographies of modified UHMWPE with 15 wt.% Cu(II) chelate of add1 were obviously lighter than those of corresponding pure UHMWPE, and the volume loss of wear of UHMWPE (MW = 3 million) modified with 15 wt.% Cu(II) chelate of add1 was the least, its volume loss of wear was only 75% of that of pure one and reduction of 8% of that of 2 million molecular weight UHMWPE modified with 15 wt.% Cu (II) chelate of bissalicylaldehyde-ethylenediamin. Meanwhile, the worn topographies of Ti6Al4V against modified UHMWPE exhibited more remarkable improvements than those of related pure ones. The worn topographies of modified UHMWPE (MW = 3 million) displayed the lightest wear among them.

(d) The effects of the MW of UHMWPE were obvious on reciprocating friction and wear characteristics of pure UHMWPE and modified UHMWPE. An MW of 3 million was best to increase the friction of rubbing pairs, enhance the wear resistance of pure UHMWPE and modified UHMWPE, and improve their mating properties.

(e) The friction and wear of friction pairs, including pure and modified UHMWPE/Ti6Al4V, were mainly controlled by a three-body abrasive wear mechanism. Sufficient Cu(II) chelate of add1 may restrain the groups from migrating from the lubricant calf serum to the worn surface and reduce friction and wear.

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