

Wear performance of ultrahigh molecular weight polyethylene/quartz composites

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Abstract

Ultrahigh molecular weight polyethylene (UHMWPE)/quartz composites were compression molded in the presence of organosiloxane, and then hydrolyzed. The used organosiloxane is vinyl tri-ethyloxyl silane. The gelation, the melting behavior, the crystallinity, the mechanical properties and the wear resistance of UHMWPE/quartz composites were investigated. The results showed that organosiloxane can act as a cross-linking agent for UHMWPE matrix and serve as a coupling agent for improving the bonding between the quartz particles and the UHMWPE matrix. The correlation between the various properties and the morphology of the composites has been discussed. At about 0.5 phr organosiloxane while the degree of crystallinity of the composite is at the peak value of 57%, the mechanical properties and the wear resistance of UHMWPE/quartz composites reaches their maximum.

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1. Introduction

Ultrahigh molecular weight polyethylene (UHMWPE) is an engineering plastic which has a wide spectrum of applications, particularly as a material for orthopedic prostheses due to its high strength, excellent toughness, high resistance to chemicals and physical abrasion, and low friction coefficient. Recently, approximately one million UHMWPE components are implanted worldwide annually. Metal-on-UHMWPE total joint arthroplasty becomes an effective and popular immediate pain relief and remarkable restoration of mobility for patients with disabilities.

Despite the success of total joint arthroplasty, wear is a major obstacle limiting the long-term performance of implanted UHMWPE components. It has been estimated that billions of particles are produced yearly from the surface of a total hip replacement. Recently, Kurtz

[1] has reviewed the latest development of UHMWPE for total joint athroplasty. Although UHMWPE components are in no imminent danger of wearing during a patient's lifetime, osteolysis and loosening of implants are attributed to the debris generated from the articulating surface. Therefore, wear resistance of UHMWPE has to be improved. Many attempts have been made to improve the wear resistance and mechanical properties of UHMWPE. One of these involves the peroxide and organosiloxane-induced cross-linking, (i.e. chemical cross-linking), plasma and γ -ray radiation cross-linking [2–12]. A comprehensive review on chemical-induced and radiation cross-linking has been given by Lewis [13]. Another widely used approach is to incorporate in-organic filler, cement or fiber into UHMWPE through composite technology [14–20]. For this technology, the dispersion of filled phase and the interfacial adhesion among various composite components play important roles in determining the wear resistance and the mechanical properties of these composites. In the present study, UHMWPE was reinforced by filling with in-organic quartz powders and cross-linking using vinyl tri-ethyloxyl silane.

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2. Experimental methods

2.1. Preparation of samples

UHMWPE powder used in this work was supplied by the Second Factory of Auxiliary Agents in Beijing in People's Republic of China. The molecular weight of UHMWPE is 2.7×10^6 g/mol and the particle size of quartz powders is 300 mesh. Vinyl tri-ethyloxyl silane of grade A-151, which were produced by the Chemical Factory of Wuhan University in People's Republic of China, was distilled at atmosphere pressure (b.p. 160–161°C). The peroxide initiator, dicumyl peroxide (DCP), was prior purified by recrystallization.

UHMWPE and quartz powders were mixed with a previously prepared acetone solution of organosiloxane and DCP in a high-speed mixer. The filled volume of quartz powder was set to 20% in this study. The amount of organosiloxane was varied from 0 to 1.0 phr (part of reagent per hundred parts of UHMWPE), whereas the amount of DCP was kept at the initiator concentration for organosiloxane-grafting onto UHMWPE. Acetone in the uniform slurry was removed by evaporating the slurry in an oven at 75°C for 30 min. This process has been determined to be effective in providing uniform organosiloxane and DCP dispersion on the surface of UHMWPE powders, with negligible residual acetone. The above mixtures were compression-molded into plates with dimensions of $180 \times 180 \times 5$ mm³ under a pressure of 15 MPa at 200°C. Then, the UHMWPE/quartz composite plates were immersed in boiling water for at least 8 h.

2.2. Gelation measurement

The gel ratio of the UHMWPE/quartz composites was determined by measuring the insoluble content using the extraction method. Samples were extracted with boiling xylene for 72 h, then washed with ethanol and dried under vacuum at 80°C to a constant weight. The gel ratio was calculated by the following equation:

$$\text{Gel ratio(\%)} = \frac{W_3 - W_1}{W_2 - W_1} \times 100\%, \quad (1)$$

where W_1 is the weight of quartz in the sample, W_2 the weight of the sample before extraction, and W_3 the weight of the sample after extraction.

2.3. Differential scanning calorimetry

Differential scanning calorimetry (DSC) measurements were conducted in a Perkin-Elmer DSC-7 instrument at a heating rate of 10°C/min under dry nitrogen atmosphere. Prior to the DSC recording, all samples were heated to 220°C, and kept at this temperature for 3 min to eliminate the influence of their

previous thermal history. After they were quenched to an ambient temperature, the samples were heated from room temperature to 220°C, and the DSC readings were recorded.

The degree of crystallinity (X_c) of the UHMWPE/quartz composite was calculated using the formula below:

$$X_c(\%) = \frac{\Delta H}{\Delta H_{100}} \times 100\%, \quad (2)$$

where ΔH is the heat of fusion corrected for one gram of UHMWPE in the composite, and ΔH_{100} is the heat of fusion for 100% crystalline UHMWPE taken as 289 J/g according to Ref. [10].

2.4. Mechanical properties and morphology observations

The UHMWPE/quartz composite plates were machined into dog-bone shape tensile bars. The tensile behavior was determined using an Instron tester (model 4206) at room temperature under a cross-head speed of 1 mm/min. Izod impact specimens with dimensions $65 \times 13 \times 5$ mm³ were also cut from the plates. They were tested by a Ceast pendulum impact tester. Blunt notch with a notch tip radius of 0.25 mm was introduced to the impact specimens with a Ceast notch opener.

The morphology of fracture surface of the sample was examined by using a scanning electron microscope (SEM, JEOL JSM 820). The samples were fractured after immersion in liquid nitrogen. All fractured surfaces were coated with a thin layer of gold prior to the SEM examination.

2.5. Wear testing

The wear testing of the composite was conducted on a computer controlled pin-on-disk wear testing machine of model TEER-PD-I. A schematic diagram of the machine is shown in Fig. 1. Samples of 60 mm in diameter and 6 mm in thickness were cut from the composite plates. A sample was placed on the rotating sample table with a stationary wear ball as the counterface subjected to an induced load. The wear ball was made of silicon nitride with a diameter of 3 mm. For each test, the conditions used were: tracking diameter of 4 mm, linear speed of 21 mm/s, 30 N load, temperature of 38°C, and rotating speed of 100 rpm. Two sets of wear tests were performed. One of them was to use distilled water as a lubricant while the other was to adopt a fetal bovine serum (Invitrogen, Carlsbad, CA cat. #26140-079). Weight loss from the samples was computed from profilometry measurements of the wear tracks.

2.6. Cytotoxicity test

Human muscle cells (American Type Culture Collection, Manassas, VA) were seeded into 96-well tissue

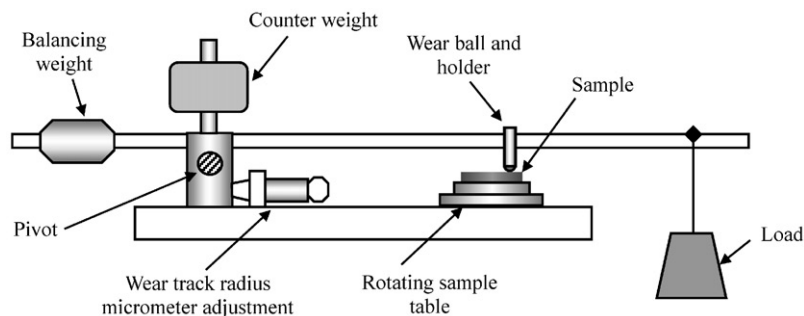


Fig. 1. Schematic diagram of pin-on-disk wear testing apparatus.

culture plates (Costar, Cambridge, MA) at a concentration of 2000 cells/well and cultured with Dulbecco's modified Eagle's medium supplemented with 4 mM L-glutamine, 4.5 g/l glucose, 10% fetal bovine serum and 10 units/ml Penicillin/Streptomycin (Invitrogen, Carlsbad, CA) was used as a culture medium. The quartz/UHMWPE wear debris was sterilized under UV for 24 h to prevent from bacterial and fungal contaminations. Totally 6 mg of sterile debris was dissolved in 1.5 ml culture medium and then subjected to serial dilution from 4 mg/ml to 0.4 μ g/ml. The cells were grown in a humidified incubator with 5% CO₂ at 37°C overnight for attachment and then in an exchange medium with sterile debris in different concentrations. After 3 days incubation, the cell viability versus the control cells without debris incubation was determined by MTT assay. 50 μ l of 5 mg/ml MTT (3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide, Sigma, Dorset, UK) was added into each well and incubated for 4 h. Dimethyl sulphoxide of 100 μ l (DMSO, Sigma, Dorset, UK) was added to each well and was shaken for 1 h before the optical density was measured by a BioRad 550 microplate reader (BioRad, Hercules, CA) at 570 nm with reference at 630 nm.

3. Results and discussions

3.1. Influence of organosiloxane on gelation of UHMWPE/quartz composites

Fig. 2 shows that the gel ratio of UHMWPE/quartz composites depends on the organosiloxane content. Before hydrolysis, the gel ratio of UHMWPE/quartz composites increases from 0 to about 45% monotonically with the organosiloxane content. After hydrolysis, the gel ratio of UHMWPE/quartz composites increases remarkably, and is higher than that before hydrolysis. The results indicate that the organosiloxane acts as a cross-linking agent as well as a coupling aid. This is because the vinyl tri-ethyloxyl silane was grafted onto the UHMWPE chain as well as coupled with quartz in

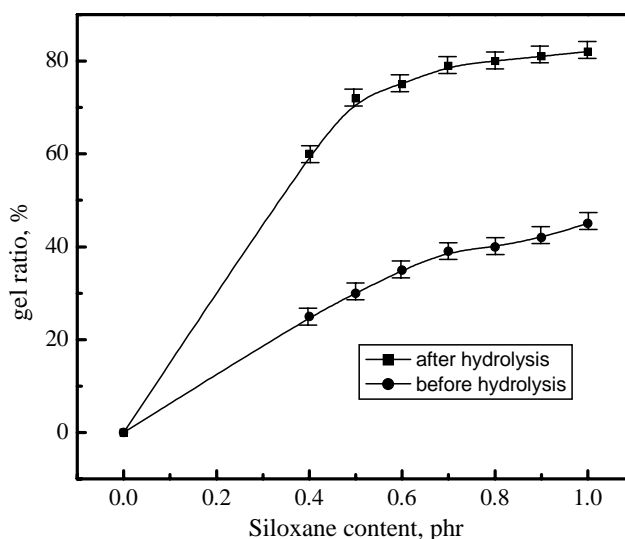


Fig. 2. Effect of organosiloxane content on the degree of gel of UHMWPE/quartz composite.

the first step of the process. The quartz powders prevent the UHMWPE from removal during the extraction. When the UHMWPE/quartz composite plates were then immersed in boiling water, the ethyloxyl groups in the organosiloxane were hydrolyzed to hydroxyl groups. The hydroxyl groups on neighboring chains then condensed together to form the organosiloxane-induced cross-linking of UHMWPE in the UHMWPE/quartz composite plates. When the organosiloxane content is 0.6 phr, the gel ratio of UHMWPE goes up to about 80%. Further increase in the organosiloxane content, the gel ratio of UHMWPE/quartz composites increases very slowly, and gradually approaches a steady value.

3.2. Thermal properties

The melting temperature (T_m) and the degree of crystallinity (X_c) of UHMWPE/quartz composites with different organosiloxane contents were determined from the DSC heating thermograms. The results are shown in

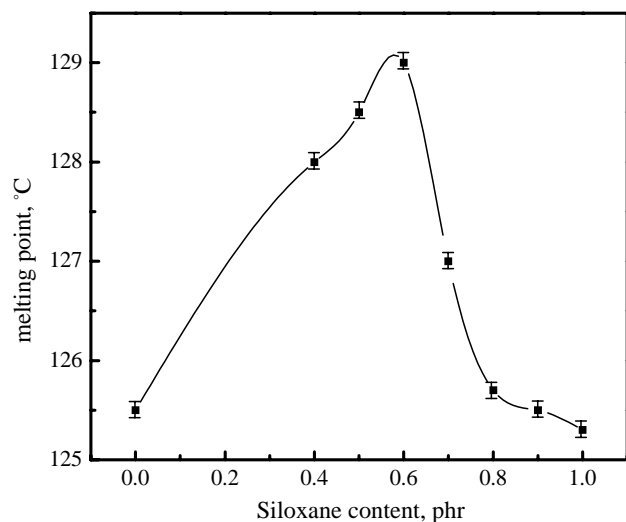


Fig. 3. Effect of organosiloxane content on melting point of UHMWPE phase in composite.

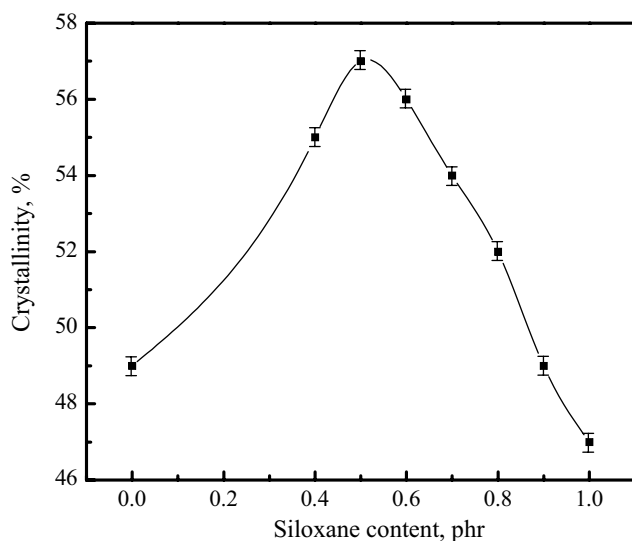


Fig. 4. Effect of organosiloxane content on degree of crystallinity of UHMWPE phase in composite.

Figs. 3 and 4. Apparently, at low content of organosiloxane, T_m and X_c of UHMWPE/quartz composites increase with increasing content of organosiloxane. After the content of organosiloxane is up to 0.6 phr, T_m and X_c of UHMWPE/quartz composites drop significantly with further increase in the content of organosiloxane. This phenomenon is similar to the behavior of organosiloxane-crosslinked UHMWPE and γ irradiated UHMWPE [4,21]. It has been well known that increase in molecular weight can increase T_m and X_c of a polymer, and the chain scission also influences the melting property and the crystallinity.

By measuring the melting point of UHMWPE, the crystalline lamellar thickness, l_c , was estimated using the

Table 1

Calculated values of l_c for organosiloxane-induced cross-linking UHMWPE

Organosiloxane content (phr)	0	0.4	0.5	0.6	0.7	0.8	0.9	1.0
l_c (Å)	133	152	157	161	144	135	133	132

Thomson–Gibbs equation [22]:

$$T_m = T_{m0} \left(1 - \frac{2\sigma_e}{l_c \Delta H_{100}} \right) \quad (3)$$

where $T_{m0} = 418.7$ K is the melting point of a hypothetical crystal of infinite size for which the surface energy effect may be neglected [10]. The fold surface energy σ_e , that relates to the surface energy of the crystal end faces at which the chains fold [10], was taken as 93×10^{-7} J/cm². The heat of fusion of the crystal ΔH_{100} was taken to be 289.3 J/g \approx 89.3 J/cm³ [10]. The calculated values of l_c are listed in Table 1. In general, larger lamellar thickness corresponds to higher melting temperature, chain regularity and crystallinity, and vice versa. From this table, it can be noticed that l_c increases to 161 Å from 133 Å after the UHMWPE/quartz composite is coupled and cross-linked by 0.6 phr organosiloxane, which leads to the increase in T_m and X_c of UHMWPE in the composite. With further increase in the content of organosiloxane, the molecular weight and l_c of UHMWPE in the composite increase, and hence X_c of UHMWPE increases at the low content of organosiloxane. However, further increase in the density of cross-linking of UHMWPE, the high-density cross-linking networks restrict the motion, fold and crystallization of molecular chains, and hence X_c of UHMWPE in the composite decreases significantly. Moreover, the high-density cross-linking leads to a decrease in the molecular weight between cross-links [7], and T_m of UHMWPE decreases in turn.

3.3. Morphology

Fig. 5 shows the SEM fractographs of the UHMWPE/quartz composites with different organosiloxane contents. From Fig. 5(a), it can be seen that the UHMWPE/quartz composite without the treatment of organosiloxane exhibits poor interfacial bonding between UHMWPE and the quartz particles. After the UHMWPE/quartz composite is treated by organosiloxane, the interfacial adhesion between UHMWPE and quartz is improved as in Fig. 5(b). From Fig. 5(c), it can be observed that, when the content of organosiloxane is 0.6 phr, the interfacial bonding in the UHMWPE/quartz composite is very well. It is because that the organosiloxane, acting as a coupling agent, improves the interaction between UHMWPE and quartz. Moreover, as discussed above, the organosiloxane also enhances

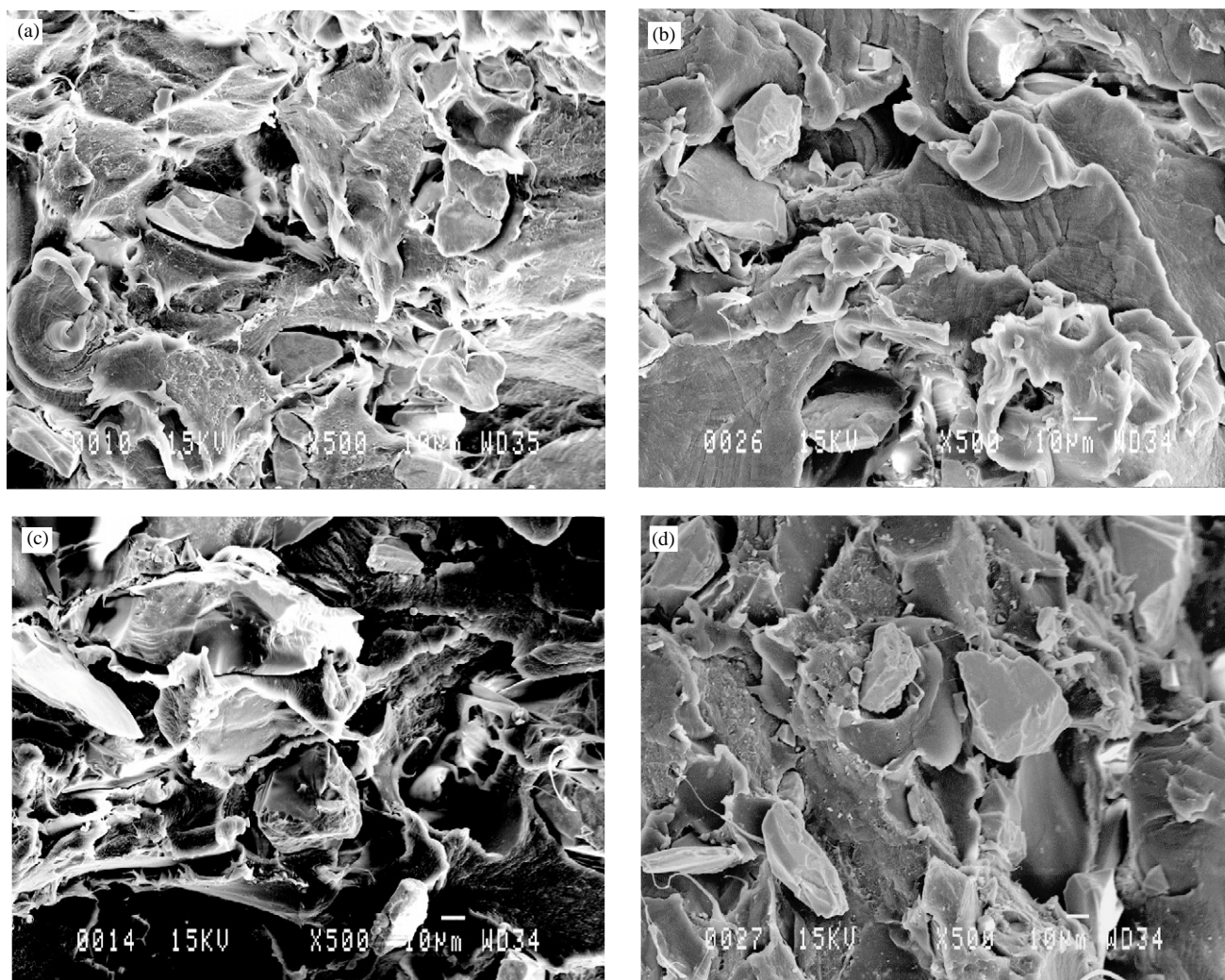


Fig. 5. SEM photographs of UHMWPE/quartz composites: (a) no organosiloxane; (b) 0.5 phr organosiloxane; (c) 0.6 phr organosiloxane; (d) 0.7 phr organosiloxane.

the cross-linking of UHMWPE. However, with further increase in the content of organosiloxane, the interfacial bonding in the composite degenerates as shown in Fig. 5(d). It indicates that excessive cross-linking of UHMWPE matrix in the composite destroys the interfacial adhesion.

3.4. Mechanical properties

The variation of modulus, tensile strength and Izod impact strength of the UHMWPE/quartz composites are plotted against organosiloxane content in Figs. 6, 7 and 8, respectively. As shown in Figs. 6–8, the modulus, tensile strength and Izod impact strength of UHMWPE/quartz composites all increase with the content of organosiloxane due to higher crystallinity, organosiloxane-induced cross-linking and network formation. As a result, the deformability is limited. With further increase in the organosiloxane content, i.e. the cross-linking density, the tensile modulus and strength of

the organosiloxane-induced cross-linking UHMWPE decrease significantly. Owing to the organosiloxane-induced cross-linking network formation, the intermolecular networks increase the number of molecules interconnecting lamella, and restrict the motion of polymer chains, leading to a decrease in the Izod impact strength of cross-linked UHMWPE. These results agree with the behaviors of organosiloxane-induced cross-linking UHMWPE.

3.5. Wear properties

The variation of weight loss of the UHMWPE/quartz composites is plotted against organosiloxane content in Fig. 9. In both cases of using the distilled water and the fetal bovine serum as lubricants, the results show that the weight loss of the UHMWPE/quartz composites decreases with the content of organosiloxane up to about 0.5 phr. However, with further increase in the content of organosiloxane, the weight loss of the

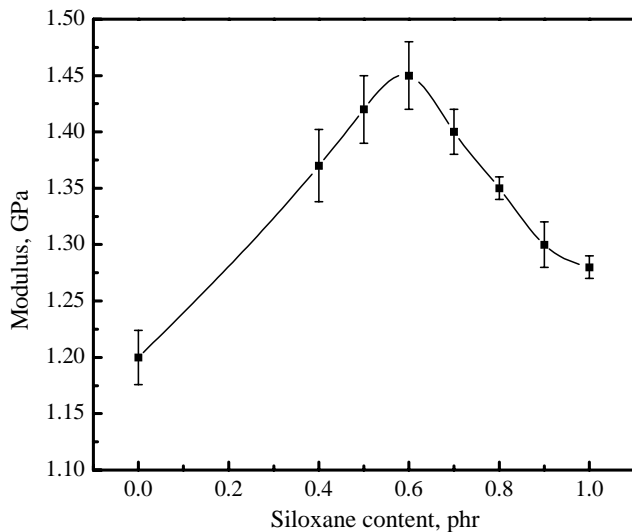


Fig. 6. Effect of organosiloxane content on tensile modulus of UHMWPE/quartz composite.

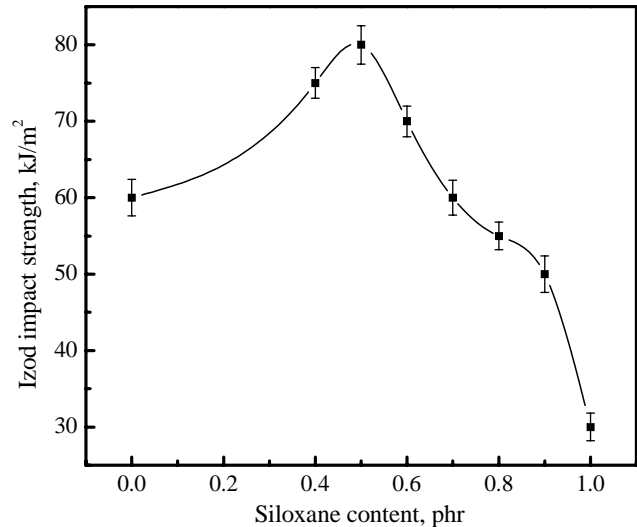


Fig. 8. Effect of organosiloxane content on Izod impact strength of UHMWPE/quartz composite.

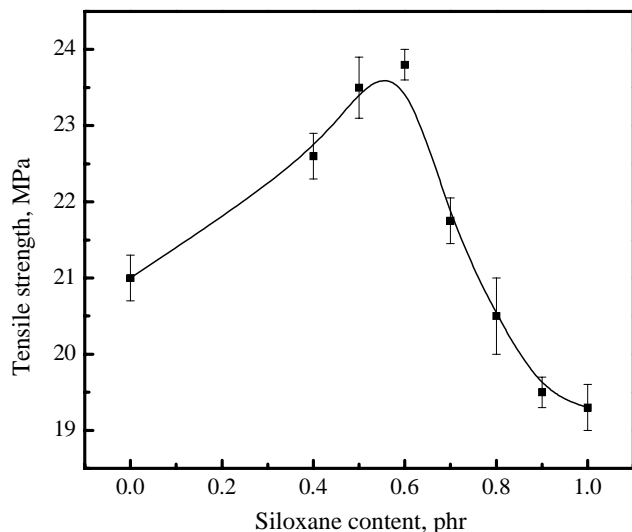


Fig. 7. Effect of organosiloxane content on tensile strength of UHMWPE/quartz composite.

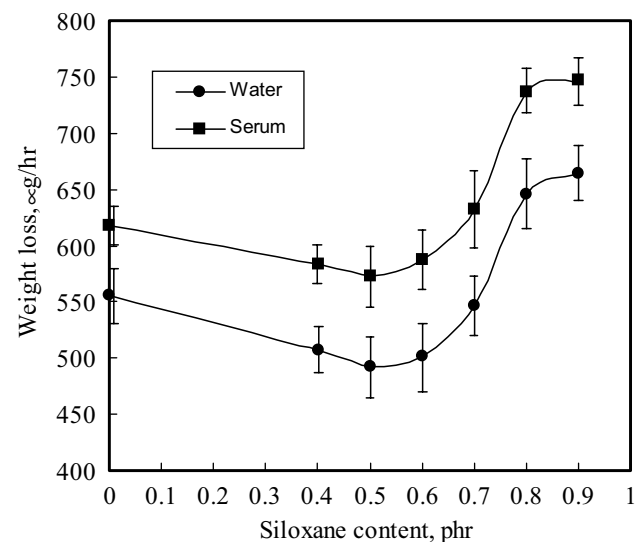


Fig. 9. Effect of organosiloxane content on wear resistance of UHMWPE/quartz composite.

UHMWPE/quartz composites increases remarkably. In other words, the maximum wear resistance of the composite can be obtained at about 0.5 phr organosiloxane. The wear rate of the serum-based test is generally higher than that of the water based one. Similar findings about other particulate composites, such as PTFE/alumina and PTFE/CoCr composites, have also been reported [23].

In general, wear in polymer materials occurs as a result of strong adhesion interaction, abrasive, fatigue, macro-shearing, thermal and thermo-oxidative interaction, corrosion, cavitation and so on [24]. The phenomenon of the wear in polymeric material is so complex that a model with fine details is difficult to be

established. In practice, a single basic mechanism is always accompanied by the occurrence of other types of wear. The types of wear caused by adhesive and abrasive have been undergone better investigation than the others. According to the mechanism of the adhesive wear [25], the volume of wear can be expressed by

$$\text{Volume of wear} = \frac{kWd}{H} \quad (4)$$

Regarding the abrasive wear [25], the volume of wear can be expressed as

$$\text{Volume of wear} = \frac{k_a W d \mu}{H \sigma \varepsilon} \quad (5)$$

where k and k_a are the coefficients of the adhesive and abrasive wear, respectively. w is the load, d is the sliding distance, and μ is the frictional coefficient. H , σ and ε are the hardness, the tensile strength and the elongation at break of material, respectively.

From Eqs. (4) and (5), the volume of wear depends upon the bulk properties of polymeric material as well as the surface properties. The better the mechanical properties of polymer are, the better its wear resistance will be. As mentioned above, the organosiloxane-induced coupling among UHMWPE, quartz and cross-linking of UHMWPE increases the modulus, the tensile strength and the Izod impact strength of the composites at low content of organosiloxane. This leads to an improvement in their wear resistance. When the content of organosiloxane is greater than the critical value, the high density of cross-linking decreases the modulus, the tensile strength and the impact strength of the composites, which leads to deterioration in wear resistance. Therefore, the organosiloxane content at 0.5 phr can produce maximum wear resistance for the UHMWPE/quartz composites.

3.6. Cytotoxicity test

In vitro toxicity tests on UHMWPE/quartz wearing debris show no adverse effects associated with 72-h incubation. The lethal dose is found to be higher than 1.25 mg/cm^2 growing area as shown in Fig. 10. No observable phenotypic changes of the tested cells could be identified under the microscope. This result suggests that the UHMWPE/quartz composite has only mild toxicity at a relatively high concentration up to 4 mg/ml . With these promising results in mechanical properties

and biocompatibility, UHMWPE/quartz may be suitable for the development of biomedical components and used for total joint replacement.

Nevertheless, the biocompatibility and toxicity of materials containing quartz is far diverse [26–28]. There are some factors affecting the cell toxicity test, including impurity of the resulted debris, chemical compositions, and physical form, especially the sizes of particles that are in contact with the cells [29–31]. Therefore, a more comprehensive test including a long-term evaluation of implantation into rabbits or rats should be carried out before carrying out a pre-clinical trial for a variety of surgical and dental applications.

4. Conclusion

UHMWPE/quartz composites were compression molded in the presence of organosiloxane, and then hydrolyzed. The results showed that the organosiloxane acts as a cross-linking agent for UHMWPE as well as a coupling aid for the quartz particles and the UHMWPE matrix. At low content of organosiloxane, the melting point and crystallinity of the UHMWPE phase in UHMWPE/quartz composites increase due to the molecular cross-linking of UHMWPE matrix. Moreover, the interfacial adhesion between the quartz and UHMWPE matrix is improved by the coupling effect of organosiloxane. The mechanical and wear resistant properties are improved subsequently by the improved interface and the cross-linking of matrix. However, at the high content of organosiloxane, these performances of the UHMWPE/quartz composites become worse due to the excess cross-linking of UHMWPE matrix. Compared with the water test, the wear rate of the composite is higher in the serum test. For both lubricants, the wear resistance of the UHMWPE/quartz composites is maximized at 0.5 phr organosiloxane. The cytotoxicity evaluation shows that the wearing debris has only mild toxicity at a relatively high concentration up to 4 mg/ml . However, recent reports on the biocompatibility and toxicity of materials containing quartz are very diverse. Therefore, a long-term and detailed evaluation of animal implantation is suggested before any pre-clinical trials are preformed.

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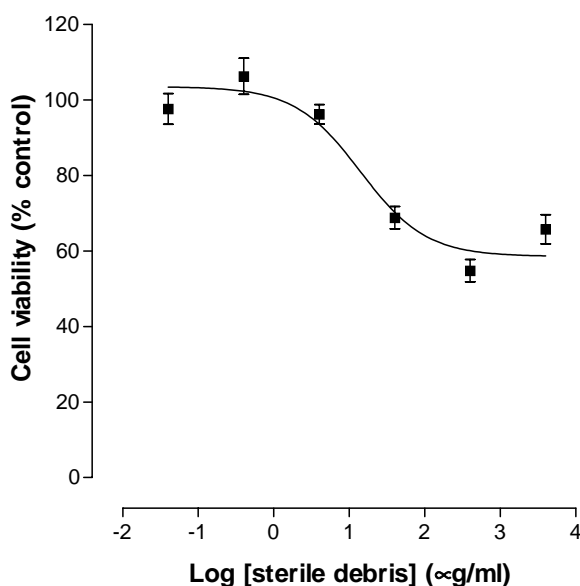


Fig. 10. Cytotoxicity evaluation of wearing debris.

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