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Wear of nano-TiO_2/UHMWPE composites radiated by gamma ray under physiological saline water lubrication

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Abstract Nano-TiO_2/UHMWPE composites were prepared by hot press procedure, and then radiated by gamma ray in dose of 120 kGy, 250 kGy and 500 kGy. The hardness of the composites was initially determined. Subsequently the wear against a CoCrMo alloy counterface were tested in a knee simulator under physiological saline lubrication. The morphologies of the worn surfaces were examined with optical microscope. The structure of the samples was determined by IR and XRD. The results showed that the wear rate of the composite UHMWPE decreased when filled with proper amount of nano-TiO_2 and with the radiation dose.

Introduction

The ultra-high molecular weight polyethylene (UHMWPE) has several excellent properties, thus it has been chosen as the orthopaedic bearing material in total joint replacements for over 40 years. Nevertheless the wear of UHMWPE and the resulting wear debris induced tissue responses that lead to osteolysis and aseptic loosening are now recognized as one of the most important factors in failure of joint replacements [1].

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Many studies have been carried out to improve the tribological properties of UHMWPE and reduce wear debris. In some studies, UHMWPE was radiated by gamma ray and the wear resistance was found to be improved. However, radiation was shown to accelerate the oxidation and increase the material's brittleness [2–7]. Some other researchers tried to improve the property of UHMWPE by filling other materials including UHMWPE fiber and carbon fiber [8–10], and found improved wear resistance. However, there are few studies on filling with nano-particles [11]. Ion implantation can also improve the tribological properties of UHMWPE and increase surface hardness of UHMWPE [10, 12–16].

In this paper, the UHMWPE samples were filled with various contents of nano-TiO_2 particles and then the resultant composites were radiated by gamma ray in different doses. The effects of TiO_2 content and radiation dose on structure, wetting ability, hardness and wear properties were investigated.

Experimental

Materials

The UHMWPE powder of 5,000,000 molecular weight was supplied by, Shanghai Institute of Chemistry. The TiO_2 nano-particles were supplied by Nanjing High Technology Nano Co. Ltd. (HTTi-01). It has an average granularity of 5 nm, and specific surface area lager than 120 m^2/g.

Preparation of UHMWPE and its composites

UHMWPE powder and TiO_2 nano-particles were intensively mixed in a QM-1SP ball mill with different percentages, then hot pressed into a cylinder at about 250 °C for 2 h. The bearing surface of the samples was polished, then cleaned by alcohol, dried and kept in an airproof bag for the following experiments.

In this study, UHMWPE samples were filled with four different amounts (1%, 3%, 6% and 10%) of nano-TiO_2 powder.

Radiation process

Some of the samples prepared using the methodology outlined in 2.2 were radiated by gamma ray with three doses of 120 kGy, 250 kGy and 500 kGy. After irradiation, the color of the samples became a little darker than those not radiated.

Wear test

The wear of the UHMWPE composite obtained in 2.2 and 2.3 against a CoCrMo counterface was tested on a cylinder-on-plane machine simulating a knee joint designed and built in house (Fig. 1) under physiological saline solution lubrication. A constant load of 1062 N is applied and the frequency is 1 Hz. The range of the angular motion of the CoCrMo cylinder is 60°. After the wear test, the morphologies of worn surfaces were examined with optical microscope.

Results and discussion

The effect of filling nano TiO_2 on the contact angel and hardness of UHMWPE

The contact angle and hardness of filled and unfilled UHMWPE specimens are shown in Table 1. The contact angle decreased after filled with TiO_2 except the one filled with 10% TiO_2. However the hardness of all the filled samples increased with the percentage of TiO_2.

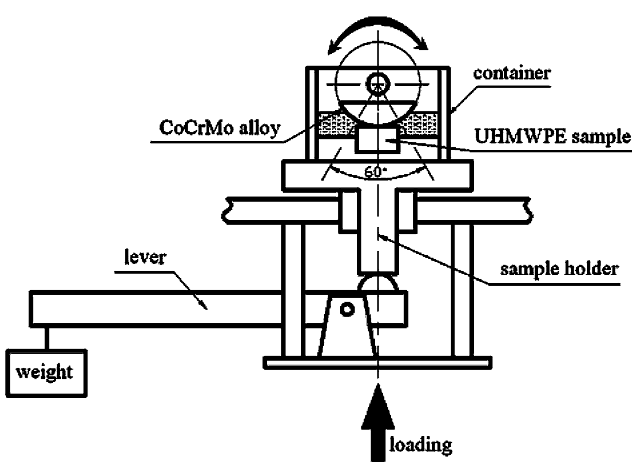


Fig. 1 The structure of the knee simulator

Table 1 The contact angel and hardness of UHMWPE composites

TiO_2 content(wt%)	Contact angle(eθ)	Hardness(HRR)
0	87° ± 4°	18 ± 2
1	83° ± 2°	20 ± 3
3	78° ± 3°	26 ± 3
6	81° ± 2°	23 ± 2
10	87° ± 5°	25 ± 2

The effect of filling nano TiO_2 and radiation on the crystallinity of UHMWPE

The structures of samples were analyzed using XRD as shown in Figs. 2 and 3. From these figures, it is clear that a

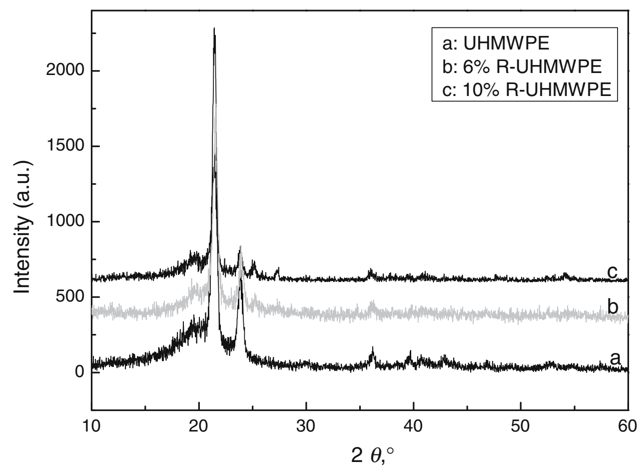


Fig. 2 XRD pattern of UHMWPE with different filling amount

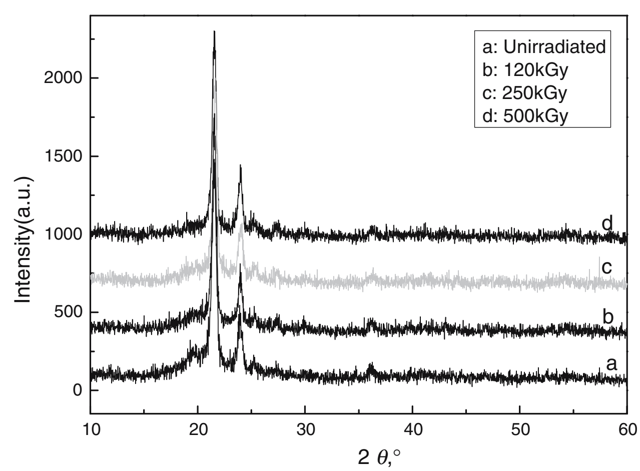


Fig. 3 XRD pattern of 6% TiO_2/UHMWPE composites radiated by gamma ray

similarity existed between the curves of filled and unfilled samples, as well as between irradiated and unirradiated ones. All these samples exhibited two sharp peeks at $2\theta = 21.5°$ and $2\theta = 24.0°$, showing that the composite UHMWPE specimens obtained in the present study have a crystalline structure. And the other blunt peeks show the amorphous structure in UHMWPE.

The ratio of the areas below sharp peeks and the ones below blunt peeks represents the crystallinity. So the crystallinities of the samples can be calculated from Figs. 2 and 3. The results are shown in Figs. 4 and 5.

Figure 4 shows that the crystallinity of UHMWPE increased significantly after filled with a small amount of TiO_2 and only slightly with further increasing filling amount. For the 6%TiO_2/UHMWPE specimens radiated by gamma ray, the crystallinity increased until the radiation dose reached to 250 kGy (Fig. 5).

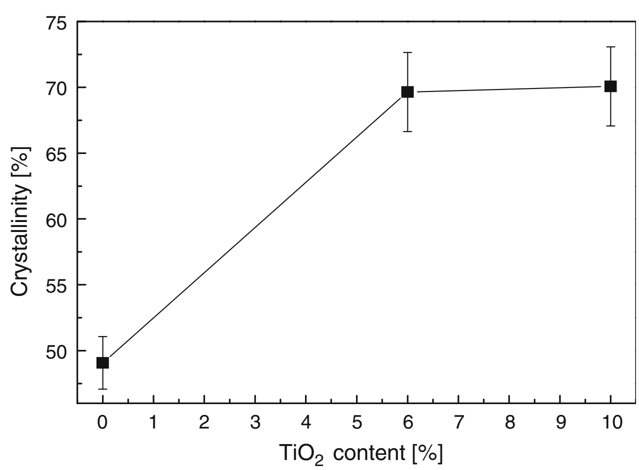


Fig. 4 Crystallinity of UHMWPE with different filling contents

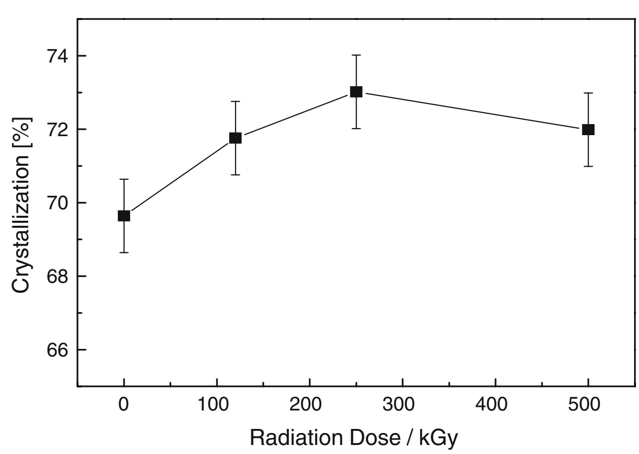


Fig. 5 Crystallinity of 6% TiO_2/UHMWPE composites radiated by gamma ray with different doses

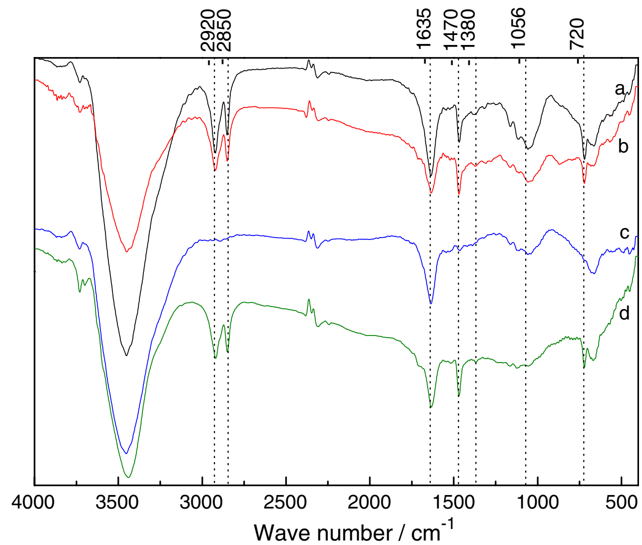


Fig. 6 results of infrared absorption spectrum test, (**a**) pure UHMWPE (**b**) UHMWPE radiated by 500 kGy gamma ray (**c**) UHMWPE filled with 6%TiO_2 (d) 6% TiO_2/UHMWPE composites radiated by 500 kGy gamma ray

The results of IR test

The filled and unfilled samples were tested using infrared absorption spectrum, and the results are shown in Fig 6.

The spectra shown in Fig. 6, allows the ratios between radicals of –COC– and (–CH_2 + –CH_3) to be calculated and the results are shown in Table 2.

It can been seen from Table 2 that the amount of –COC– in unfilled UHMWPE samples increased by 14% after the radiation. However, the amount of –COC– in 6%TiO_2/UHMWPE composites decreased 2.5% after the radiation.

The effect of filling nano TiO_2 on the tribological properties of UHMWPE

The unirradiated samples were tested firstly and the result is shown in Fig. 7. It can be seen that the wear rate of the composites decreased after filled with nano TiO_2, the one filled with 6% TiO_2 has the lowest wear rate, about 77% of the unfilled specimens.

Table 2 Ratio of peek area between different radicals

Radical	Area ratio			
	UHMWPE	UHMWPE 500 kGy	6% TiO_2	6% TiO_2 500 kGy
–COC– : (–CH_2 + –CH_3)	0.43	0.50	1.19	1.16

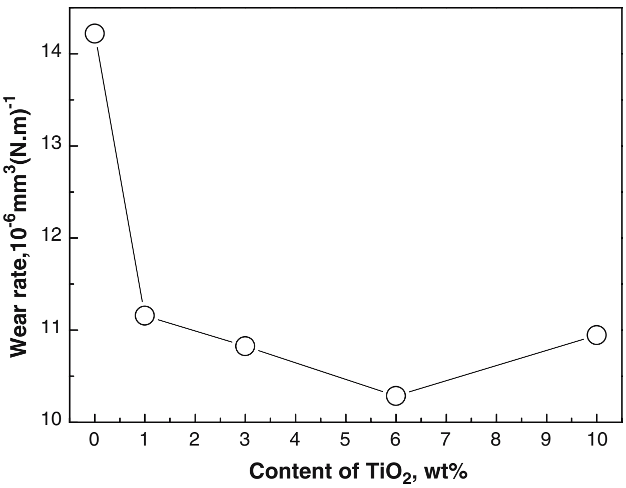


Fig. 7 Wear rate of UHMWPE with different filling amount

The wear rates of UHMWPE and 6%TiO_2/UHMWPE composites radiated by gamma ray are shown in Fig. 8. It can be seen that the wear rate decreases with the increasing

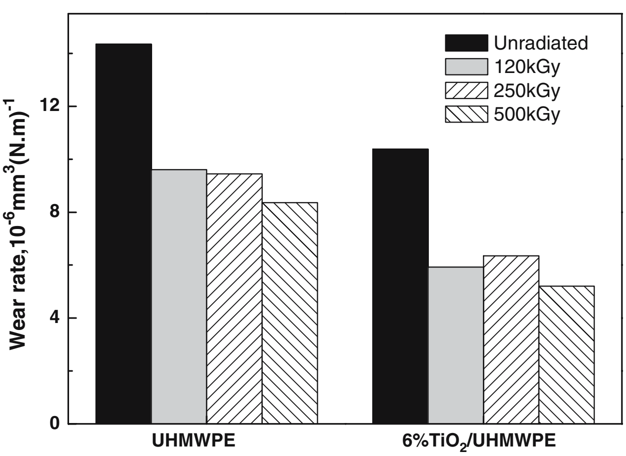


Fig. 8 Wear rate of UHMWPE and 6% TiO_2/UHMWPE composites radiated by gamma ray

of the radiation dose, the lowest wear rate associated with the 6%TiO_2/UHMWPE composites irradiated with 500 kGy gamma ray and only about 30% of the unfilled and unirradiated samples. In the radiated 6%TiO_2/UHMWPE composites samples, the one radiated with 250 kGy gamma ray has the highest wear rate, and this may be associated with its high crystallinity (Fig. 5).

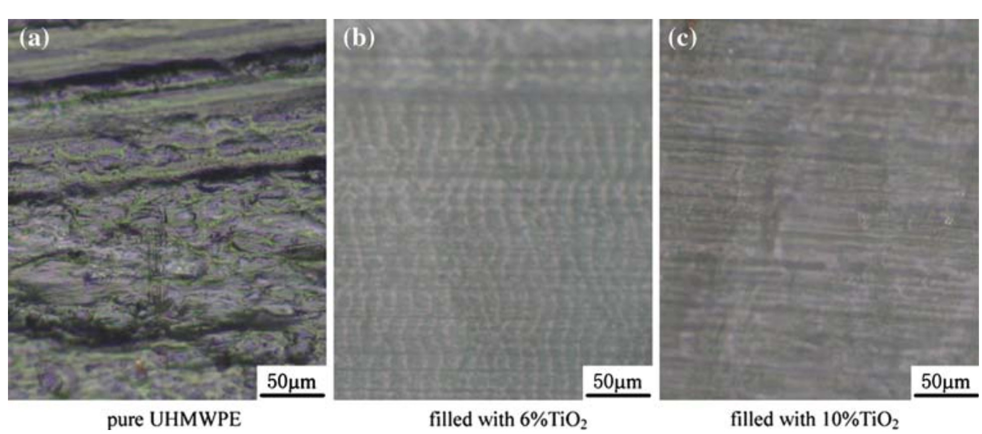
Figure 9 shows the morphologies of worn surfaces. There are severe desquamation and ploughing on the surface of unfilled UHMWPE (Fig. 9a). However, on the surface of composites filled with 6%TiO_2, there are only some flat ploughing and slight fatigue and the surface is smooth as a whole (Fig. 9b). While, on the surface of composites filled with 10%TiO_2, block desquamation can be seen and the ploughing is deeper than that of 6%TiO_2/UHMWPE composites, but flatter than that of unfilled UHMWPE (Fig. 9c). All these imply that agglomeration was introduced due to filling with too many nano-particles.

Overall discussion

As the results of wear tests show, tribological properties of UHMWPE can be improved markedly by filling with proper amount of nano-TiO_2 (Fig. 7). This can be explained that the filling particles link the UHMWPE molecular chains by Van Der Waals force and hydrogen bonds, and consequently improve the mechanical properties, especially the shear modulus which improves tribological properties [9, 11]. And the wear rate decreases further with increasing radiation dose (Fig. 8). That is because the radiation introduces crosslinking in UHMWPE molecular chains [4], improves the mechanical properties further, and overall tribological properties can be improved significantly.

From the results of IR test for filled and unfilled samples, the amount of –COC– in unfilled UHMWPE increased by 14% after the radiation. However, for 6%TiO_2/UHMWPE composites the amount decreased by 2.5%. All

Fig. 9 Pictures of wore surfaces (**a**) pure UHMWPE, (**b**) filled with 6% TiO_2 and (**c**) filled with 10% TiO_2



these suggest that filling with nano-TiO_2 has inhibiting effect on the oxidization during radiation, leading to significant improvement on the tribological properties of the composite materials (Fig. 8).

Conclusions

1. The crystallinity of UHMWPE increased significantly after filled with TiO_2, and slightly with the further increasing filling amount. And the crystallinity of 6%TiO_2-UHMWPE increased until the radiation dose to 250 kGy.
2. The wear rate of the composites decreased after filled with nano TiO_2 and the one filled with 6% TiO_2 had the lowest wear rate, about 77% of the unfilled one. The wear rate decreased further with increasing radiation dose, and the lowest wear rate was associated with the composite filled with 6%TiO_2 and irradiated with 500 kGy gamma ray, only about 30% of the unfilled and unirradiated sample..
3. Filling with nano-TiO_2 has inhibiting effect on the oxidization during radiation, and after radiation the wear rate of filled sample decreased by about 50% of the unfilled and unirrdiated specimens.

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