Effect of Gamma Ray Irradiation on Processability and Properties of Ultra High Molecular Weight Polyethylene

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Received 18 March 2010; accepted 14 May 2010
DOI 10.1002/app.32821
Published online 19 August 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Ultra high molecular weight polyethylene (UHMWPE) has been widely used in many fields due to its outstanding properties. However, it is virtually impossible to be processed by the conventional method due to its high molecular weight and very tight chain entanglement. To solve this problem, a new method was proposed in this article. Gamma ray irradiation was adopted to cause the oxidation degradation of UHMWPE. The degraded products which generated *in situ* and dispersed in UHMWPE evenly were utilized as self-lubricant and heat transfer intermediary. These low molecular weight fractions thus could improve the processability of UHMWPE. The effects of irradiation dose on the structure and properties of UHMWPE were studied by fourier transform infrared (FTIR) spectroscopy, gel content measurement, wide angle x-ray diffraction (WAXD), Haake torque rheometer, mechanical properties measurements and sliding wear tests. The experimental results showed that gamma ray irradiation caused oxidation degradation of UHMWPE. Under appropriate irradiation condition, the processability of UHMWPE could be improved substantially while most of its excellent properties could be kept. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 1542–1547, 2011

Key words: UHMWPE; gamma ray irradiation; melt fluidity; processability

INTRODUCTION

Ultra high molecular weight polyethylene (UHMWPE) has been widely used in many fields due to its outstanding physical and mechanical properties such as high strength, low creep, low friction coefficient, low abrasion, reduced wear, and good resistance to fatigue. However, because of its high molecular weight and very tight chain entanglement, UHMWPE does not flow even above its melting temperature (T_m). Thus, it is virtually impossible to be processed by the conventional method of screw extrusion, injection molding or blow molding. To make it suitable for conventional processing method, improving processability of UHMWPE has been the research subject in recent decades.[1–7]

Incorporating a small amount of processing aids, such as stearate or PE wax, has been used to enhance the processability of UHMWPE.[1–3] These processing aids could form a lubricating film between UHMWPE and metal surface of processing machine. However, these processing aids are difficult to be interposed between the entangled macromolecule chains or blocks of UHMWPE. Furthermore, the instability of these low molecule agents and the ease of transferring to the extrudate surface are very harmful to some applications, especially in medical area.

Zhao et al.[4] utilized thermotropic liquid crystalline polymer (TLCP) to modify the properties of UHMWPE. Because of strong shear-thinning effect and molecular orientation of TLCP along the flow direction, the strength and stiffness, as well as the flowability of UHMWPE were improved. However, the high cost of LCP made this approach unacceptable.

Other efforts to reduce the melt viscosity of UHMWPE include blending it with conventional polyethylene which generally has lower average molecular weight.[5–7] When the blend is heated to the melt point of the conventional polyethylene, UHMWPE component is suspended in the liquid phase of conventional polyethylene and is possible to be processed by the conventional method. However, a small quantity of conventional polyethylene could not sufficiently enhance the flowability of UHMWPE. While an effective amount of polyethylene could improve the flowability of UHMWPE significantly, it will also affect some of the most desirable properties of UHMWPE seriously.

Radiation processing involves the use of natural and man-made sources of high energy radiation on an industrial scale. The basis of radiation processing is the ability of high energy radiation to produce

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reactive cations, anions, and free radicals in the materials.[8] The radiation processing of polymer includes polymerization, grafting, crosslinking, and degradation. Compared with conventional chemical methods, radiation processing is more efficient and requires no solvent and chemical agent.

The effect of gamma ray irradiation on the properties of UHMWPE has been discussed since the late 1970s for the purpose of crosslinking and sterilization of medical disposables.[9–11] In these cases, the oxidative degradation of UHMWPE is undesirable and people often try to avoid it. Therefore, the manufactured products are usually irradiated under nitrogen atmosphere and high irradiation dose rate.

A new method to improve the fluidity of UHMWPE was studied in this article. Gamma ray irradiation was adopted to degrade UHMWPE to a suitable extent. The degraded products generated *in situ* in UHMWPE were utilized as self-lubricant and heat transfer intermediary to improve its processability. The crosslinking of UHMWPE was undesirable for our purpose. For avoiding it, UHMWPE powder was irradiated under low irradiation dose rate in air. The effects of irradiation dose on the structure change of UHMWPE were investigated through FTIR and WAXD. The processability, mechanical, and wear properties of gamma ray irradiated UHMWPE were studied as well in this article.

EXPERIMENTAL

Materials

UHMWPE (M-II), with a viscosity average molecular weight of 2.5×10^6, was supplied by the second auxiliary agent factory of Beijing (Beijing, China).

Gamma ray irradiation

Irradiation was performed in air at room temperature with ^{60}Co gamma source. Irradiation dose ranged from 1 to 150 kGy and dose rate was 1 kGy/h.

Measurements and characterization

FTIR analysis

FTIR spectra were recorded on a Nicolet-560 FTIR spectrometer (Nicolet). The samples were prepared by mixing UHMWPE powder and ground KBr and then pressed in a sheet. All infrared spectra were scanned from 4000 to 400 cm^{-1} with a resolution of 4 cm^{-1}.

Gel content measurement

The gel content was determined with a Soxhlet extractor according to ASTM D2765. Samples were refluxed in xylene close to its boiling point (about 138°C) for at least 72 h, until the sample reached a constant weight.

$$\text{Gel content} = W_2/W_1 \quad (1)$$

where W_1 was initial weight of the sample and W_2 was weight of the insoluble gel.

Haake torque measurement

A Haake torque rheometer (Rheocord 90) with a twin-roll mixer was used. Irradiated UHMWPE powders were added into the mixer through a top-mounted loading hopper, torque and temperature were recorded immediately after loading. The mixer temperature was 250°C and roller speed was 60 rpm.

Mechanical properties measurements

To measure mechanical properties, powdery samples were compression molded into sheets under 10 MPa at 190°C for about 8 min. The tensile properties of the blends were examined with an Instron 4302 universal testing machine (Instron) at 23°C with a crosshead speed of 100 mm/min. Tensile test specimens were cut into dumbbell shape. The size of specimens and test conditions followed ASTM D268. In each test, at least five specimens were tested and the average was reported. An XJ-40A tester (Wuzhong Testing Equipment, China) was used to carry out the impact fracture measurements. The samples were prepared and notched according to ASTM D 256. In each test, at least seven samples were tested and the average was reported.

Wide angle x-ray diffraction (WAXD)

WAXD samples were prepared by compression molding of powdery samples into 1mm thick sheets under 10 MPa at 190°C for about 8 min. WAXD analysis was performed by use of a MaxIIIA (Rigaku) wide angle X-ray diffractometer (Ni-filtered CuKa radiation). The accelerating voltage and electric current used were 40 kV and 30 mA, respectively.

Scanning electron microscopy (sem) observations

A JSM 5900 LV scanning electron microscope (JEOL, Tokyo, Japan) was used to observe the morphology of the specimens.

Wear measurement[12]

Sliding wear tests were conducted by use of a MM200 wear tester (Affiliated Factory of Shanghai Polytechnic University, China) at room temperature according to Chinese GB3960-83. The schematic

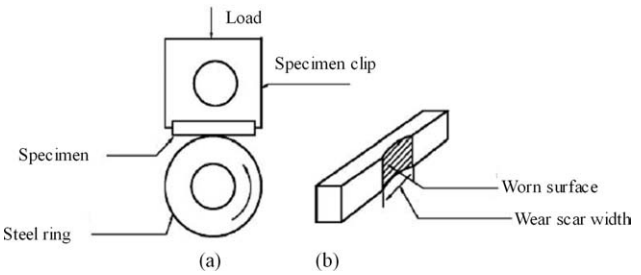

Figure 1 Schematic diagram of wear testing (a) scheme of MM200 model friction and wear tester; (b) worn surface of specimen.

diagram of wear test was shown in Figure 1. The diameter and thickness of the steel ring was 40 and 10 mm, respectively. Its surface roughness (Ra) was 0.015 μm. The rotation speed of the steel ring was 200 rpm during operation. The specimen and the steel ring were washed with acetone and dried naturally before testing. Friction torque was recorded every 5 min, and friction coefficient was calculated as follows:

$$\mu = T/(M \times R) \quad (2)$$

where, μ was the average friction coefficient, T was average friction torque (kg cm^{-1}), M was load (kg) and R was radius of the ring (cm^{-1}).

RESULTS AND DISCUSSION

For polyethylene, irradiation in air may cause crosslinking, chain branching and oxidative degradation. The oxidation degradation during irradiation is controlled by two factors: one is the generation rate of free radicals, which depends on the irradiation dose rate; the other is the diffusion of the oxygen inside the bulk of the material, which depends on sample thickness.[13,14] In this article, UHMWPE powder (the particle size is about 300 μm) was irradiated at a low dose rate (1 kGy/h) to avoid the undesirable crosslinking. From Table I, it could be seen that there was no gel formed in gamma ray irradiated UHMWPE (γ-UHMWPE) even for irradiation dose up to 150 kGy. This indicated that our γ-UHMWPE was absent significant amounts of crosslinked products in the whole irradiation dose range.

Figure 2 showed the FTIR spectra of UHMWPE irradiated under different irradiation doses. Through gamma ray irradiation, oxygen-containing groups (mainly carbonyl groups, situated at 1715 cm^{-1} in FTIR spectra) were introduced onto the molecular chains of UHMWPE. With the increase of irradiation

TABLE I
Effect of Irradiation Dose on Gel Content of UHMWPE

Irradiation dose (kGy)	0	10	30	50	70	100	150
Gel content (%)	0	0	0	0	0	0	0

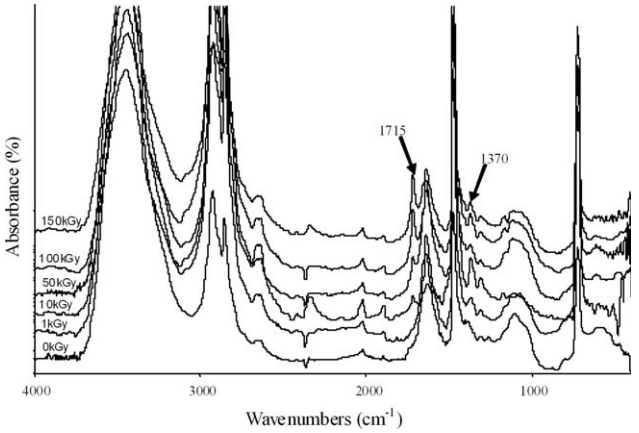

Figure 2 FTIR spectra of irradiated UHMWPE (dose rate: 1 kGy/h).

dose, the peak of the group intensified. Carbonyl group (C=O) contents could be evaluated by $A_{C=O}/A_{CH2}$ ratio, where the $A_{C=O}$ and A_{CH2} were the areas of absorption peaks at 1715 and 1370 cm^{-1} in the FTIR spectra, respectively. With increasing irradiation dose, the $A_{C=O}/A_{CH2}$ ratio of irradiated UHMWPE increased (Fig. 3). The FTIR results suggested that the level of oxidation of UHMWPE could be controlled by adjusting the irradiation dose.

Haake torque reflects the viscosity of the material being processed and is an indication of its processability.[15,16] The effect of irradiation on the processability of UHMWPE was characterized by Haake torque and the results were shown in Figure 4. The blending torque was clearly influenced by irradiation dose. The torque-time curves of the irradiated UHMWPE (10 kGy) and irradiated UHMWPE (30 kGy) exhibited similar torque-time curves to rigid PVC. According to literatures,[17,18] the points A and B on the torque-time curve were caused by loading

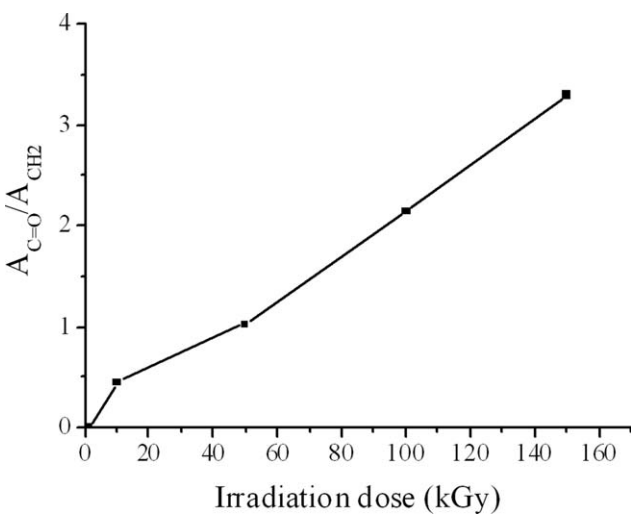

Figure 3 The oxidation index of UHMWPE at different irradiation dose.

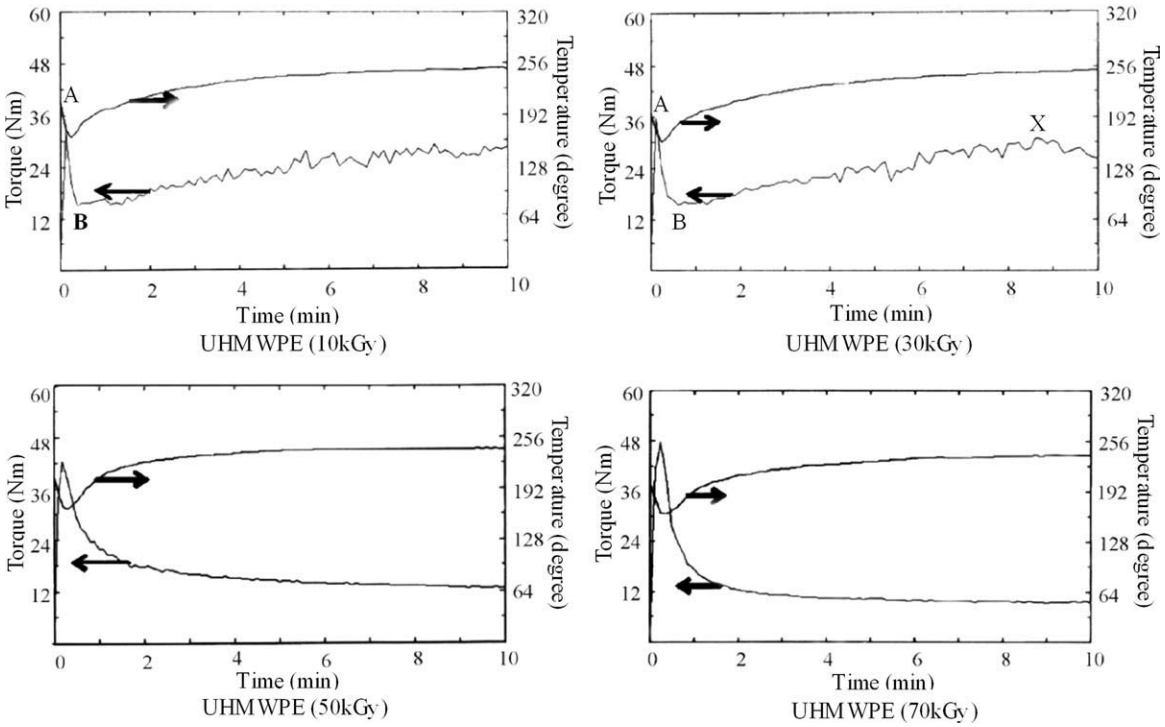

Figure 4 Torque of irradiated UHMWPE at different irradiation dose.

and free flow of material, respectively. Point X was caused by compaction and the onset of fusion. The period between the loading point (A) and the fusion point (X) was defined as the fusion time. In case of UHMWPE (10 kGy), the fusion time was very long and onset of fusion could not be observed during 10 min mixing. For UHMWPE (30 kGy), the fusion time was nearly 9 min and the torque value was high. The unstable torque curves indicated that the sample could not form a single melt phase. The torque-time curves of the irradiated UHMWPE (50 kGy) and irradiated UHMWPE (70 kGy) exhibited similar torque-time curve to common PE.[19] The fusion time was short and their torque curves were stable and smooth. On the torque-time curve, the stabilization zone is the region in which there is no torque fluctuation for a period of time. In this region, it is believed that a single melt phase has been formed and the torque value in this region is directly related to the melt viscosity. It could be seen in Figure 4, the irradiated UHMWPE (50 kGy) and UHMWPE (70 kGy) reached the stabilization zone after mixing about 5 min and 3 min, respectively. Compared with the curve of UHMWPE (50 kGy), UHMWPE (70 kGy) had lower torque value. The Haake torque results indicated that irradiation allowed the fusion process occurring more quickly and uniformly.

Haake torque result could be partly explained by the result of SEM observation of the original UHMWPE powder. Figures 5 revealed that UHMWPE particles appeared to be composed of a large number of smaller units with the microgaps among them and were interconnected by fibrils. The gaps that exist between the minor particles and the

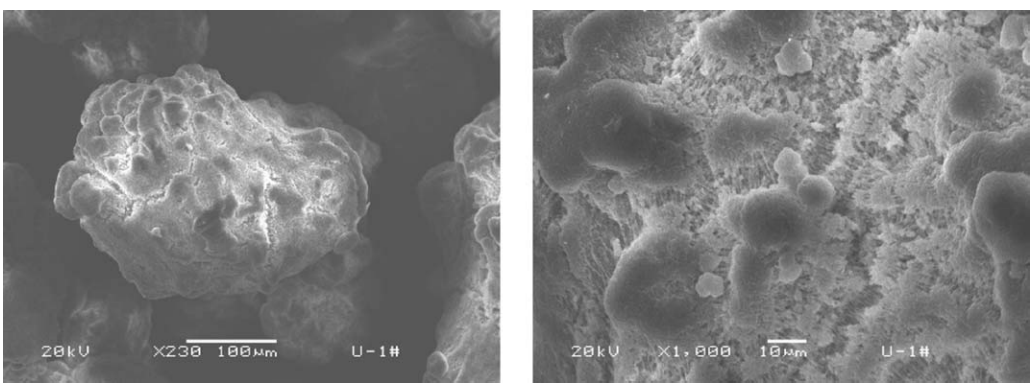

Figure 5 SEM micrograph of the surface of UHMWPE powder.

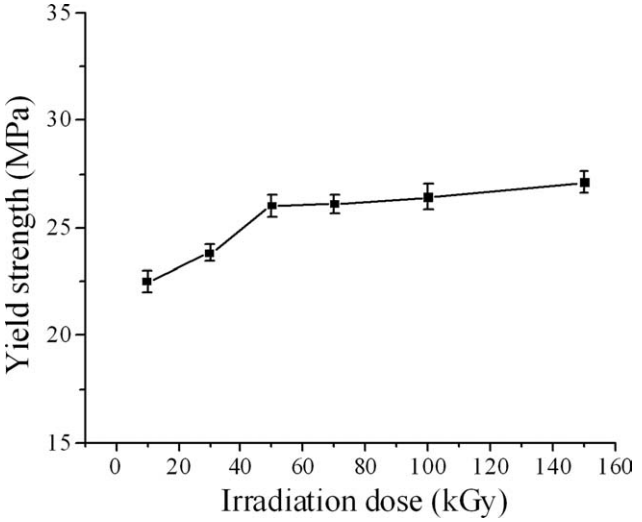

Figure 6 Yield strength of UHMWPE vs. irradiation dose.

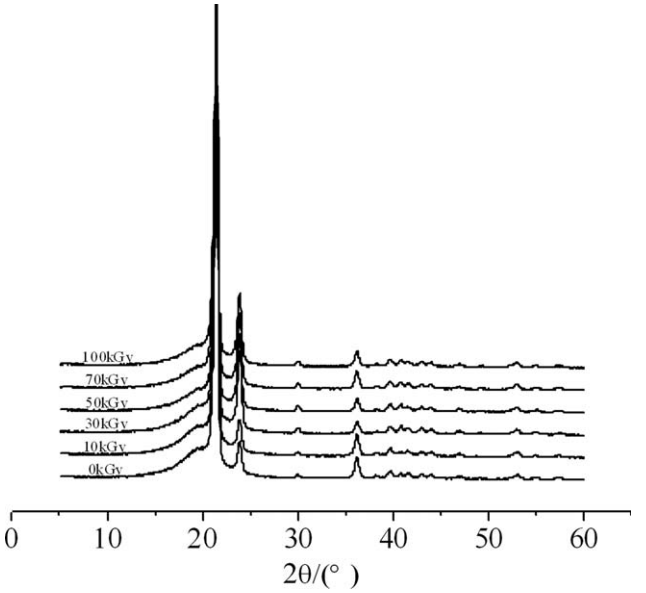

Figure 7 WAXD patterns of irradiated UHMWPE powders.

low mobility of the molecular chain retarded the heat transmission within the material during processing. Therefore, the time to melt unirradiated UHMWPE into a homogenous phase was very long. In the case of gamma ray irradiated UHMWPE, oxidized products were generated *in situ* and dispersed in UHMWPE evenly. These low molecular weight fractions of UHMWPE, due to higher mobility of molecular chain, could act as the self-lubricant and heat transfer intermediary, and thus increased the processability of UHMWPE.

It is well known that the excellent properties of UHMWPE are mainly attributed to its high molecular weight. In this article, to improve its processability, some molecular chains of UHMWPE were broken as self-lubricant by irradiation. This might deteriorate the desirable properties of UHMWPE. To find out an optimal irradiation dose, which could improve the processability of UHMWPE and also had little effect on the properties of UHMWPE, it was necessary to investigate the effect of irradiation dose on the properties, especially the mechanical and frictional properties of UHMWPE.

The effects of irradiation dose on the tensile yield strength and notched Izod impact strength of UHMWPE were shown in Figure 6 and Table II, respectively. With the increase of irradiation dose, the yield strength of UHMWPE increased and the notched Izod impact strength decreased gradually (Table II). While the irradiation dose was lower than 50 kGy, the desired impact strength of UHMWPE could be kept.

The yield strength of irradiated UHMWPE varied with the irradiation dose suggested that irradiation might have some effect on the crystallinity of UHMWPE. To prove it, WAXD was adopted to investigate the crystalline behavior of irradiated UHMWPE. X-ray diffraction patterns of irradiated UHMWPE were shown in Figure 7. The crystallinity of UHMWPE was calculated by the following equation[20]:

$$W_{c,x} = (I_{110} + 1.42I_{200})/(I_{110} + 1.42I_{200} + 0.75I_a) \quad (3)$$

where, I_{110}, I_{200}, and I_a were the integrating intensities of the (110) peak, (200) peak, and the noncrystalline regions, respectively. To determine the exact integrating intensities, a deconvolution procedure was performed. Table III listed the d-spacings of the several main crystalline planes and crystallinity of

TABLE II
Notched Izod Impact Strength of Irradiated UHMWPE

Irradiation dose (kGy)	Notched Izod impact strength (J/m)
0	>1000
10	>1000
30	>1000
50	>1000
70	653
100	576

TABLE III
WAXD Analysis of Irradiated UHMWPE

Irradiation dose (kGy)	Crystallinity (%)	d-spacing of UHMWPE crystalline plane (Å)		
		110	200	020
0	70.8	4.144	3.725	2.480
10	77.4	4.146	3.725	2.479
30	78.4	4.143	3.725	2.479
50	83.5	4.145	3.727	2.479
70	84.5	4.146	3.727	2.480
100	84.7	4.145	3.727	2.480

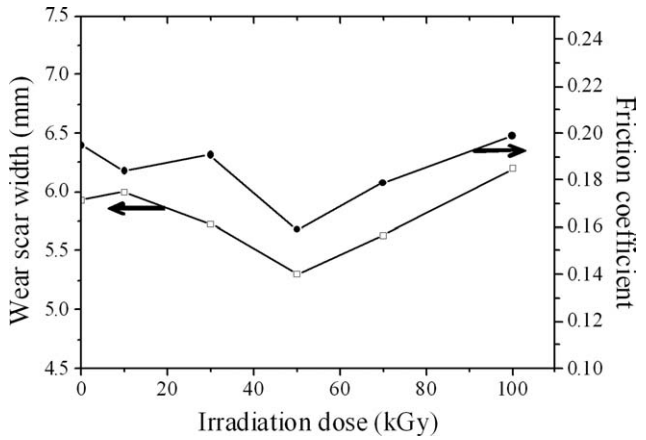

Figure 8 Effect of irradiation dose on frictional properties of UHMWPE.

the irradiated UHMWPE. After irradiation, the crystalline plane (110), (200), (020), and the d-spacing of irradiated UHMWPE were almost unchanged. With increasing irradiation dose, the crystallinity of irradiated UHMWPE increased. Compared Figure 6 with Table III, it could be found that with the increasing irradiation dose, the changes of the crystallinity and yield strength of UHMWPE almost had the same trend. This suggested that the increase of yield strength of irradiated UHMWPE should be mainly attributed to its increase of crystallinity.

Low friction coefficient is another excellent property of UHMWPE. Figure 8 showed the dependence of friction coefficient and wear scar width of UHMWPE on the irradiation dose. The results indicated that with the increase irradiation dose, the friction coefficient and wear scar width of the irradiated UHMWPE decreased. When irradiation dose was 50 kGy, the friction coefficient and wear scar width of the irradiated UHMWPE reached a minimum value. The decrease of friction coefficient and wear scar width of the irradiated UHMWPE might be attributed to the increase of crystallnity. When irradiation dose was higher than 50 kGy, the friction coefficient and wear scar width of the irradiated UHMWPE increased with the increase irradiation dose. This could be explained by the excessive degradation of UHMWPE.

CONCLUSIONS

Gamma ray irradiation caused the oxidative degradation of powdery UHMWPE at a low dose rate. The level of oxidation degradation of UHMWPE could be controlled by adjusting irradiation dose. Through oxidation degradation, the processibility of UHMWPE was improved. With the increase of irradiation dose, the processability, crystallinity, and yield strength of irradiated UHMWPE increased while the notched Izod impact strength decreased. With the increase of irradiation dose, the friction coefficient and wear scar width of the irradiated UHMWPE decreased and reached a minimum value when irradiation dose was 50 kGy.

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