A Crosslinking Method of UHMWPE Irradiated by Electron Beam Using TMPTMA as Radiosensitizer

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ABSTRACT: Trimethylolpropane trimethylacrylate/Ultra high molecular weight polyethylene (TMPTMA/UHMWPE) composite and pure UHMWPE plates were made by compression molding and electron beam (EB) irradiation crosslinking methods. Fourier transform infrared spectroscopy (FTIR), Soxhlet extractor, electromechanical tester, and wear tester were used for the characterization of the structure, mechanical properties, and tribological performance of the crosslinked UHMWPE. FTIR analyses show that *trans*-vinylene (965 cm^{-1}) absorption increases with the increasing dose and the *trans*-vinylene intensity of TMPTMA/UHMWPE is higher than that of UHMWPE at the same dose, and Soxhlet experiments reveal that gel fraction increases with the increasing dose, both proving that crosslinking took place in all the irradiated samples. The results of the tensile tests indicate a significant decrease in elongation at break, but the stress of UHMWPE increases to 47 MPa at 10 kGy and then decreases with the increasing dose. The stress of TMPTMA/UHMWPE composites keeps at about 39 MPa before 50 kGy and then decreases with the increasing dose because of plasticization effect. The stress changes indicate that crosslinking and degradation occurred at the same time. Wear rate of 100 kGy 1% TMPTMA/UHMWPE is 1.76×10^{-7} mg/Nm, only 23.5% of wear rate of 0 kGy UHMWPE and 44.2% of wear rate of 100 kGy UHMWPE. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

INTRODUCTION

Ultra high molecular weight polyethylene (UHMWPE) is a linear and highly entangled polyethylene with an average molecular weight more than 1.5×10^6 g/mol. Excellent properties in terms of high resistance to chemicals, physical abrasion, low fiction coefficient, and high impact strength have made UHMWPE to be used in the areas of mechanism, transportation, colliery oil field, and medicine to replace metals. Among them, a special and the most important application is the replacement of damaged articulating cartilages. However, the structure of UHMWPE also originates many problems, like weak creep and fatigue strength compared with metal and bone materials. Therefore, the wear resistance and anticreep properties of UHMWPE must be improved to prolong the life of the total joint replacement. So wear modification methods of UHMWPE summarized in Figure 1 have been developed.

Comparing with crosslinking, the most advantage of using particle additives (such as fiber,[1] Pt-Zr,[2] Cu,[3] Zr[4]) to improve wear resist-ance is the avoidance of free radical generation and accelerated oxidation. However, it remains to be seen how much wear reduction and whether they degrade impact properties as much as crosslinking does. The major challenge is the toxicological effect on the body. Further, the dispersion of the filling phase and the interfacial adhesion between various composite components plays an important role in influencing the wear resistance of the composite.

The applications of Di-alkyl peroxides [(R—OO)nR′] (such as dicumyl peroxide (DCP)[5] or benzoyl peroxide[6]), silane (DCP as initiator),[7] and 2.5-dimethyl-2.5-di-(t-butyl-peroxy) hexyne-3[8] in UHMWPE have caught great attentions. Despite the evidence of improved wear resistance of peroxide-crosslinked UHMWPE, questions have been raised about its long-term stability to oxidative degradation, so members of the orthopedic community have diverted their attention to radiation-crosslinked UHMWPE to improve its resistance to long-term oxidation.

Although some scientists have done researches on the application of polyethylenes crosslinked by silane chemistry in total hip
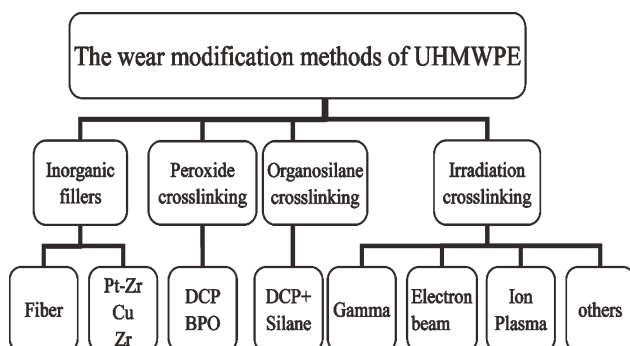
Figure 1. The wear modification methods of UHMWPE.

arthroplasty,[9–14] little information is available on the crosslinking of UHMWPE induced by organosilane, not to mention in the clinical evaluations. In a paper,[7] UHMWPE was crosslinked by vinyl tri-ethyloxyl silane with the purpose of improving the wear resistance property. The abrasion loss of UHMWPE decreases to 0.8% when the pure UHMWPE is 1.25%. The result is not so ideal, more efforts should be done.

Crosslinking of UHMWPE is done in commerce through the use of gamma or electron beam (EB) irradiation under certain atmospheres along with a thermal treatment with doses range from 50 to 105 kGy. The irradiation creates free radicals, through removal of hydrogen and chain breaking, which can recombine together to produce the crosslinked structure. However, the consumption of free radicals by crosslinking at room temperature is a slow process, and in the presence of oxygen the free radicals are consumed more through oxidative reactions to form carbonyl groups (C=O) which cause scission of UHMWPE. Postirradiation thermal processing,[15,16] which occurs below the melt transition is annealing and above is remelting, is conducted to reduce free radicals to minimize the potential for postirradiation oxidation. This treatment can cause the decay of free radicals and enhancement of crosslinking, but it can also change the semicrystalline structure which may affect fracture toughness and other mechanical properties.

The main problem is to prevent the oxidation in and after irradiation process through the analysis above. So some scientists use inert atmospheres (such as nitrogen or a vacuum)[16,17] or add radical scavengers (such as vitamin E,[18–20] hindered amine light stabilizer[21]) to catch the free radicals which can prevent the oxidative degradation. Plasma/ion treatment[22–24] (such as Argon) method which is an efficient and environmental friendly process is also used to modify polymer surfaces without changing the bulk composition. Recently, someone irradiated UHMWPE in the presence of acetylene[25] or 1,7-octadiene[26] to increase the molecule crosslinking density.

However, the methods above need long time to process and also the processes are complicated. In addition, the high molecular weight (more than 1.5×10^6 g/mol) and linear, highly entangled structure (Melt Flow Index = 0) make it difficult to mix additives with UHMWPE in a two-roll mill or a mixing mill which can be used in other types of PE. So it needs to use different methods to process the compound when UHMWPE is

mixed with other additives. In this article, one method is issued to reduce the irradiation dose of UHMWPE through adding trimethylolpropane trimethylacrylate (TMPTMA) as radiosensitizer which can increase the crosslinking density. The addition of TMPTMA into UHMWPE can get the same crosslinking effect under lower irradiation dose. When the irradiation doses reduce, the residual free radicals trapped in the amorphous region drop, the oxidation probability of UHMWPE during use can be reduced, and then the mechanical properties can be preserved. Some antioxidants (1010) can be added into UHMWPE to prevent the oxidation in the process of irradiation and during use of TMPTMA/UHMWPE. To research the changes of chemical structure of TMPTMA/UHMWPE and the reaction mechanism of crosslinking induced by EB, the antioxidant is not added into UHMWPE in the paper. In this work, pure ethyl alcohol was used to dissolve TMPTMA and then dried to disperse TMPTMA on the surface of the UHMWPE powders uniformly. Then the specimens were made by melting compounding method and then irradiated by EB to enhance crosslinking density. The method is simple, fast and can make radiosensitizer well dispersed in the UHMWPE.

MATERIALS AND METHODS

Sample Preparation

The preparation of X-TMPTMA/UHMWPE samples could be described in Figure 2. UHMWPE (M_c = 2,000,000, SLL4020) powders were mixed with a previously prepared alcohol solution of TMPTMA in a high speed mixer. The concentration of TMPTMA was varied from 0, 0.5 to 1%. Alcohol in the uniform slurry was removed by evaporating the slurry in a vacuum oven at 80°C for 1 h. The process had been proved to be effective in providing uniform TMPTMA dispersion on the surface of UHMWPE powders, with negligible residual alcohol. The above mixture was compression-molded into plates with dimensions of $100 \times 100 \times 6$ mm^3 (or 1 mm thickness sheet for tension test, 100 μm thickness film for IR) under a pressure of 15 MPa at 200°C for 30 min. Then the plates packed with a PE bag were irradiated by an EB generator (GJ-2E-EB, 2 MeV, 10 mA) by passing the oven with a dose rate of 5 kGy per pass. The oven had an aluminum foil window through which EB passed the oven to irradiate on the surface of the plates. The irradiation doses varied from 10 to 200 kGy. The specimens on the transmission mechanism could transmit along with transmission rail which was 3 m long after every 5 kGy irradiation, and there was a forced air cooling machine blowing the specimens in irradiation process. So, the temperature of the specimens could be controlled
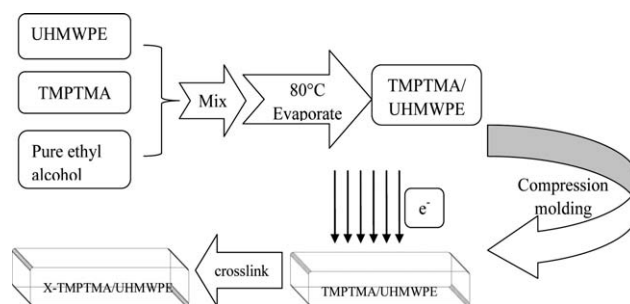

Figure 2. Experiment process.

and would barely affect the activity of the free radicals and the mobility of UHMWPE chains.

Fourier Transform Infrared Spectroscopy

The materials were studied by Fourier transform infrared (FTIR) spectroscopy (Spectrum 100, Perkin Elmer, CT). The FTIR spectrum was recorded in transmission mode with a 0.4 cm^{-1} resolution. To detect the occurrence of crosslinking, the region of the spectrum between 2000 and 600 cm^{-1} was analyzed, especially in vinyl double bonds area (=C=C= stretching for vinylidene group about 1632 cm^{-1}) and the *trans*-vinylene groups area (about 965 cm^{-1}). The peak at 720 cm^{-1}, a combination band associated with in-plane rocking vibration of =CH$_2$, was used as an internal standard, because it can be regarded as unaffected by minor changes in the polymer structure. The sample thickness is 100 μm.

M_c, and gel Fraction

Equilibrium swelling experiments[27,28] were performed in *o*-xylene with 0.1 mass % Irganox 1010 (Ciba Geigy) added as an antioxidant. The samples (w g) were kept at 130°C for 24 h and then weighed, w_2. After cooling to room temperature in the Soxhlet Extractor, the specimens were dried in a vacuum oven at 130°C to reach a constant weight, w_1. The swell ratio (q) was calculated from the weight ratio between the swollen and the dried extracted gel according to eq. (1).

$$q = 1 + \frac{(w_2 - w_1)/\rho_s}{w_1/\rho_p} \quad (1)$$

ρ_s, the density of *o*-xylene (130°C, 0.768 g/cm^3), ρ_p, the density of UHMWPE (here 0.908 g/cm^3 was used).

The values stated below are the average of three tests. With the steady-state swell ratio (q), the crosslink density (v_d) was computed using Flory's network theory expressed by eq. (2).

$$v_d = \frac{\text{In}(1 - q^{-1}) + q^{-1} + \chi_f q^{-2}}{V_1(q^{-1/3} - 0.5q^{-1})} \quad (2)$$

Flory's interaction parameter for *o*-xylene–PE at 130°C with $\chi_F = 0.33 + 0.55/q$, the molar volume of *o*-xylene $V_1 = 138$ cm^3/mol. Equation (3) was applied to calculate the molar mass between adjacent crosslinks (M_c).

$$M_C = \frac{\rho_P}{v_d} \quad (3)$$

Here, χ_F is the Flory–Huggins Interaction Parameter.

The percentage of crosslinking can be characterized by gel fraction. Gel fraction of the TMPTMA crosslinking UHMWPE was determined by measuring the insoluble using the extraction method. Gel fraction was calculated by eq. (4).

$$\text{Gelfraction}(\%) = \frac{\text{extractedsampleweight(g)}}{\text{sampleweight(g)}} \times 100\%$$
$$= \frac{w_1}{w} \times 100\% \quad (4)$$

Tension Tests

Tensile tests were performed on all samples with a Universal Electromechanical Tester (Instron 4465, Instron Corp., MA) with a crosshead speed of 250 mm/min at 25°C. Barbell type specimens
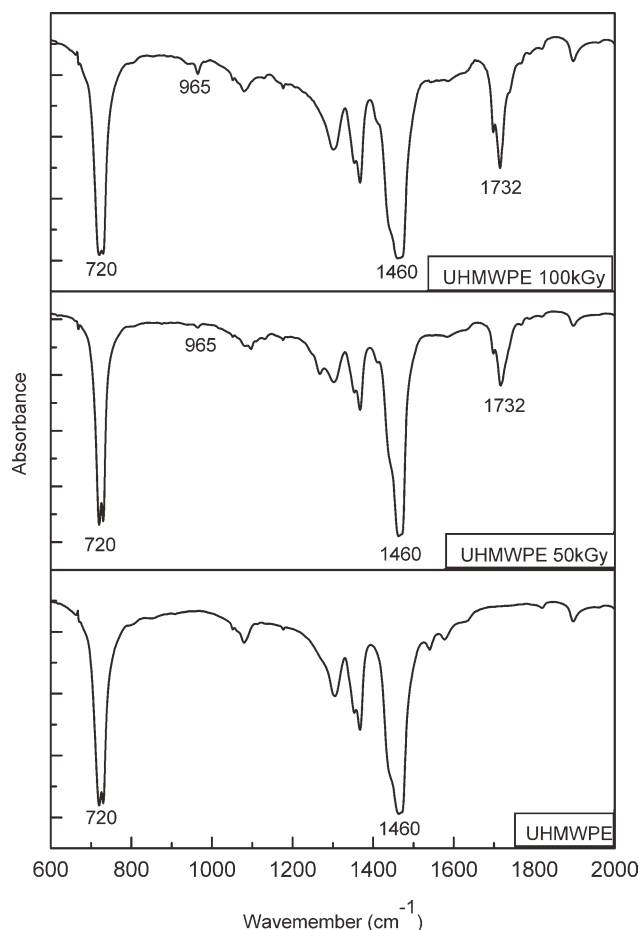
Figure 3. FTIR spectra of UHMWPE specimens irradiated to 50 kGy, 100 kGy, and initial UHMWPE specimen.

were punched out from 1 mm thickness sheets, according to ASTM D638-00.

Wear Tests

The tribological performances of the materials were evaluated by a pin-on-plate wear tester (M2000-A type), the dimension of the steel ring is ($d_1 = 40$ mm) × ($d_2 = 16$ mm) × (thickness = 10 mm), the dimension of the specimens is 30 × 7 × 6 mm^3, The rotate speed of the machine is 200 circles/min, the load is 20 kg, the environment temperature is 23 ± 5°C.

RESULTS AND DISCUSSION

FTIR Analysis

The peak changes of functional groups in UHMWPE and TMPTMA/UHMWPE before and after irradiation are showed in Figures 3 and 4. Figure 3 reports the FTIR spectra of the pure UHMWPE films irradiated in air to 0, 50, and 100 kGy, respectively. Figure 4 shows the FTIR spectra of TMPTMA/UHMWPE films irradiated in air to 0, 50, and 100 kGy, respectively. After irradiation by EB, both spectra demonstrate the presence of new absorption bands which are not attributable to the original polymer.[29]

The bands at 720 cm^{-1} (=CH$_2$ in-plane rocking vibration) and 1460 cm^{-1} (=CH$_2$ scissor vibration), which represent ─CH$_2$─
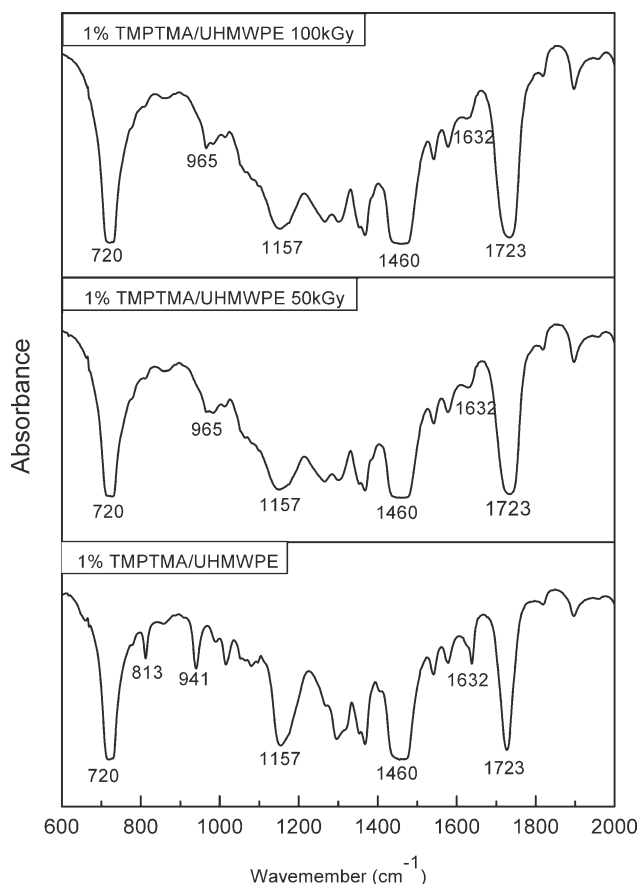
Figure 4. FTIR spectra of 1% TMPTMA/UHMWPE specimens irradiated to 50 kGy, 100 kGy, and initial 1% TMPTMA/UHMWPE specimen.

in UHMWPE and TMPTMA/UHMWPE, have no obvious changes, illustrating that the main structure of UHMWPE has not undergone any changes in the irradiation process. The *trans*-vinylene absorption band appears at 965 cm^{-1} on the spectra of irradiated UHMWPE and its intensity increases with the increasing dose, and TMPTMA/UHMWPE composite has the same phenomenon at 965 cm^{-1}, showing that the reaction took place in UHMWPE in the irradiation process. In Figure 3, in the region of carbonyl groups (1732 cm^{-1}) which is attributable to irradiated UHMWPE, the peak appears and becomes wider following the increasing irradiation dose. In Figure 4, the carbonyl groups absorption (C=O, 1723 cm^{-1}) becomes wider after irradiation. These show the oxidation reaction of UHMWPE with O_2 happened in the process of irradiation and after irradiation. But the phenomenon of 1723 cm^{-1} becoming wider is not as obvious as that of 1732 cm^{-1}, showing that the addition of TMPTMA has some effect of inhibitory action on oxidation.

The asymmetric C—O stretching vibration of saturated aliphatic ether (1157 cm^{-1}), the =C—H deformation of vinylidene hydrocarbon [941 cm^{-1} (in-plane), 813 cm^{-1} (out of plane)], and the =C=C= stretching for vinylidene group (1632 cm^{-1}) which come from TMPTMA indicate the presence of diffused TMPTMA in UHMWPE in Figure 4. The disappearing of the peaks of 941 and 813 cm^{-1} and the decrease in the vinyl double

bond absorption (1632 cm^{-1}) show the reaction of TMPTMA with UHMWPE in the irradiation process.

The phenomena above can be explained by Figures 5–7. Figures 5–7 show the reaction mechanisms of UHMWPE and TMPTMA/UHMWPE in the irradiation process. The crosslinking and degradation mechanisms of polyethylene in an inert atmosphere induced by EB have been widely studied in the previous studies.[26,30,31] The major effects observed are the formation of crosslinks and unsaturation when UHMWPE is irradiated by EB. Crosslinking results in the formation of a three-dimensional chemical network and, consequently, alters the mechanical properties of the polymer. The radiation-induced crosslinking has been shown to be particularly valuable in improving the wear resistance and creep performance of UHMWPE.

The interaction of EB with UHMWPE leads, through a complex energy transfer, to the scission of C—C and C—H bonds, giving H· radicals and primary and secondary macroradicals (reaction 1 and reaction 3, Figure 5). These macroradicals are dispersed throughout the amorphous phases of the polymer and likely in the crystalline phase. Only secondary macroradicals can be detected, then it is assumed that primary macroradicals undergo recombination following reaction 2 (Figure 5) in both amorphous and crystalline phase in the solid state, giving back a C—C bond, with dissipation of energy in the polymer mass. Secondary macroradicals give hydrogen elimination via intra (reaction 5, Figure 5) or intermolecular mechanisms (reaction 6, Figure 5), forming *trans*- and *cis*-vinylene internal double bonds both in the amorphous and in the crystalline phase.

Although the reaction of the formation of H-shaped crosslinks (H-crosslinks) between two secondary macroradicals (reaction 7, Figure 5) is thermodynamically feasible at room temperature, but UHMWPE is in the solid state at room temperature, so the reaction is extremely impossible to happen due to steric hindrance.

UHMWPE is not just a simple sequence of methylenes —(CH_2)—, but it also contains small but measurable concentrations of vinyl double bonds, tertiary carbons, and methyl groups. These short and long chain branches, as well as the residues of the catalyst, are incorporated in the less ordered amorphous phase, not in the crystalline lamellae. Terminal vinyl double bonds can react with secondary macroradicals according to reaction 8 (Figure 5), which leads to the formation of Y-shaped branching (Y-crosslink). Reaction 8 is exothermal,[32] with $\Delta G \approx$ −50 kJ/mol at room temperature, and it is sterically feasible, being similar to the radical polymerization of 1-butene. But when the majority of the vinyl double bonds have been consumed, reaction 8 reaches a plateau for doses higher than 100 kGy.

Because the amount of pendent double bonds cannot be increased during UHMWPE synthesis, the efficiency of crosslinking can be improved by diffusing crosslinking additives which contain reactive double bonds into the polymer.

In this work, UHMWPE diffused with TMPTMA was exposed to the increasing doses of EB. TMPTMA contains three terminal double bonds in one molecule. The reaction of the first vinyl
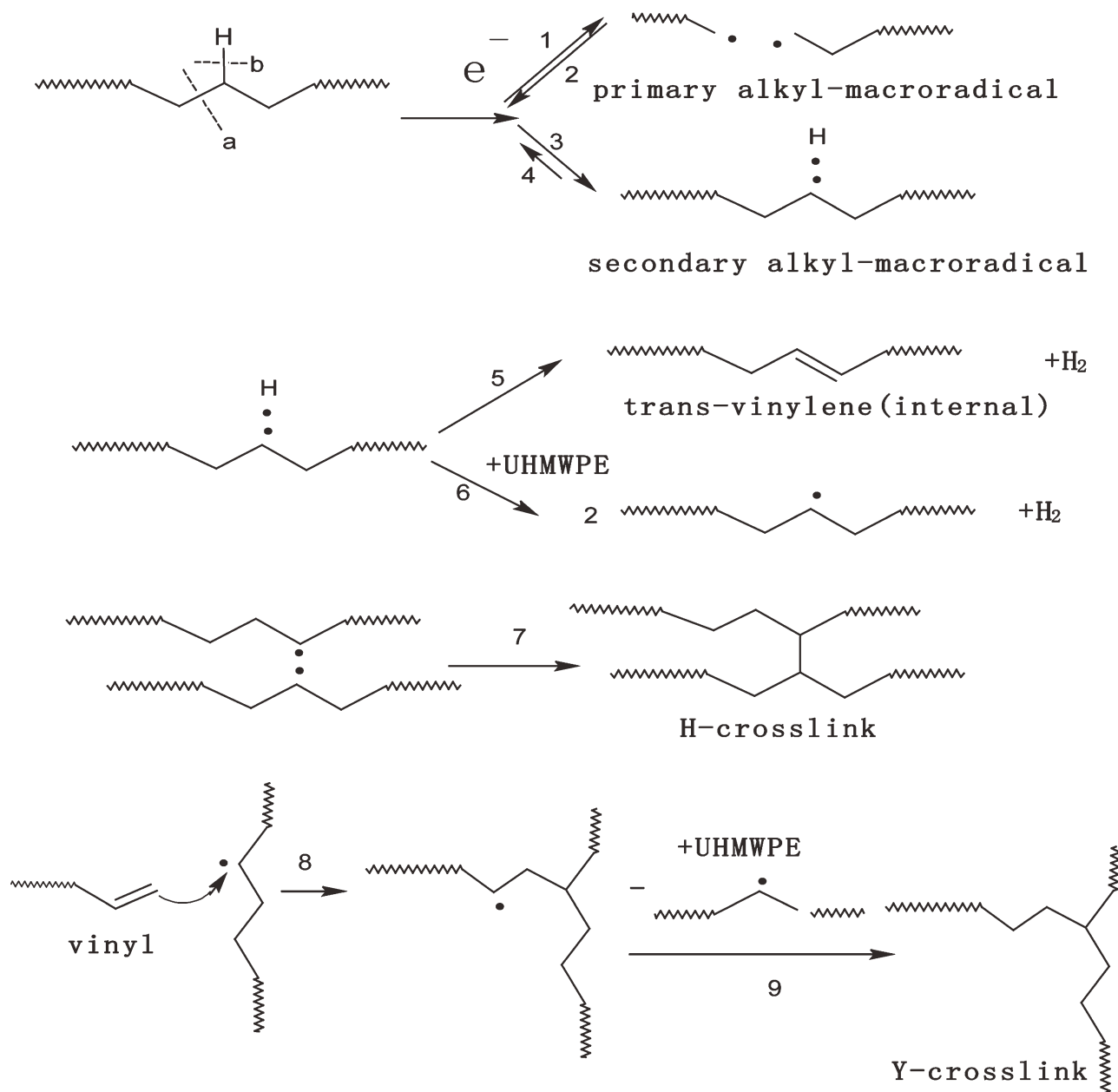
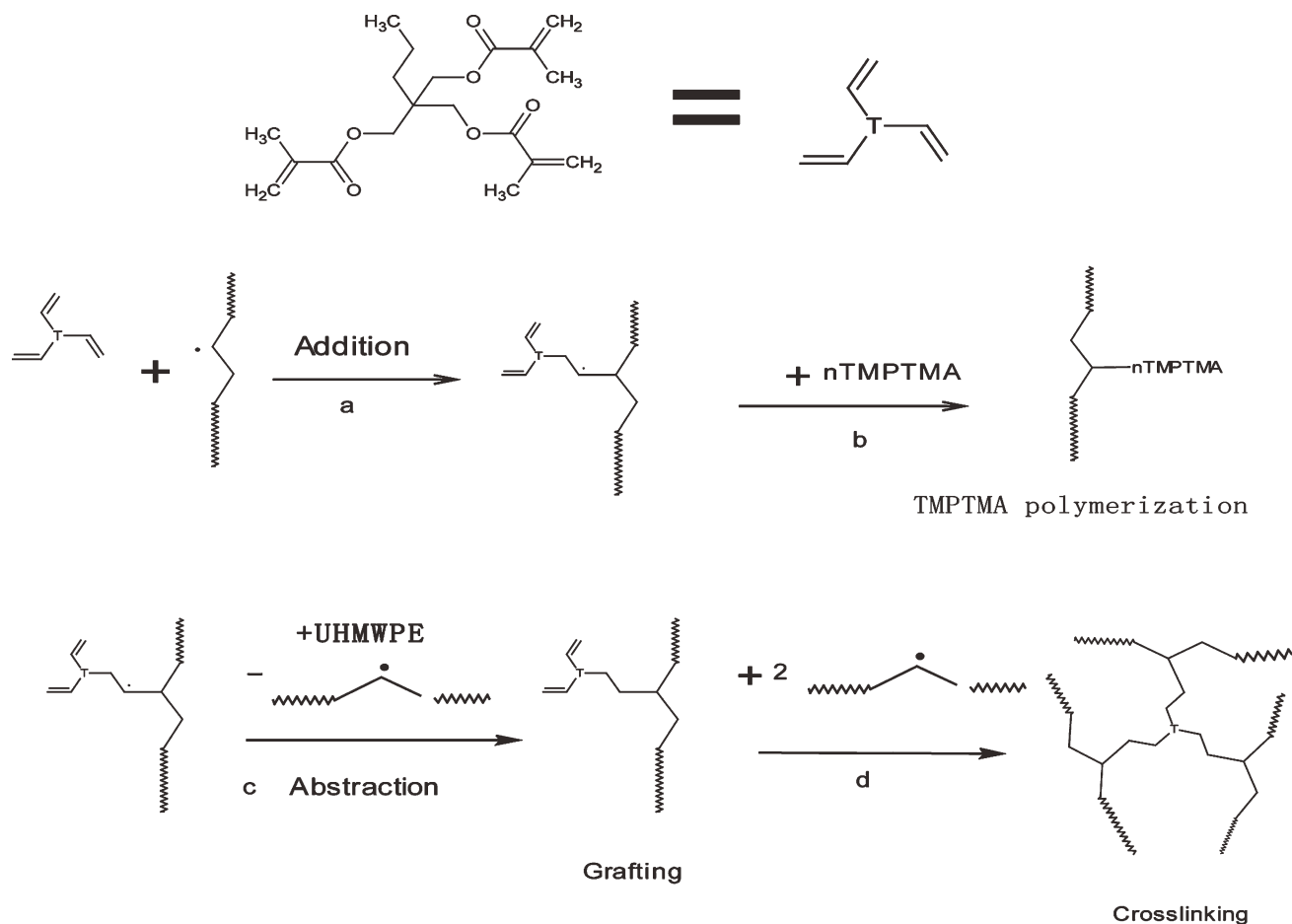**Figure 5.** The reaction mechanism of UHMWPE irradiated by electron beam.

unit results in branching (reactions a, c, Figure 6), whereas the following ones may lead to TMPTMA polymerization (reaction b, Figure 6, impossible because of the steric hindrance) and crosslinking (reaction d, Figure 6). Therefore, the crosslinking degree is dependent on the amount of pendent double bonds in the polymer and on the absorbed dose. So the addition of suitable reactive additives to UHMWPE prior to irradiation leads to an enhancement of crosslinking.

In addition, it has been well acknowledged that irradiation of UHMWPE in the presence of air leads to oxidation of the polymer and, as a result, to a loss of its superior mechanical properties. Oxygen reacts readily with alkyl radicals and forms species such as hydroperoxides, alcohols, acids, ketones, etc which can be explained by Figure 7 (Boland's cycle: oxidation scheme of

hydrocarbons).[33] The oxidation degree can be showed in FTIR (about 1730 cm^{-1}, $=C=O$ stretching vibration).[34] The extent of radiation-induced oxidation increases with the increasing dose and, in addition, with exposure time. If some additives which can increase the crosslinking density or/and reduce the irradiation dose at the same crosslinking density are added to UHMWPE, the oxidation of UHMWPE would be inhibited, so TMPTMA was added into UHMWPE in the paper.

The Effect of Irradiation Dose on Gel, q and M_c of UHMWPE and TMPTMA/UHMWPE

Figure 8 shows the relationship between the irradiation dose and gel fraction of UHMWPE and TMPTMA/UHMWPE. Figure 9 shows the relationship between the irradiation dose and q, M_c of UHMWPE and TMPTMA/UHMWPE.[25,29,35]

Figure 6. The reaction mechanism of TMPTMA/UHMWPE irradiated by electron beam.

All the irradiated samples in Figure 8, even those treated with the minimum dose by EB, are completely insoluble in xylene, indicating that crosslinking took place in all irradiated samples.

Figure 7. Boland's cycle: oxidation scheme of hydrocarbons.

It can be observed that gel fraction of UHMWPE or TMPTMA/UHMWPE increases with the increasing dose before 100 kGy and keeps almost constant with further increasing irradiation dose.
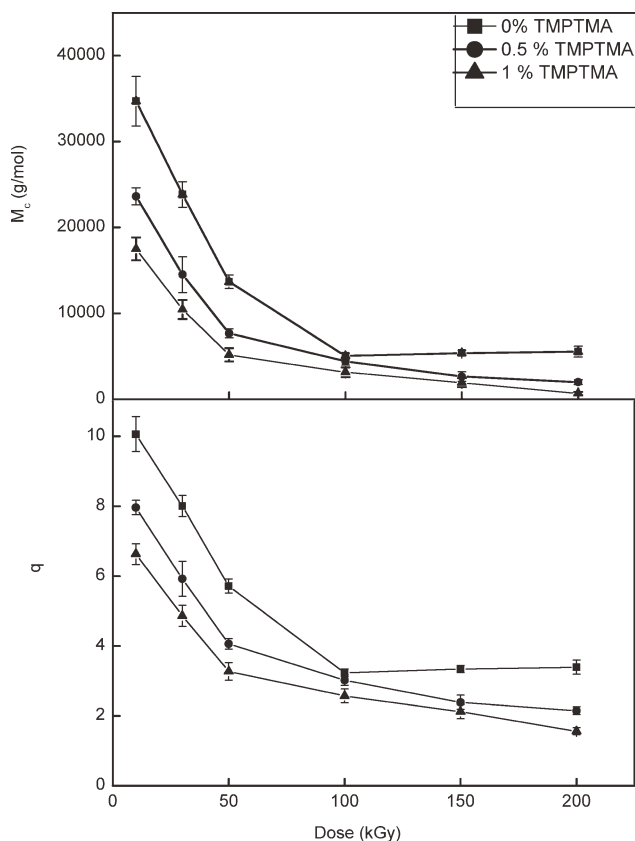
Gel fraction of pure UHMWPE is about a constant (45%) after the dose higher than 100 kGy, and also gel fraction of
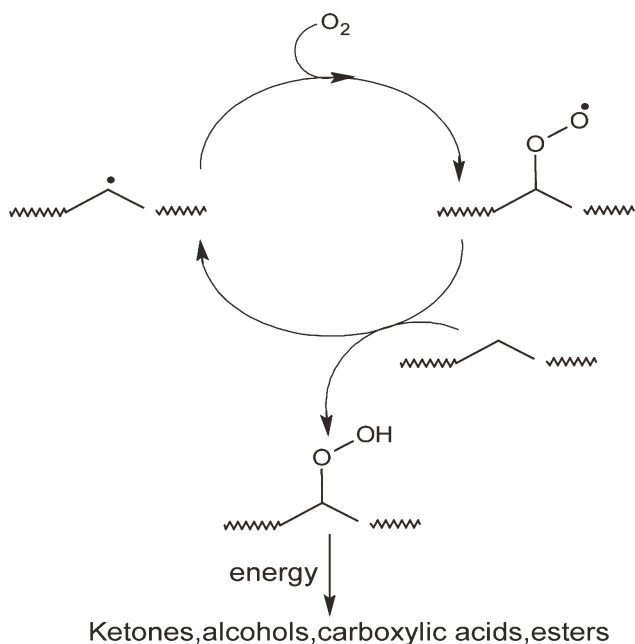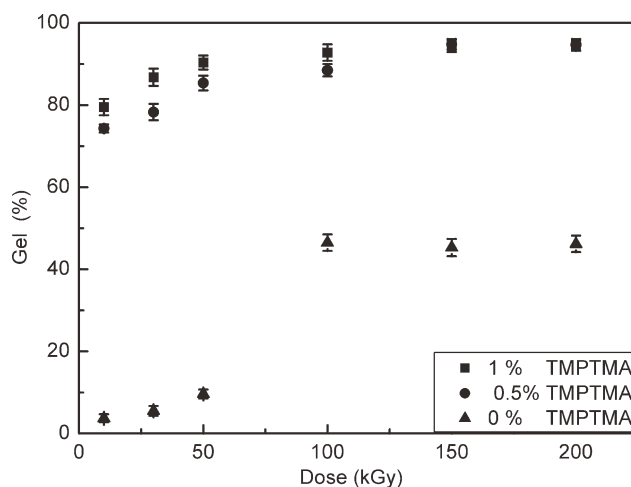
Figure 8. The effect of irradiation dose on gel fraction of TMPTMA/UHMWPE.

Figure 9. The effect of irradiation dose on q and M_c of TMPTMA/UHMWPE.

TMPTMA/UHMWPE (about 95%), indicating the radiosensitizer TMPTMA can promote crosslinking of UHMWPE. The latter is much higher than the former not only at the lower dose but also at the higher dose. In TMPTMA/UHMWPE composites at the same dose, the more the content of TMPTMA, the higher gel fraction, but after 100 kGy, there is less difference at the higher dose, gel fraction is at the same level (about 95%).

As the irradiation dose increases, the concentration of the free radicals increases and, as a consequence, the crosslinking density increases, forming a three-dimensional crosslinked insoluble and infusible network. On the other hand, the swelling ratio (q) decreases rapidly with the increasing dose as shown in Figure 9, meaning that less space between the chains is available for the swelling. The molar mass between adjacent crosslinks (M_c) which is related to the swelling ratio can be calculated by eqs. (2) and (3) through the Flory's network theory from equilibrium swelling experiments using a Soxhlet Extractor. M_c decreases with the increasing dose. The 50 kGy irradiation leads to a molar mass of 13,675 g/mol of UHMWPE between adjacent crosslinks, and M_c of 1% TMPTMA/UHMWPE is 5175 g/mol. An increase in the irradiation dose to 100 kGy causes a further reduction to 5055 g/mol of UHMWPE, and M_c of 1% TMPTMA/UHMWPE is 3141 g/mol which corresponds to about 112 monomeric units.

When the irradiation dose increases to certain dose, gel fraction should equal to 100% and q should equal to 1 if the irradiation

process only has crosslinking. But after certain dose, gel fraction does not go up and keeps a constant value. The phenomenon above demonstrates that crosslinking and chain scission occur in the process simultaneously. The variation of gel fraction and the swell ratio with the increasing dose is due to oxidation-induced chain scission and loosening of the network. In high dose samples, the radical concentration is on the high level, more chain scission reactions are induced and will continue for some time after irradiation. However, considering the fact that the scission reactions are supposed to compete with crosslinking for higher radiation doses, the increase in the extent of cross-linking can be accounted for by the fact that chain scissions lead to entanglement couplings which act as crosslinks. Normally, the main chain degradation is accompanied by crosslinking, however, many factors such as molecular weight, degree of crystallinity, concentration of free radicals, and degree of oxidation, can influence the mechanism. Investigation of such factors is in progress. The tensile stress test results can give some explanation in this article.

Tensile Properties

Figure 10 shows the relationship between the irradiation dose, tensile stress, and elongation at break of TMPTMA/UHMWPE and UHMWPE specimens. An overall decrease in the elongation at break is observed with the increasing irradiation dose. The tensile stress increases at the first stage with the increasing irradiation dose, and then decreases with the increasing irradiation dose. The phenomenon can be explained by the structural
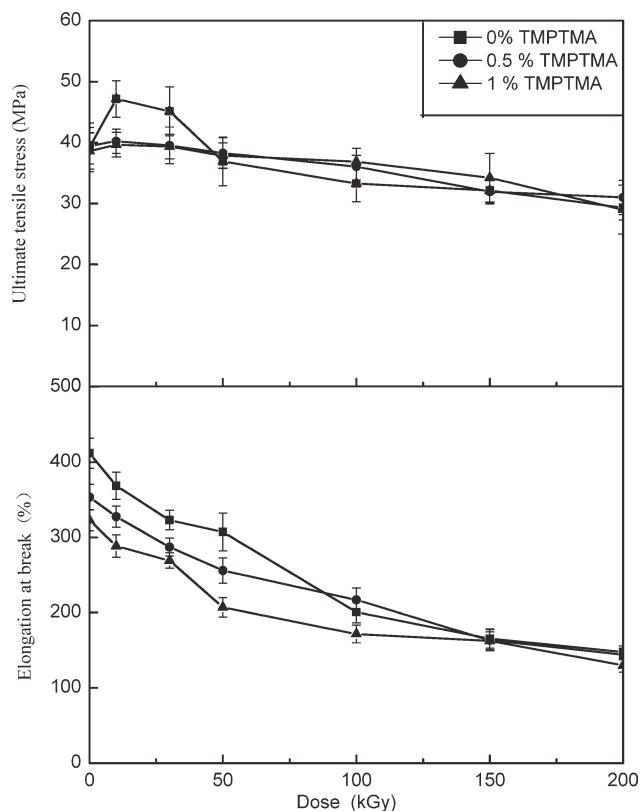
Figure 10. The effect of dose on tensile stress and elongation at break of TMPTMA/UHMWPE.
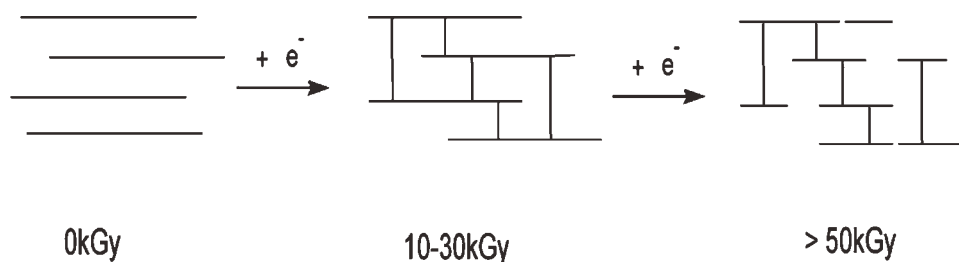
Figure 11. The structural changes of UHMWPE with the increasing doses.

changes of the specimens showed in Figure 11. Figure 11 shows the structural changes of UHMWPE with increasing doses.

In the unirradiated UHMWPE or TMPTMA /UHMWPE, there are no conjunction chemistry band points between the molecule chains. After irradiation by EB, crosslinking and chain scission occur simultaneously in the polymer.

The crosslinking reaction is the main reaction at the low irradiation dose range (show in Figure 11, 10–30 kGy) in UHMWPE, so after 10–30 kGy irradiation, the tensile stress of the irradiated UHMWPE (47 MPa, 10 kGy) is higher than that of unirradiated UHMWPE (39 MPa). The crosslinking reaction can be demonstrated by the increasing gel in Figure 8, and the decreasing M_c in Figure 9.

TMPTMA/UHMWPE composites keep the stress at about 39 MPa and almost have no change of the tensile stress below 50 kGy irradiation. If other factors are not in consideration, the phenomenon can be interpreted by the fact that crosslinking and chain scission take the same effect on the stress of TMPTMA/UHMWPE composites in the irradiation process. But the crosslinking density of TMPTMA/UHMWPE composites increase with the increasing dose showed in Figures 8 and 9, and TMPTMA has plasticization effect on UHMWPE, so the facts both should be considered. After subtracting the plasticization effect of TMPTMA on UHMWPE, the phenomenon should be described as that the crosslinking reaction is the main reaction at the low irradiation dose range (shown in Figure 11, 10–30 kGy) in TMPTMA/UHMWPE composites. The stress of TMPTMA/UHMWPE is lower than that of UHMWPE at the same irradiation dose in Figure 10 referring to that the addition of TMPTMA has plasticization effect on UHMWPE.

After 50 kGy irradiation, the tensile stress of the irradiated UHMWPE decreases with the increasing irradiation dose, and the TMPTMA/UHMWPE composites have the same trend. The phenomenon can be illustrated that the chain scission reaction is the main reaction at the high irradiation dose (show in Figure 11, >50 kGy). In Figure10, although the tensile stress of the TMPTMA/UHMWPE composites decreases smoothly, it is higher than that of UHMWPE at the same irradiation dose.

The tensile stress of TMPTMA/UHMWPE composites is lower than that of UHMWPE before 50 kGy irradiation and then higher after 50 kGy irradiation. The phenomenon can be explained that the plasticization effect weakens the effect of the

crosslinking reaction on UHMWPE before 50 kGy, plasticization effect disappears gradually after the consumption of TMPTMA by crosslinking reaction. The promotion of the crosslinking reaction on UHMWPE by the addition of TMPTMA begins to take more effect after 50 kGy when irradiated by EB.

Although the main chain crosslinking reactions accompanied by the scission reactions are the main changing reasons of the tensile stress and elongation at break in the irradiation process, many other factors such as molecular weight, degree of crystallinity, concentration of free radicals, and degree of oxidation should be taken into consideration. The measurement error should also be considered. Here the main chain crosslinking and scission reactions are concerned mainly in the paper.

Wear Rate

Figure 12 shows the relationship between the irradiation dose and wear rate of 1% TMPTMA/UHMWPE (50, 100 kGy) and the wear curves of irradiated UHMWPE (0, 100 kGy) specimens.

The wear rate of irradiated UHMWPE (at 100 kGy) is about 3.98×10^{-7} mg/Nm which is about half of the rate of unirradiated UHMWPE [7.5×10^{-7} mg/Nm], indicating that the crosslinking method of UHMWPE irradiated by EB is useful to decrease the wear rate.

The wear rate of 1% TMPTMA/UHMWPE (at 50 kGy) is about 1.88×10^{-7} mg/(Nm) which is about 25.1% of the wear rate of
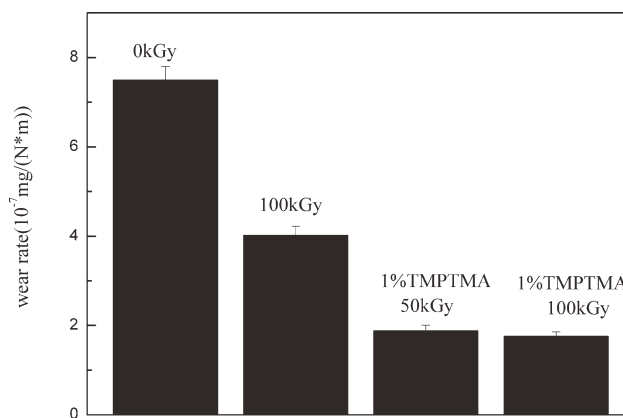
Figure 12. The relationship between the irradiation dose and wear rate of UHMWPE and 1% TMPTMA/UHMWPE.

unirradiated UHMWPE and about 47.2% of the wear rate of irradiated UHMWPE (at 100 kGy), indicating that the addition of TMPTMA into UHMWPE plays an important role and TMPTMA is a promotion of crosslinking in the irradiation process.

Wear rate of 100 kGy 1% TMPTMA/UHMWPE is about 1.76×10^{-7} mg/(Nm), less than wear rate of 50 kGy 1% TMPTMA/UHMWPE [1.88×10^{-7} mg/(Nm)], but it is about 23.5% of wear rate of unirradiated UHMWPE and about 44.2% of wear rate of 100 kGy UHMWPE, which can be explained by gel fraction curves showed in Figure 8. In Figure 8, gel fraction of 100 kGy 1% TMPTMA/UHMWPE is almost as much as that of 50 kGy 1% TMPTMA/UHMWPE. So 50 kGy is enough for the irradiation of UHMWPE with TMPTMA as radiosensitizer. The wear data prove that the addition of TMPTMA into UHMWPE promotes the crosslinking reaction. So when TMPTMA is added into UHMWPE, the irradiation dose can be reduced to get the same crosslinking density. On the other hand, the reduction of the irradiation dose can reduce the oxidation reaction in and after irradiation, indirectly being the protection of the UHMWPE matrix.

CONCLUSIONS

The results of this study confirm that the addition of TMPTMA radiosensitizer which provides three additional vinyl double bonds per molecule into UHMWPE enhances the crosslinking of TMPTMA/UHMWPE compared with pure UHMWPE irradiated by EB. M_c decreases with the increasing dose. The irradiation at 50 kGy led to a molar mass of 13,675 g/mol of UHMWPE between adjacent crosslinks, and that of 1% TMPTMA/UHMWPE is 5175 g/mol. An increase in the irradiation dose to 100 kGy caused a further reduction to 5055 g/mol of UHMWPE, and M_c of 1% TMPTMA/UHMWPE is 3141 g/mol which corresponds to about 112 monomeric units. Gel fraction increases to 95% at 100 kGy, which is higher than that of UHMWPE (about 45% at 100 kGy).

The tensile stress of TMPTMA/UHMWPE composite kept at about 39 MPa before 50 kGy.Wear rate of 100 kGy 1% TMPTMA/UHMWPE is 1.76×10^{-7} mg/(Nm), only 23.5% of wear rate of 0 kGy UHMWPE and 44.2% of wear rate of 100 kGy UHMWPE. So the crosslinking method of UHMWPE irradiated by EB using TMPTMA as radiosensitizer can be used to improve the wear rate of UHMWPE.

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