Radiation enhanced modification of HDPE for medical applications

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Comparison of gamma irradiation induced change in properties in terms of thermal and mechanical properties between two grades of HDPE and UHMWPE was carried out. It was found that the responses to irradiation of two grades of HDPE investigated were close whereas a difference in response was found between HDPE and UHMWPE. The irradiation dose that caused the lowest wear and highest hardness for UHMWPE was 500 kGy. When irradiation dose was above 500 kGy, no significant changes in wear and hardness properties were observed. The irradiation dose for HDPE, both 2208J and 7000F, that caused the wear resistance and hardness comparable to irradiated UHMWPE at 500 kGy was 1000 kGy. In addition, the dose of 750 kGy was needed for HDPE to achieve the similar level of wear resistance as non-irradiated UHMWPE.

1. Introduction

Ultra high molecular weight polyethylene (UHMWPE) is a group of polyethylene that is composed of extremely long backbone chains forming entanglements, which act as molecular defects and pseudo-crosslinks giving UHMWPE excellent toughness. The existence of such entanglements is believed to be the reason for its high wear resistance and toughness [1]. For years, this material has been selected as a material of choice for fabricating bearing surface in various arthroplasties. These components have performed well in clinical use, but concerns about wear and the effect of wear particles on the longevity of the prosthesis has been raised over years.

Improvement of materials to increase wear resistance in terms of process modification, new materials development and sterilization technology have been carried out by many investigators. Crosslinking of polyethylene is a method used to improve the wear resistance and has been received increased interest recently due to the confirmation by many institutions that crosslinking can dramatically reduce wear [2–6]. Crosslinking can be formed by either chemical or radiation technique for example ionizing radiation, peroxide chemistry or silane chemistry. However, radiation crosslinking is probably more flavored since it does not add any chemicals which potentially can cause problems with biocompatibility if the chemical is not treated or stabilized properly [7, 8]. Gamma irradiation which has been used as one of the sterilization methods for medical devices has been reported as a method that can form crosslinks to reduce the wear of UHMWPE if the dose is sufficiently high and the oxidation and amount of free radicals could be prevented or reduced by controlled atmosphere irradiation or thermal treatment [2, 3, 5, 7, 8].

However, due to its high viscosity, processing of UHMWPE has to be carried out with care and controled manner. Manufacturing related defects for example internal inconsistencies or dead zones and non-fused area have been reported for UHMWPE that caused the adverse effect on properties of implant made of UHMWPE [7, 9]. High density polyethylene (HDPE) is of the same family of UHMWPE, but molecular weight is less. Therefore, it is easier to process due to lower viscosity, greater creep resistance, but is less wear resistant. Therefore, the use of HDPE with improved properties as an alternative material has been considered. The study of silane-crosslinked HDPE was reported to improve creep resistance and wear resistance at high sliding velocities under unidirectional and multidirectional motions compared to uncrosslinked UHMWPE [10]. Crosslinked HDPE also shows a higher resistance to crack initiation, but lower resistance to crack propagation [11, 12]. However, improvement of HDPE by irradiation for medical application which is the current technique for increasing wear resistance of UHMWPE is less studied. This investigation is thus aimed to improve the properties of HDPE via crosslinking by gamma irradiation in a vacuum condition followed by thermal annealing to

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TABLE I Properties of raw materials as supplied by manufacturers

Properties	HDPE 2208J	HDPE 7000F	UHMWPE
Density (g/cm^3)	0.962	0.956	0.928
Stress at yield (MPa)	33	28	20–24
Stress at break (MPa)	17	39	32–48
Elongation at break (%)	> 500	> 500	250–400
Modulus (MPa)	1100	1000	703–1054

reduce the amount of oxidation and remained free radicals as a possible alternative for UHMWPE in medical applications.

2. Materials and methods

2.1. Raw materials

Materials used in this study were HDPE (grades 2208J and 7000F, Bangkok Polyethylene Co., Ltd, Bangkok, Thailand) and UHMWPE (Hoechst GUR 4150, Siam Cast Nylon, Co. Ltd, Bangkok, Thailand). HDPE was in the form of pellets while UHMWPE was supplied as ram extruded billet. The properties of materials according to the manufacturers are listed in Table I.

2.2. Sample preparation

HDPE pellets were compression molded into 5 mm thick sheet at 190 °C and then cut into rectangular bars (size $180 \times 25 \times 5\,mm^3$). In the case of UHMWPE, the as-received billet was machined into bars similar to HDPE. All materials were then packed in vacuum sealed polyethylene bags. They were then put into the aluminum container (15 cm in diameter and 18 cm in depth) before placing the container into the chamber of gamma irradiation machine (Gamma cell 220, Office of Atomic Energy for Peace, Bangkok, Thailand) that has approximately dose rate of 7 kGy per hour. Materials were exposed to gamma ray at 250, 500, 750 and 1000 kGy. After irradiation, all materials was then annealed at 120 °C for 2 h to reduce the number of free radicals remaining within the materials.

2.3. Calorimetric measurement

Melting endotherm and crystallinity of the samples were characterized by differential scanning calorimeter (Perkin-Elmer DSC4). The samples were put in aluminum pans and heated from room temperature to 220 °C at the heating rate of 20 °C min^{-1}. The samples were dwelled at 220 °C for 5 min to erase the thermal history and then cooled down to 30 °C. They were reheated to 220 °C for a second cycle. Data were collected continuously and then analyzed by the DSC analysis program. Crystallinity of all polyethylenes were derived from the ratio of the measured heat of fusion of the polyethylene fraction to the heat of fusion for the finite crystals, 293 J g^{-1}.

2.4. Wear test

Wear test was carried out on the pin on disc type machine (Plint TE 79) with load of 20 N at room temperature. HDPE and UHMWPE was employed as a pin with the dimension of 5 mm in diameter and 21 mm in height. The disc was polished stainless steel which was covered by silicon carbide paper that has a roughness of 0.8395 μm. The disc was rolled at various speed, which depend on distance between the center of disc and the pin to keep the contact speed at 0.28 m/s and tested distance at 5000 m. Control pins were also used in order to measure any weight change due to moisture or temperature variation.

2.5. Hardness measurement

The samples were indented at 23 °C/55% RH by using Hardness Tester (Instron-Wolpert Model 930/25) with a ball indenter according to Rockwell R method. The hardness value was calculated automatically via the program in the machine which used load cell and LVDT to measure the force and displacement respectively. Five indentations were made at different parts of the specimens for each test. The values were then averaged.

3. Results

3.1. Thermal properties

In the case of non-irradiated material, UHMWPE showed higher first melting peak temperature than both types of HDPE which showed comparable values of melting temperature, Fig. 1. After exposure to gamma radiation, only UHMWPE showed an increase in melting temperature with increasing dose. Fig. 1 also shows the effect of irradiation on the second melting peak temperature after reheating. It can be seen that all grades of polyethylene showed a decreasing trending with increasing irradiation dose. However, UHMWPE showed more decrease at the similar level of dosage while both grades of HDPE showed similar, but lower degrees of decrease.

The relationship between the degree of crystallinity and dose of irradiation exposure is shown in Fig. 2. It could be seen that HDPE initially had higher degree of crystallinity than UHMWPE. After irradiation, all types of polyethylene showed no change in first heating cycle crystallinity with increasing irradiation dose. The crystal-

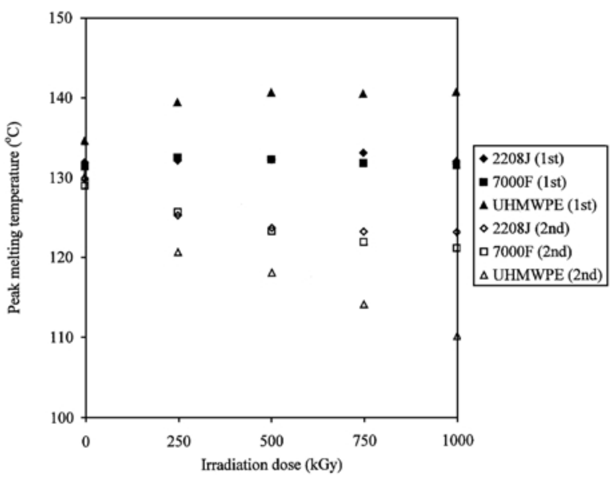

Figure 1 Effect of irradiation dose on the peak melting temperature of polyethylenes (first and second heating).

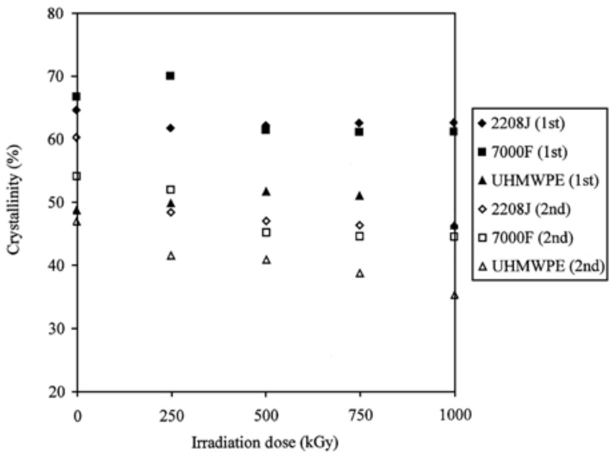

Figure 2 Effect of irradiation dose on the crystallinity of polyethylenes (first and second heating).

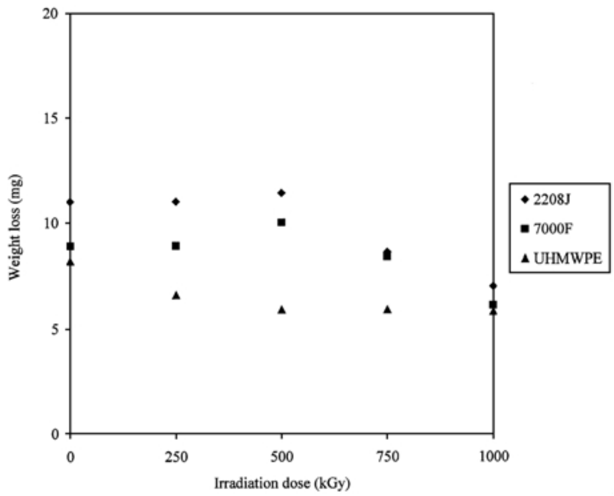

Figure 4 Effect of irradiation dose on the wear performance of polyethylenes.

linity of irradiated HDPE remained higher than UHMWPE. In the second heating cycle, all types of polyethylene displayed a clear decrease in crystallinity with increasing irradiation dose. The degree of decrease seemed to be similar for all materials. The crystallinity of HDPE remained higher than UHMWPE at all dose levels.

3.2. Wear characteristic

Fig. 3 shows the comparison of friction coefficient among three grades of polyethylene. In case of non-irradiated materials, UHMWPE has higher coefficient of friction than both types of HDPE. After irradiation, the friction values of both HDPE slightly increased with increasing irradiation dose. However, the friction of UHMWPE seemed to remain constant independent of the level of irradiation.

Fig. 4 displays the effect of radiation on wear of polyethylene materials after wear test. In the unirradiated state, UHMWPE showed the highest wear resistance followed by 7000F and 2208J HDPE. After irradiation the wear of UHMWPE decreased with increasing irradiation dose and started to level off at the dose of 500 kGy. Further increase in irradiation dose produced insignificant effect on the wear of UHMWPE. In the case of HDPE, both grades did not show any change in wear resistance when the irradiation was less than 750 kGy. However, when the dose was above 750 kGy, the weight loss started to decrease and approached the level of wear of UHMWPE at the dose of 1000 kGy.

3.3. Hardness

Fig. 5 shows the influence of gamma irradiation dose of three different types of polyethylene on the Rockwell hardness values. It can be seen that HDPE grade 2208J showed the highest hardness followed by HDPE grade 7000F and UHMWPE respectively. Increasing irradiation dose results in the increase in hardness for all materials. UHMWPE shows the greatest increase in hardness, approximately 50%, whereas both grades of HDPE show only about 10% increase.

4. Discussion

The comparison of the effect of gamma irradiation on three grades of polyethylene investigated in this study clearly shows the influence of the initial molecular weight and crystallinities. In the case of crystallinity, UHMWPE has lower crystallinity than both grades of HDPE which have comparable crystallinity. After irradiation, all types of polyethylene show insignificant

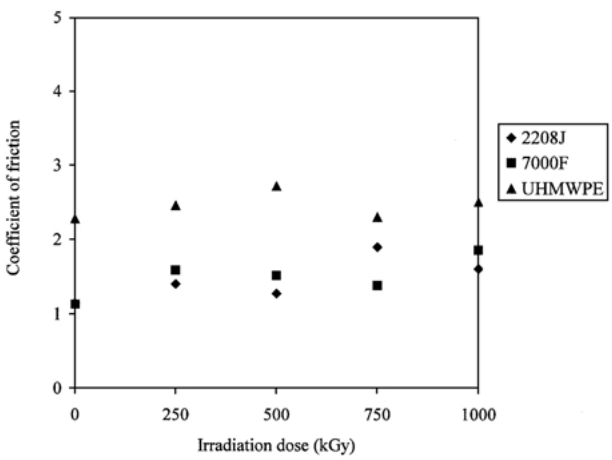

Figure 3 Effect of irradiation dose on the coefficient of friction of polyethylenes.

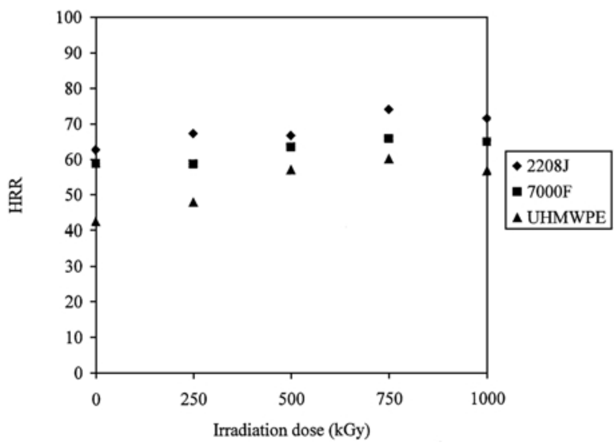

Figure 5 Effect of irradiation dose on the Rockwell hardness of polyethylenes.

changes in crystallinity even at 1000 kGy which is the highest irradiation dose used in this study. This effect is likely due to the fact that irradiation below the melting point allows crosslinks to occur within the amorphous part of the material whereas more radicals are likely to be trapped in its crystalline phases. The radiation did not alter the physical appearance of the crystals, nor did it affect their dimensions. Crystallinity was thus preserved [13]. However, in the case of melting temperature, UHMWPE showed an increase in melting temperature after irradiation, but neither grades of HDPE showed any change. The increase in peak melting temperature of UHMWPE rises instantly at 250 kGy dosage, but leveled off at higher doses. This effect can be explained from molecular mechanism of the scission of tie molecules by high energy irradiation which caused a relief of stress in the crystal to which the tie molecules are attached. This results in the increase in crystal perfection and thus the increase in melting temperature is observed. This effect is greater for polyethylenes which contain more tie molecules. Therefore, the increase in melting temperature of UHMWPE is greater than HDPE [14].

The evidence of crosslink formation can be indirectly approximated by studying the thermal properties of polymers. Crosslinking creates structures that resist alignment into crystalline regions. This also increases the viscosity which will affect the kinetic of crystallization. Therefore, reheating the crosslinked polymers will show decreases in crystallinity and melting temperature of materials in the second heating cycle compared to the first heating since crosslink structure prevents the recrystallization of polymers after cooling from the first heating cycle. The more crosslinks the greater decrease in the crystallinity and melting temperature [14]. It can be seen that UHMWPE showed the greatest decrease in melting temperature in the second heating cycle with increasing irradiation dose whereas HDPE, both 2208J and 7000F, showed less decrease respectively. All polyethylenes also show greater decrease in crystallinity with increasing dose. This signifies that the crosslink structure is formed by irradiation with various amounts depending on the type of polyethylene and irradiation doses.

It was proposed that the formation of crosslinks is the factor that causes the reduction in wear of UHMWPE since the resistance to orientation softening was increased [15]. The difference in amount of crosslinking and efficiency of crosslink formation, thus affect the wear resistance of materials. From thermal analysis by DSC, it can be assumed that UHMWPE has higher efficiency in forming crosslinks when irradiated with Co-60 than HDPE. This is obviously due to the fact that crosslinking occurs mainly in the amorphous region of polyethylene. In polymers with lower initial crystallinity, radiation is much more effective in forming a gel than in samples with highly developed crystallinity [16]. Since UHMWPE is less crystallized than HDPE, it has greater ability to form crosslink.

Although it has been suggested that multidirectional hip simulators can represent better *in vivo* wear profile and resistance value, wear test in this study was carried out on a unidirectional pin-on-disk machine. This was done as a screening and comparative test to simulate the abrasive wear which is one of the crucial wear modes in artificial joints [17]. From the results, although the coefficient of friction of HDPE is lower, UHMWPE has greater wear resistance than 7000F and 2208J HDPE respectively regardless to the non-irradiated or irradiated specimen. However, increasing the irradiation dose did further increase the wear resistance of all materials. Wear of UHMWPE was reduced instantly and then leveled off at doses above 500 kGy. In contrast, wear of both grades of HDPE did not show any decrease at this dose level, but started to decrease evidently after the irradiation dose was 750 kGy. To reach the similar value of lowest wear of UHMWPE in this study, both grades of HDPE need to be irradiated as high as 1000 kGy whereas 500 kGy is needed in the case of UHMWPE. This dissimilarity in the level of irradiation is obviously due to the greater crosslink formation ability and efficiency of UHMWPE compared to HDPE. This range of irradiation is consistent with previous investigations that the lowest wear of UHMWPE was observed at 500–750 kGy [2].

When the comparison is made between non-irradiated UHMWPE and irradiated HDPE to see how much irradiation is required to cause HDPE as wear resistant as non-irradiated UHMWPE which is the materials of choice used to produce joint replacement nowadays, it can be seen that dose of 750 kGy is needed for HDPE to wear at the similar level as non-irradiated UHMWPE. Although 7000F HDPE is more wear resistant than 2208J in non-irradiated state and low irradiation dose, wear at 750 kGy and higher is not different significantly. This may be caused by the crosslinking which has been formed similarly in both HDPEs once the irradiation dose is sufficiently high. Therefore, in the case of HDPE, irradiation above 750 kGy was needed to improve its wear property approaching the property of UHMWPE.

Not only wear resistance property is important for the improvement of bearing surface for joint replacement materials, other properties are also needed to be studied so the change will not adversely affect the working of such materials. It has been reported that although the wear resistance of UHMWPE can be reduced by irradiation induced crosslinking, the increase in brittleness of irradiated UHMWPE is commonly found. Decrease in tensile strength and elongation at break, but increase in hardness were observed when UHMWPE was irradiated [2, 5, 7]. These trends were also observed in this study as well for UHMWPE. Rockwell hardness of UHMWPE was increased 50% after irradiation dose of 500 kGy. Higher doses did not cause significant change further. In contrast, hardness of both grades of HOPE only slightly increased after irradiation, approximately 15%. This result can be interpreted that HDPE becomes less hard and possibly less brittle when irradiated compared to UHMWPE which can be the advantage of HDPE in irradiation improvement.

5. Conclusions

Wear property of HDPE could be improved by gamma irradiation at different doses to approach the similar level of non-irradiated and even irradiated UHMWPE with limited change in hardness compared to UHMWPE. However, higher irradiation dose was needed for HDPE due to its higher initial crystallinity which retard the crosslink efficiency. Further studies in other aspects, however, are needed to ensure the possibility of implementing HDPE which is easier to be processed and higher creep resistance as an alternative for UHMWPE in medical applications.

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