Proceeding of the Korean Nuclear Society Spring Meeting
Kori, Korea, May 2000

Radiation Crosslinking of Ultra High Molecular Weigh Polyethylene

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ABSTRACT

The effect of g-irradiation on the thermal and mechanical properties of ultra high molecular weight polyethylene (UHMWPE) used in orthopedic implants was investigated. UHMWPE was recrystallized with different cooling conditions for the purpose of enhancing the crosslinking extent of the polymer after g-irradiation. UHMWPE was irradiated with gamma ray to a dosage of 10 kGy to 500 kGy in air and nitrogen atmosphere. Differential scanning calorimetry, tensile characterization, creep deformity and wear were examined to determine the mechanical properties of the irradiated UHMWPE specimens. The crystallinity of the irradiated samples was increased with irradiation dose. The irradiated UHMWPE after recrystallization in a quenching condition had a higher crosslinking extent compared with the irradiated UHMWPE after slowly cooling. The irradiated UHMWPE after quenching had a lower wear rate than the irradiated UHMWPE after recrystallization in a slowly cooling condition, and the wear rate of UHMWPE decreased with irradiation dose up to 250kGy, which showed about 40% of the wear rate of nonirradiated UHMWPE.

INTRODUCTION

Ultra high molecular weight polyethylene (UHMWPE) is currently the polymer most often used in orthopedic prostheses. Its primary application has been in the acetabular cup component of the total hip replacement, but it has also found extensive use as a bearing surface in knee, ankle, shoulder, wrist prostheses, and as a prosthetic cruciate ligament (Grood et al., 1976). UHMWPE is the current material for use as a bearing surface in total joint replacements. Also although bulk UHMWPE is considered the biocompatable polymer, wear debris that is released into the tissue immediately surrounding the biomaterial can cause a foreign body reaction. Although the short-term function of UHMWPE implants is satisfactory, their long-term performance has been a concern for many years. UHMWPE is a viscoelastic material, and the problems with the polymer originate from some of its inherent weaknesses like creep and fatigue compared with the metal stem and the cortical bone. Therefore , the wear and creep of such articulating materials must be reduced for improving long-term device performance, for more active patients. To date, the generally suggested approaches to increase the mechanical properties of UHMWPE have been several categories such as crosslinking and composite technology. Carbon fiber was used to reinforce UHMWPE to reduce its creep deformation. However, examination of carbon fiber-reinforced polyethylene surfaces revealed that the composite had no advantage over the plain polyethylene surface, since surface unevenness from the protruding carbon fibres was also observed in the new materials. Meng Deng et al. investigated the physical properties of UHMWPE fibre/UHMWPE matrix composites. It was found that the tensile strength and modulus, and creep resistance were significantly increased after incorporating UHMWPE fibers into a UHMWPE matrix. However, the wear properties of the composites were found to be similar to plain UHMWPE (Deng M, 1997).

It is well known that there exists serious chain entanglements within UHMWPE, which causes the morphology of UHMWPE to be different from that of conventional linear polyethylene. γ-irradiation introduces free radicals into polyethylene(Dole, 1972). These free radicals can in turn lead to cross-linking and chain scission of the polymer. The dominance of one of these mechanisms over the other is highly dependent upon the radiation environment. It is suggested that radiation-induced crosslinking primarily occurs in the amorphous region and forms an insoluble network to an extent dependent on the contact

between the crystalline lammellae. Efforts to solve the wear problem in UHMWPE have spurred numerous studies into the structure, morphology, and mechanical properties of the polymer at every stage of its production from original resin into stock material and final fabricated form. But scientific developments to improve the wear resistance of the polymer are therefore increasingly necessary. Shen et al. reported that chemical crosslinking of UHMWPE led to a reduction on crystallinity and to a marked improvement in wear(Shen et al., 1996). High pressure crystallization was employed to produce UHMWPE components with an increase in mechanical properties such as yield stress and Young's modulus (Li and Howard, 1991). However, this material, known as Hylamer (DePuy-Dupont Orthopaedics, Newark, DE), has again not shown any improvement in laboratory wear tests(McKellop et al., 1992) despite enhanced creep resistance and an increase in resistance to fatigue crack growth(Champion et al., 1994). Clinical results also indicate that Hylamer does not demonstrate increaesd resistance to wear in total-hip-replacement prostheses compared with conventional UHMWPE(Chmell et al., 1996). Oonishi reported that wear tests using a hip simulator test machine were performed on crosslinked UHMWPE cups irradiated with widely different levels of γ–irradiation up to 10000 kGy. This result was that the more crosslinking the better wear resistance in UHMWPE.(Oonish et al, 1992). Then there is a question what is the result of combined adverse oxidation effect and advantageous crosslinking effect on the wear performance. Though high level of γ-irradiation process enhances the level of crosslinking but the oxidation continues as the aging time increases and this progressive oxidative degradation. (Lee, 1999). These conflicting results imply that the effects of γ-irradiation on the wear and on the microstructural changes in UHMWPE are not clearly known. So in this study, the radiation process of UHMWPE was investigated to elucidate clearly radiation crosslinking effect on the wear of prostheses. The structure of polyethylene is well known to be variable according to the processing method, such as cooling conditions which is related to the formation of the crystallinity. So in the present work, UHMWPE was recrystallized with different cooling conditions for the purpose of enhancing crosslinking extent of the polymer after γ-irradiation. The purpose of the present study is to investigate the effects of the γ-irradiation on the mechanical properties of UHMWPE, irradiated at a dose of up to 500 kGy.

EXPERIMENTAL

Materials

Material used in this study was UHMWPE supplied by Saxin corporation, Japan in sheet form. The molecular weight of UHMWPE was 5.5 million. The dimensions of UHMWPE samples were 250 mm in length, 20 mm in width and 2 mm in thickness.

Processing

UHMWPE specimens were melted in a oven at 180 ℃. For slowly cooled samples, the oven was allowed to cool to room temperature over a period of three hours. Quenched samples were obtained by dropping the molten samples into a pool of water.

g- irradiation procedure

UHMWPE samples were irradiated by γ–ray to total doses of 10, 120, 250 and 500 kGy at a dose rate of 3.0 x 10^3 Gy/hr at room temperature in two different environments; namely, nitrogen and air. The nitrogen gas environment was created by evacuating and filling an aluminum container sealed with silicon rubber with nitrogen through a needle.

Relative crystallinity

The relative crystallinity of the specimen was measured using differential scanning calorimetry(DSC) (DSC-7 Series Thermal Analysis System, Perkin Elmer). Heating runs were conducted from 50℃ to 200 ℃ at a rate of 10 ℃/min in nitrogen. The weight of the sample was around 9 mg. Heat of fusion was obtained by integrating the area under the endothermic peak. The percentage crystallinity of specimen was determined by assuming a value 288 J/g for the heat of fusion for a fully crystalline polyethylene material.

Crosslinking measurement

Percentage of crosslinking was determined by measuring the insoluble content using the extraction method. Samples were extracted with boiling xylene, for 72hr, then washed with ethanol and were dried

under vacuum at 80°C to a constant weight.

Polymer surface analysis

Surface oxidation on the UHMWPE samples before and after irradiation was verified by Fourier transform infrared spectroscopy in the attenuated total reflectance mode (FT-IR-ATR) and electron spectroscopy for chemical analysis(ESCA). ESCA for verifying the presence of peroxide onto UHMWPE by irradiation was performed with a V. G. SCIENTIFIC ESCALAB MK II spectrometer using MgKα X-ray radiation at 1253.6 eV operating at 10^{-9} mbar and photoelectron takeoff angles of 60 degrees. The control and irradiated UHMWPE samples were cut to form 6 mm disks, and then were introduced into the UHV spectrometer chamber. MgKα radiation was used with an analyzer operating at a constant band pass energy of 20 eV. The spectrometer was calibrated by assuming the binding energy of the Au $4f_{7/2}$ line to be 83.9 eV with respect to the Fermi level. Survey scans (0 to 1200 eV) were recorded for each sample to obtain a qualitative elemental analysis. Following spectra acquisition, peak identification and quantification were achieved using V. G. SCIENTIFIC ESCALAB package software. High resolution spectra for the carbon-1s and oxygen-1s were also obtained and computer curve-fitted employing a Gaussian model, using the same package software, to obtain the best binding energy values. To take into account some shifting caused by charging of the sample surface, all spectra were adjusted taking the carbon-1s peak at 284.6 eV as reference for the adventitious carbon contamination.

Mechanical characterization

Tensile test

The irradiated UHMWPE and the control were subjected to tensile mechanical testing following ASTM standard D638(Jacobs et al, 1992). The tensile properties of the samples at room temperature were evaluated using an Instron universal mechanical tester (Model 1130), 1 week after γ–irradiation. A crosshead speed of 100 mm/min and a gauge length of 50 mm were used. The specimen load was sensed by a 500 kg capacity Instron Type-A load cell. This cell was mechanically calibrated by precision standard weights prior to testing each set of samples. From these experiments, tensile strength and elongation of all the samples were obtained. An average of 5 specimens were tested. All tensile tests were run under time mode.

Creep test

Creep tests in compression were performed on plain UHMWPE by using a digital indicator of monitoring central deflection as shown in Figure 1. Rectangular specimens, 2 mm thickness by 20 mm width, were mounted on supports 85 mm apart. A central load of 0.037 MPa was applied to the specimens. The creep test lasted 1800 sec for compressive creep.

Wear test

As shown in Figure 2, the ball-on-flat reciprocating type testing apparatus was used to test wear. A stainless ball of 6.35mm diameter was used for the ball-on-flat reciprocating type testing apparatus. The surface of UHMWPE specimen was polished. All tests were done under a contact pressure of 0.33 MPa for 72 hr (777,600 cycles) with water as lubricant. The sliding distance was 1.4×10^4 m. In this study, the wear rate was determined by penetration depth of an indentor into the polymer as defined in eq.(1).

Wear rate (mm $.m^{-1}$)
= Penetration depth / Sliding distance (1)

The digital indicator of monitoring central deflection was used to measure the penetration depth of an indentor of the UHMWPE specimens.

RESULTS AND DISCUSSION

Influence of radiation on percent crystallinty of UHMWPE

UHMWPE has both a crystalline and an amorphous region. Unlike the short chain lengths of high-density polyethylene, the long chain lengths of UHMWPE hinder the ability of the molecules to order themselves into crystalline arrays, thus limiting the crystalline percentage. The crystallinity can be easily

calculated with the use of differential scanning calorimetry. The peak temperature corresponds to the melting of the material, and the area under the curve in the heat of fusion of the material. The heat of fusion(H_f)of 100 percent crystalline polyethylene has been reported to be 288 joules per gram. Therefore, the crystallinity percentage can be calculated by the equation of (H_f of sample/288) x 100.

It is known that the crystalline regions of any polymer form lamellae, which may organize further to form larger structures called spherulites. The lamellae of UHMWPE are composed of folded polyethylene chains. Following irradiation, the melting behavior was studied by differential scanning calorimetry. Figure 3 shows the percent crystallinity of the UHMWPE sheets which were recrystallized under slowly cooling and quenching conditions, and then irradiated to various doses under nitrogen or air atmosphere. From calorimetry, the crystallinty of the non-irradiated samples recrystallized under slow cooling and quenching was 52%, 40%, respectively. The percent crystallinity of UHMWPE which was irradiated by γ-ray in the presence of air, increased much more with an increase in radiation dose up to 500 kGy, comparing with specimens irradiated in nitrogen atmosphere. In addition to crosslinking during exposure to ionizing radiation, polyethylene undergoes chain scission under certain conditions, as in the presence of oxygen. As a consequence, the crystallinity of UHMWPE increases as the scission of tie molecules permits polymer chains in noncrystalline regions of the polymer to fold and crystallize, as well as to allow increasing perfection of existing folded-chain crystallites. It was suggested that irradiation-induced scission of tie molecules permits recrystallization of broken chains from the noncrystalline regions, and results in an increase in the degree of crystallinity and an increased perfection of existing folded chain crystallites.

As a result of its very high molecular weight, the crystallinity of UHMWPE is much lower than is typical of linear polyethylene i.e. ca 75%. This is attributed to the large number of entanglements present in UHMWPE. Because UHMWPE has a high rate of crystallization, the long entangled chains of UHMWPE do not have sufficient time to disentangle and fold into the growing crystallites, thereby resulting in a larger number of tie molecules and entanglements in the amorphous region between crystallites. There is a concomitant reduction in the number of loose chain folds in the crystallites of UHMWPE compared with those of HDPE.

Influence of radiation on cross-linking of UHMWPE

Polyethylene, when exposed to high energy irradiation, is a crosslinking type polymer, and the formation of the intermolecular links is very common. These crosslinks form mainly in the amorphous region in the polymer, possibly the crystal fold surface and also in the crystallites. Radiation-induced cross-linking had been suggested to occur preferentially at the fold surfaces of folded-chain lamellae or in the amorphous phase of bulk materials. As shown in Figure 4, The degree of crosslinking, as measured by the gel fraction, remaining after boiling in solvents like xylene, which can be achieved by a given radiation dose in the polymer, depends on the irradiation condition. The irradiation in nitrogen gave a positive effect on gel content compared with the polymer irradiated in air. In the presence of oxygen, it can diffuse into the polymer material and continuously feeds oxidative degradation reactions. Thus the crosslinking yield is reduced. At 500 kGy, insoluble contents of 98% are formed in the rapidly quenching state. Whereas insoluble contents formed in the slowly cooled condition are 90%. The inert gas packaging eliminates radiation induced oxidative-degradation and also maximizes the free radical recombination process, leading to an increased level of crosslinking.

The reason why the higher crosslinking percent was made in the quenched UHMWPE can be attributed to that radiation-induced crosslinks are formed essentially in the amorphous regions in UHMWPE.

The changes in the chemical structure of UHMWPE with irradiation were examined by FTIR-ATR and ESCA. Oxidation was characterized by analysis of the carbonyl peak located between 1689 and 1756cm^{-1}. Figure 5 shows the FTIR-ATR spectra of control and UHMWPE irradiated in nitrogen atmosphere after quenching. The stretching peaks of the carbonyl group(>C=O) at 1730 cm^{-1} increased slightly with increasing radiation dose. The intensity of carbonyl group of UHMWPE irradiated in air environment after quenching was stronger than that of UHMWPE irradiated in nitrogen as shown in Figure 6 This means the much more oxidation occurs in UHMWPE irradiated in air environment compared with that irradiated in nitrogen environment.

Figure 7 shows ESCA survey scan spectra of control and UHMWPE which was irradiated in nitrogen and air environment after recrystallization under quenching. Carbon-1s spectra of the surfaces for each

UHMWPE was investigated by using ESCA(Figure 7). The C1s spectra data are resolved into four characteristic peaks. The peaks at 288.6, 287.3, 286.3, and 284.6 eV on the surfaces of the samples indicate the functional groups of COO, C=O, C-O and C-C. The oxidation onto the UHMWPE surface was also detected by an increase in the C-O, C=O and COO contribution. The intensity of the C-O peak relative to the C-C peak was seen to increase with the irradiation dose of the sample. From the results of Figure 5-7, it was found that the degree of irradiation-induced oxidation was influenced by the irradiation condition and dose.

Influence of radiation on physical properties of UHMWPE

Figures 8, 9 show the tensile strength and elongation at break when UHMWPE sheets were recrystallized under slowly cooling and quenching conditions, and then irradiated up to 500 kGy under nitrogen and air. As shown in Figure 8, UHMWPE irradiated in nitrogen after recrystallization in slowly cooling conditions had higher tensile strength compared with the irradiated UHMWPE after quenching. It can be contributable to the higher cristallinity in slowly cooling conditions. Its tensile strength increases with increasing irradiation doses up to 120 kGy, but then it gradually decreased with increases in radiation dose, and levelled off. On the other hand, the tensile strength of UHMWPE recrystallized in rapidly quenching conditions increased continuously with the radiation dose. The elongation at break decreased owing to the increase in cross-linking structure of polymer chains as irradiation dose increased. The tensile properties of irradiated UHMWPE were similar regardless of irradiation conditions, i.e. in nitrogen and air atmosphere(Figures 8,9).

Figure 10-11 showed the results of creep tests after UHMWPE specimens were recrystallized under slowly cooling and quenching conditions, and then irradiated to various doses under nitrogen or air atmosphere. The amount of compressive creep was determined by monitoring the central deformation of specimen when a central load of 0.037 MPa was applied to the specimens during1800sec. In general, the vertical positions of the curves indicate the elastic response of the materials, and slopes of the curves indicate the creep response. The deflection rate of the irradiated specimen decreased in proportion to the radiation dose.

Effects of the irradiation dose on wear rates were examined after UHMWPE specimens were recrystallized under slowly cooling and quenching conditions, and then irradiated to various doses under nitrogen or air atmosphere(Figure 12,13). Results showed that a linear wear rate of irradiated UHMWPE decreased with irradiation dose up to 250 kGy regardless of the irradiation condition. However, UHMWPE irradiated under the nitrogen environment had a lower wear rate than UHMWPE irradiated under air environment. The least wear rate was obtained when UHMWPE specimens were recrystallized under quenching conditions, and then irradiated under nitrogen atmosphere. The wear rate decreased with irradiation dose up to 250kGy, which showed about 40% of the wear rate of non-irradiated UHMWPE. This result might be attributable to its high cross-linking extent. The data of wear rates were in a good agreement with the results of the percentage of cross-linking. These results indicate that prostheses made from UHMWPE crosslinked by radiation will have mechanical properties that resist against mechanical deformation and abrasion. Creep has been shown to be a major component of the total deformation (wear plus creep) occurring in UHMWPE acetabular cups.

CONCLUSIONS

UHMWPE was recrystallized with different cooling conditions for the purpose of enhancing crosslinking extent of the polymer after γ-irradiation. UHMWPE was irradiated with gamma ray to a dosage of 10 kGy to 500 kGy in air and nitrogen atmosphere. Differential scanning calorimetry, tensile characterization, creep deformity and wear were examined to determine the mechanical properties of the irradiated UHMWPE specimens. The crystallinity of the irradiated samples was increased with irradiation dose. The irradiated UHMWPE after recrystallization in a quenching condition had a higher crosslinking extent compared with the irradiated UHMWPE after recrystallization in a slowly cooling condition. The irradiated UHMWPE after quenching had a lower wear rate than the irradiated UHMWPE after recrystallization in slowly cooling condition, and the wear rate of UHMWPE decreased with irradiation dose up to 250kGy, which showed about 40% of the wear rate of nonirradiated UHMWPE. From these experimental results, we expect that a

novel UHMWPE having the enhanced crosslinking extent after γ-irradiation will be used to extend the useful life of artificial joints.

Acknowledgement
This present work was supported by the Nuclear R&D Program from Ministry of Science & Technology, Korea.

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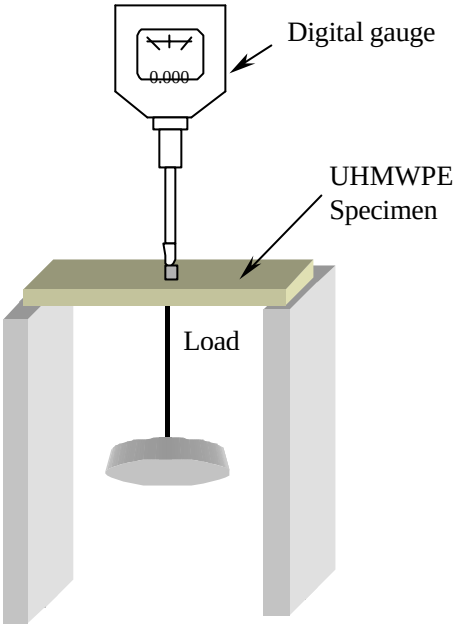

Figure 1. Schematic diagram of the creep testing apparatus.

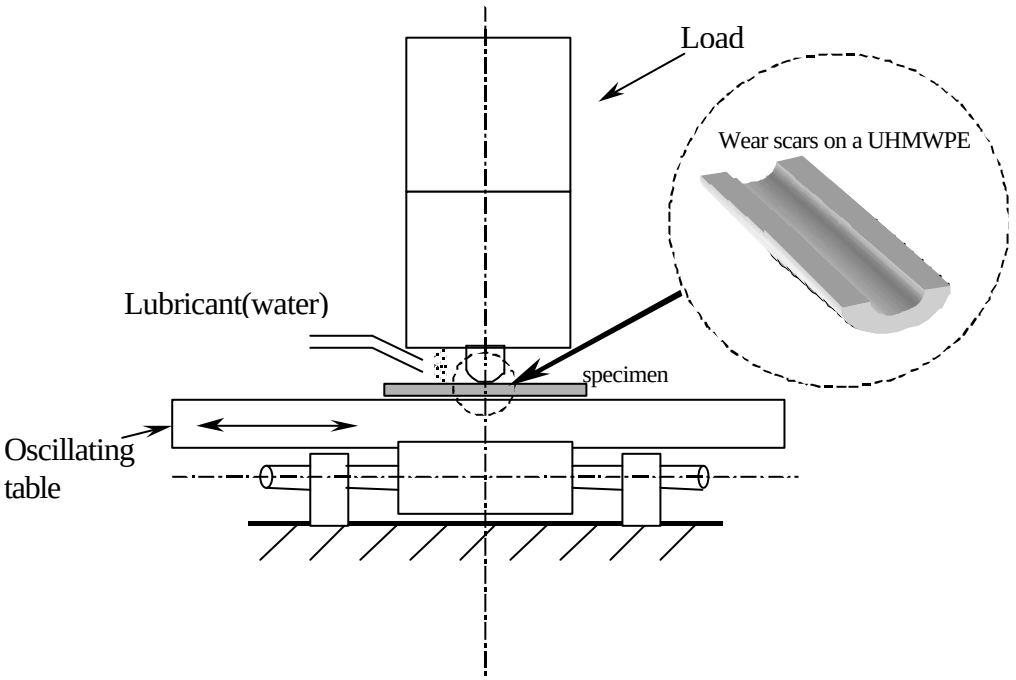

Figure 2. Schematic diagram of the ball-on-flat reciprocating type wear testing apparatus.

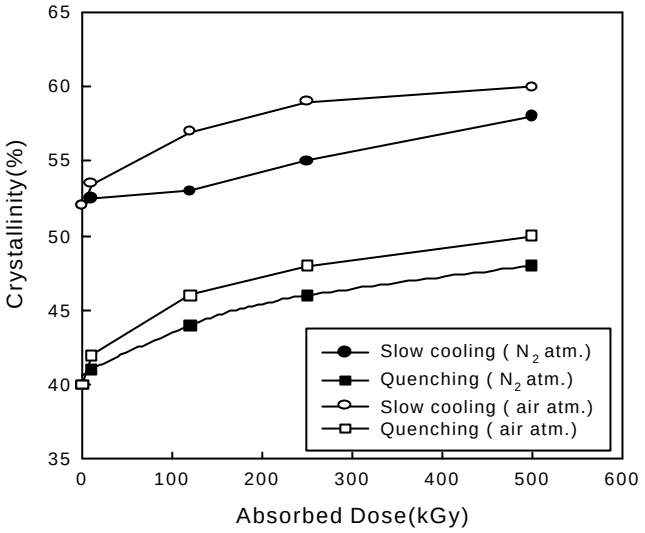

Figure 3. Effects of irradiation on crystallinity of the UHMWPE recrystallized under slow cooling and quenching conditions and irradiated in nitrogen or air atmosphere.

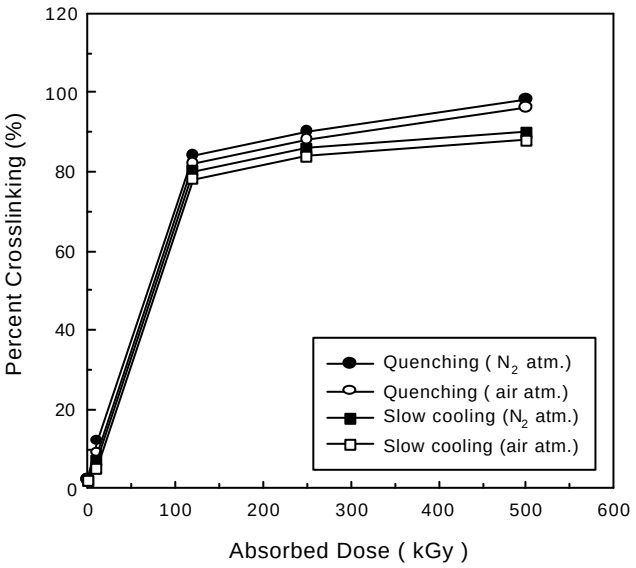

Figure 4. Effects of irradiation on the crosslinking of the UHMWPE recrystallized under slow cooling and quenching conditions (irradiated in nitrogen or air atmosphere).

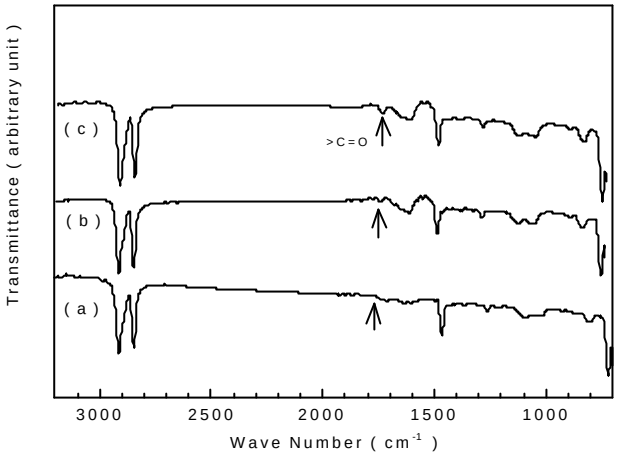

Figure 5. FTIR-ATR spectra of (a) UHMWPE-control, (b) UHMWPE-120 kGy irradiated in nitrogen and (c) UHMWPE-250 kGy irradiated in nitrogen after quenching.

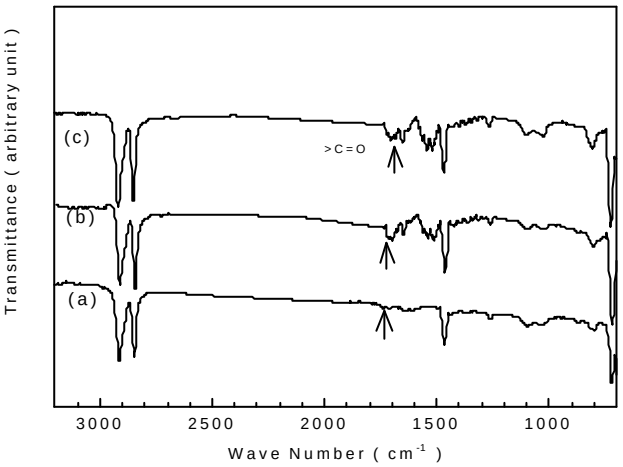

Figure 6. FTIR-ATR spectra of (a) UHMWPE-control (b) UHMWPE-120kGy irradiated in air (c) UHMWPE-250kGy irradiated in air after quenching.

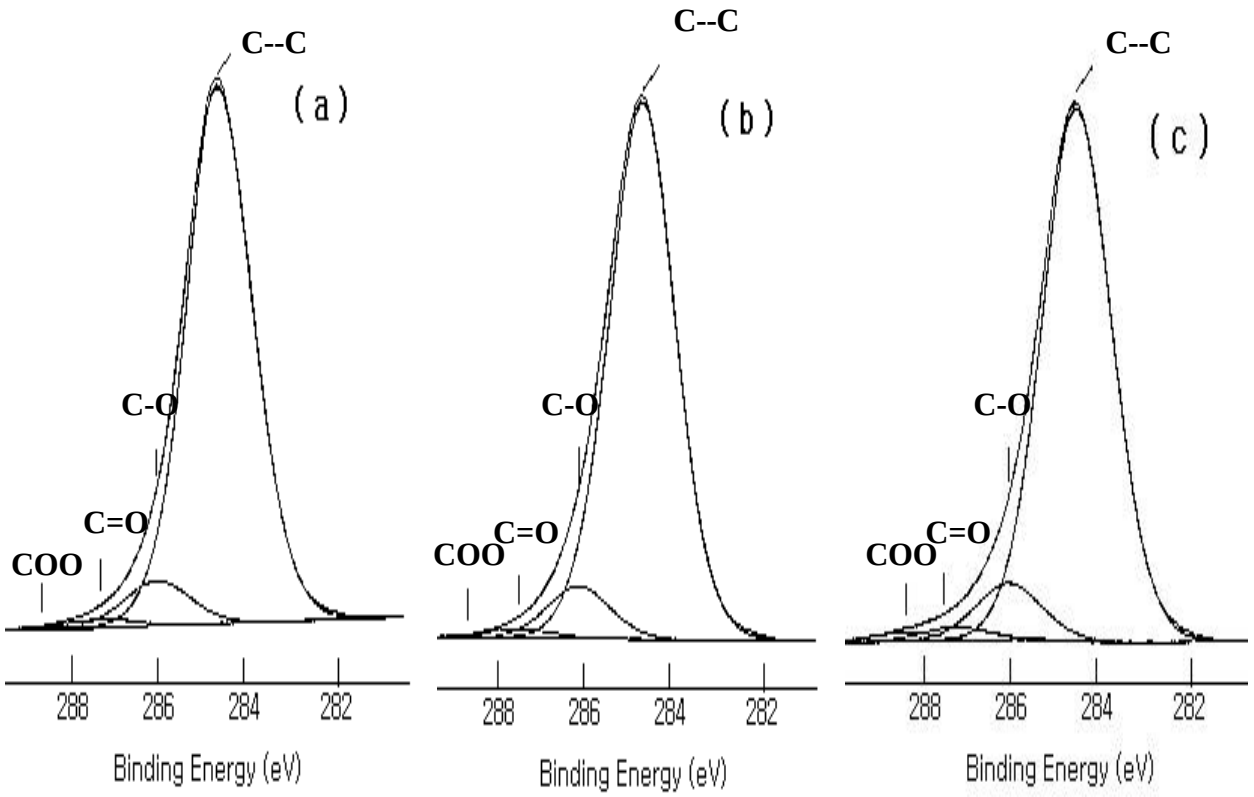

Figure 7. ESCA spectra of carbon 1s core level scan spectra of (a) UHMWPE-control (b) recrystallized-UHMWPE-quenching-120kGy-N_2 (c) recrystallized-UHMWPE-quenching-120 kGy-air.

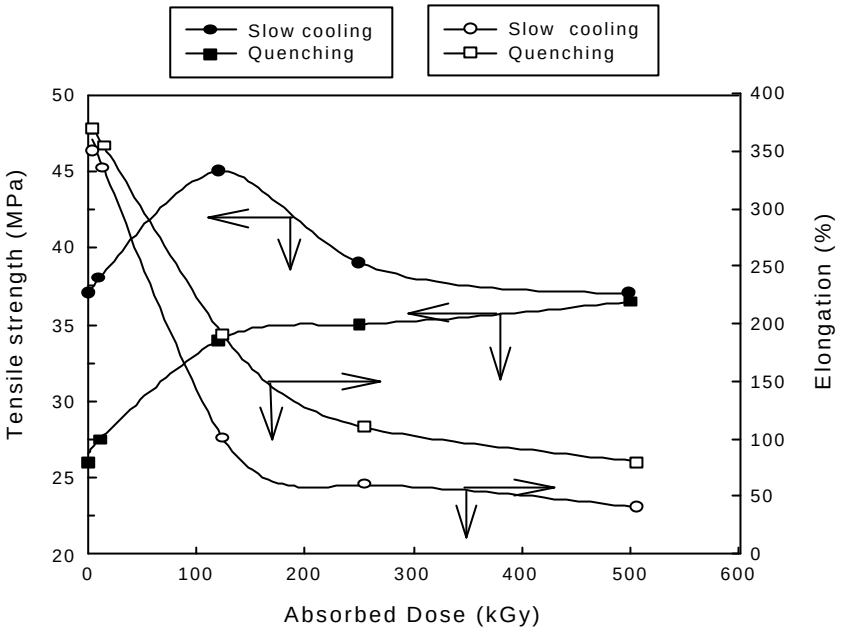

Figure 8. Effects of irradiation on tensile strength and elongation of UHMWPE recrystallized under slow cooling and quenching conditions (irradiated in nitrogen).

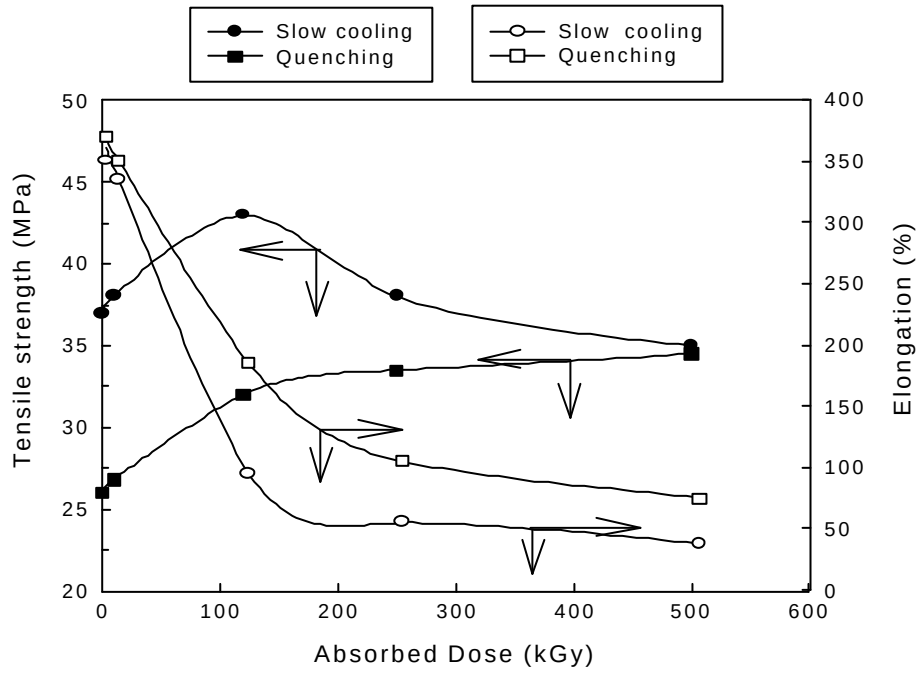

Figure 9. Effects of irradiation on tensile strength and elongation of UHMWPE recrystallized under slow cooling and quenching conditions (irradiated in air).

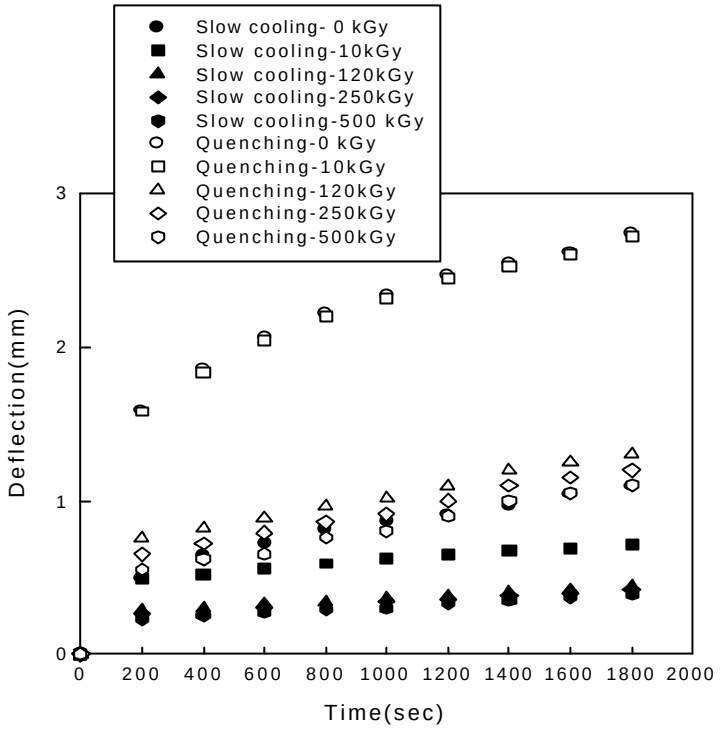

Figure 10. Effect of dose on creep of UHMWPE irradiated in nitrogen.

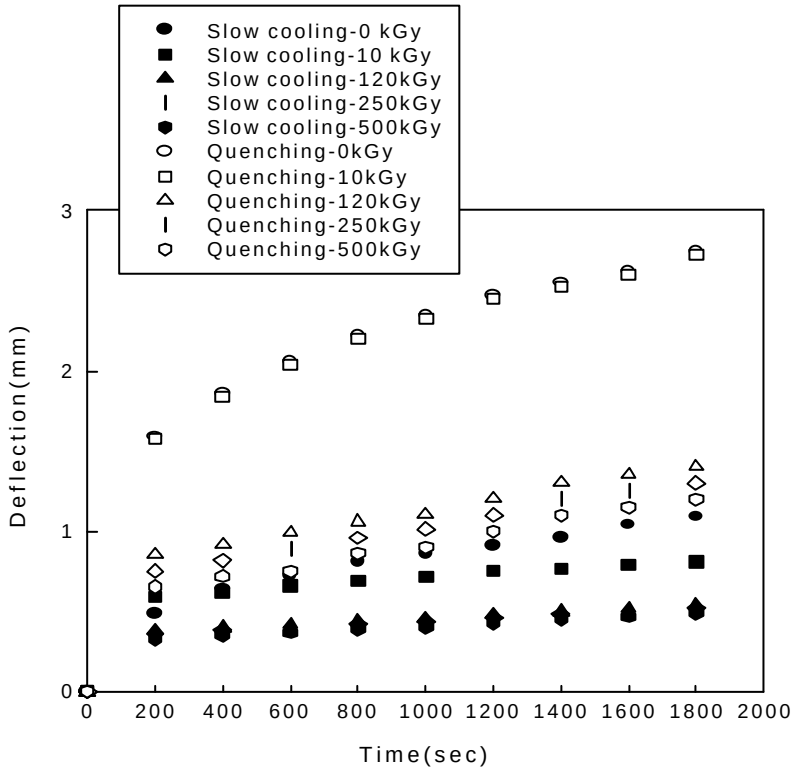

Figure 11. Effect of dose on creep of UHMWPE irradiated in air.

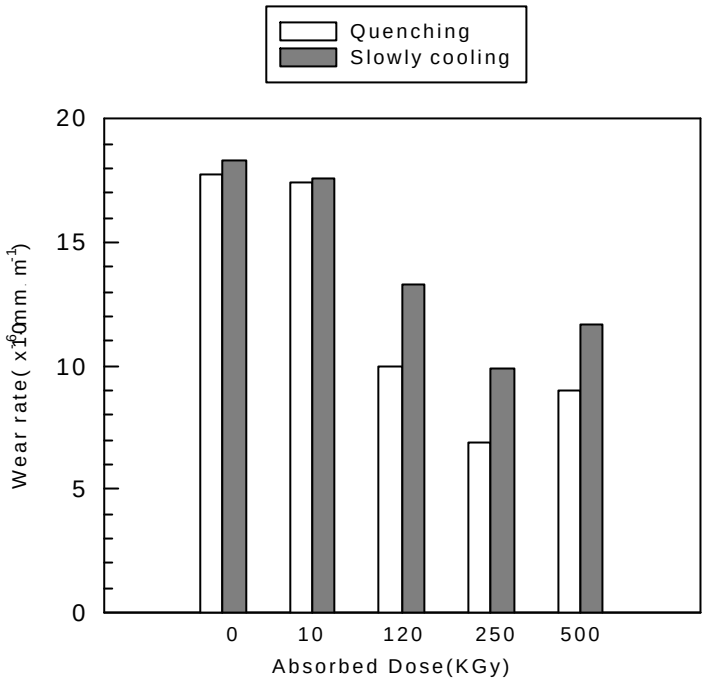

Figure 12. Effect of dose on wear rates of UHMWPE irradiated in nitrogen atmosphere.

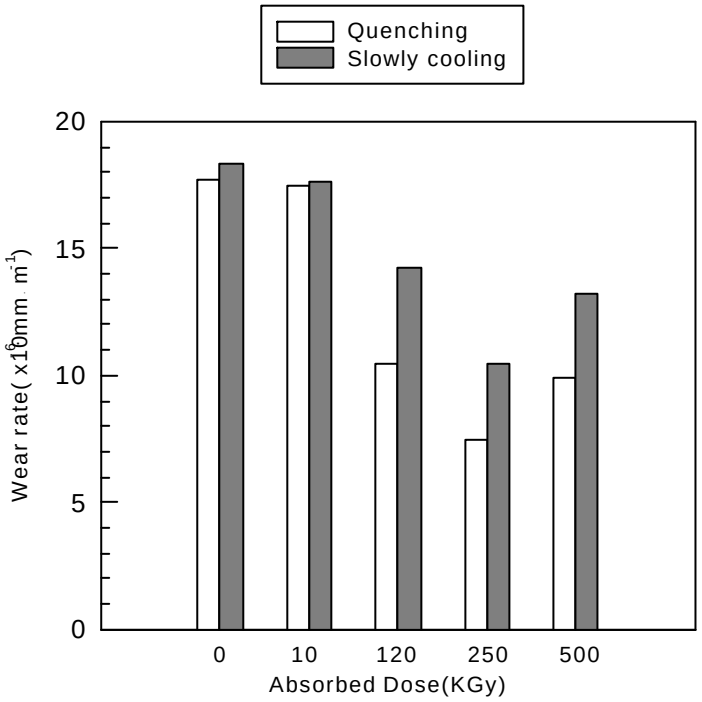

Figure 13. Effect of dose on wear rates of UHMWPE irradiated in air atmosphere.