Effects of Gamma Irradiation, Gas Environments, and Postirradiation Aging on Ultrahigh Molecular Weight Polyethylene

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SYNOPSIS

The effects of low-dose (1 to 5 Mrad) gamma irradiation in different gas environments on thermal and tensile properties, and mass of melt-crystallized ultrahigh molecular weight polyethylene (UHMW-PE) have been investigated. The gamma irradiation was conducted under four different environments, air, nitrogen, acetylene, and vacuum. Thermal parameters were investigated using differential scanning calorimetry. The results showed that both irradiation dose and environments affected the thermal and tensile properties. Gamma irradiation significantly increased the melting temperature of UHMW-PE in all cases. However, the oxidation temperatures of irradiated polyethylene was lowered in all cases except those associated with acetylene environment. The crystallinity of the polymer was increased upon irradiation. Tensile yield strength and modulus of irradiated UHMW-PE increased for all cases except those treated at 1.25 and 2.5 Mrad, and in nitrogen environment that showed a decrease in the modulus. Gamma irradiation caused a weight gain of UHMW-PE in all conditions. To further the study, the postirradiation aging effect on the irradiated polymer was examined during a period of 1 year, and the results showed that the thermal and tensile properties of UHMW-PE were, indeed, affected. The data suggests that irradiation in acetylene affects mainly the crosslinking of the polymer. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Ultrahigh molecular weight polyethylene (UHMW-PE) with an average molecular weight of 3 million has found wide application, as articulating components, in total hip and knee replacement to reconstruct the function of a diseased human joint. During long-term implantation, UHMW-PE undergoes wear and creep. Therefore, in the past 20 years, there have been some attempts to improve the material's long-term performance. One of such attempts is high-energy ionizing irradiation crosslinking, as it imparts some improvements to poly-

ethylene film, cable insulation, pipes, and foams.[1-3] The radiation effects of low molecular weight polyethylene showed an increase in melting temperature, increase in stress cracking resistance, and improvement in solvent resistance. Further, the radiation crosslinking of UHMW-PE has been investigated in an attempt to improve the mechanical properties and, thus, the survival rate of its prostheses,[4,5] but without significant success because the employed high-dose irradiation largely decreased the toughness of the polyethylene. Another reason leading to this study is that although ethylene oxide is commonly used for sterilization, at present most UHMW-PE joint components are gamma sterilized using a dose of about 2.5 Mrad. The main advantages of gamma over ethylene oxide sterilization are the relatively high effectiveness

and safety factor involved, and no posttreatment is required. However, it is expected that this method of sterilization could cause certain changes in the polymer properties.

Even low radiation dose affects the physical and structural properties of UHMW-PE.[6] It was stated that while in a vacuum or inert gas environment the main reaction of polyethylene to irradiation is crosslinking, the oxidation and/or chain scission competes with crosslinking if irradiation is done in an oxygen-containing environment.[7-10] Ultimately, oxidation leads to the degradation of polyethylene. At a low dose of less than 1.25 Mrad, the main reaction is crosslinking whether irradiation is done in air or nitrogen.[7] Acetylene gas was found to promote irradiation-induced crosslinking of polyethylene film.[18,19] Thus, if UHMW-PE is irradiated in acetylene environment, a dense crosslinking would be expected. It should be realized that a radiolytic chain scission may take place even if oxygen is not present. Crosslinking and/or chain scission not only change the molecular weight, but also change the molecular weight distribution, which also has a significant influence on the mechanical properties of polyethylene. Elimination of the high molecular weight fractions will definitely decrease the yield and failure stresses and increase the elongation at yield. Further property changes may occur during storage because latent free radicals remain after irradiation and slow oxidation of polyethylene occurs. It can be expected that the crosslinking would occur in the amorphous region or at the site of imperfect crystals based on the fact that the distance between carbon chains in a perfect alkane crystal is 0.41 nm, whereas the carbon–carbon bond distance is 0.154 nm.[11] Thus, effecting carbon–carbon crosslinking within such crystals is practically impossible. Therefore, as a general rule, crosslinking, chain scissions, and oxidation mainly occur in the amorphous component of semicrystalline polyethylene at a low irradiation dose.

Because UHMW-PE is widely used as medical devices, its gamma irradiation effect has been the topics of some researches. The study by Nussbaam and Rose[12] showed that gamma irradiation caused some change in UHMW-PE mechanical properties—the extent, however, is minimal. Under physiological dose of 2.5 Mrad, the yield and ultimate strength showed a few percent increase whether the irradiation was done in air or in nitrogen.[7] The elongation at yield and failure decreased because the crosslinking limits the molecular chain mobility. As oxygen has a strong tendency to react with radicals

formed during irradiation, its presence is expected to have a detrimental effect on the material performance, considering that the polyethylene chain β-scission is a direct result of oxidation.[13] Increasing the dose increases the oxidation.[14,15] Dumbleton and co-workers[16,17] observed that in the absence of crosslinking agents, relatively high radiation doses are required to obtain worthwhile property improvements, and at doses of 20 to 1000 Mrad, the coefficient of friction at low pressures drops noticeably. The studies by Grobbelaar, du Plessis, and Marris[4,20] showed that the creep of UHMW-PE could be drastically reduced when the polymer was irradiated at the dose of up to 50 Mrad in the presence of acetylene. Comparing the results in the presence of acetylene with those in nitrogen, they found that irradiation in acetylene gas environment had a higher efficiency in the crosslinking of UHMW-PE. As far as tensile strength, there was a slight increase with increase in radiation dose. For the thick material, the radiation crosslinking could be limited by the limited diffusion of crosslinking agents into UHMW-PE.

The previous studies have been conducted mainly using high radiation doses, and no detailed studies were reported on the effect of low-dose gamma irradiation in different gas environments on thermal and tensile properties of UHMW-PE. Therefore, the present study was directed towards examining the effects of gamma irradiation on the tensile and thermal properties, and mass of UHMW-PE using a dose range of 1 to 5 Mrad in four different environments, i.e., air, nitrogen, acetylene, and vacuum. This is to determine whether the UHMW-PE medical devices maintain their initial characteristics upon exposure to gamma sterilization, and identify means to reduce radiation sterilization damage towards improving long-term stability of UHMW-PE medical devices.

EXPERIMENTAL

Materials

A commercial medical grade UHMW-PE, GUR405™ (same as GUR415™, but without calcium stearate), in the form of fine powder was provided to us by Hoechst–Celanese Co., USA. The virgin polymer has a molecular weight of about 6 million and a bulk density of 101 g/L. The melting temperature of the unprocessed polymer, as determined by DSC using a heating rate of 10°C/min in nitrogen environment, is about 145°C. In the present

study, virgin powder GUR405® was melted and compression molded into sheets (thickness ~ 1.2 mm) using a rectangular metal frame placed between two stainless steel plates at a temperature of 180°C and a pressure of 7 MPa. A Carver Laboratory Press (Model C) was used for compression molding the polymer under ambient laboratory environment. The sample was kept at 180°C for 10 min, and then was cooled to room temperature under pressure using an electrical fan during a 2-h period.

Gamma Irradiation

Gamma irradiation was conducted on UHMW-PE at room temperature using three doses, 1.25, 2.5, and 5 Mrad, and three different irradiation gas environments, namely, air, nitrogen, and acetylene, in an irradiator having a ^{60}Co source. The irradiation rate was 0.326 Mrad/h. The experiment was also performed under vacuum. The nitrogen and acetylene environments were created by repeatedly evacuating and introducing the gas to a two-way ground joint glass vessel containing the samples. The duration for each step was about 15 min, and the process was repeated four times. To achieve vacuum, the vessel was evacuated below 1 mmHg before sealing. The vessels were then sealed. Prior to irradiation the acetylene gas pressure inside the vessel was 2.5 psi above atmospheric pressure. The nitrogen pressure was atmospheric.

Thermal Analysis

Differential scanning calorimetry (DSC) was used to examine the thermal properties of UHMW-PE. A Du Pont TA Instrument 2000 thermal analyzer with a computer data system was used for this purpose. The unit was calibrated using indium. UHMW-PE samples weighing approximately 4 mg were placed in a closed (but not airtight) aluminum pan and heated at 10°C/min from room temperature to 300°C in air. The thermal properties were measured for samples irradiated at 2.5 Mrad only. An average of three to five samples was used for each condition during DSC analysis.

Tensile Test

The compression-molded UHMW-PE sheets were converted into dumbbell-shaped tensile test specimens using a metallic cutting die. Figure 1 shows the specimen geometry. The tensile properties of irradiated specimens at room temperature were
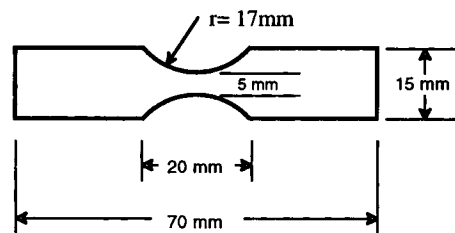
Figure 1 Tensile specimen geometry, thickness ~ 1.2 mm.

evaluated using an Instron universal mechanical tester (Model 1125). A crosshead speed of 20 mm/min and a gage length of 20 mm were used. At least four samples were used for each case.

Mass Change

The change in mass of the polymer after gamma-irradiation was examined by weighing samples before and after treatment using a scale with an accuracy of 0.001 mg. The weight change were measured only for samples irradiated at 2.5 Mrad. An average of 8 to 10 samples was used for weight measurements.

Postirradiation Aging

Considering the long-term effects of gamma radiation, the postirradiation effects on the thermal and tensile properties, and mass changes were examined for UHMW-PE samples. The samples were stored in glass bottles in a dark cabinet. The glass bottles were occasionally opened to atmosphere to make necessary measurements. The postirradiation effects were monitored over a period of 1 year.

Statistical Analysis of Data

The experimental data were subjected to a through statistical analysis,[21] assuming a general linear model between response and treatment. Three factors (radiation dose level, gas environment, and postirradiation time) were statistically analyzed to determine their effects on the properties of UHMW-PE. The analysis of variance was first run to see if there were significant changes in properties within the groups after treatment. If the answer was yes, then the multiple comparison (Fisher's least significant difference) was conducted to compare the properties between any two subjects within the group. This revealed significant changes in the
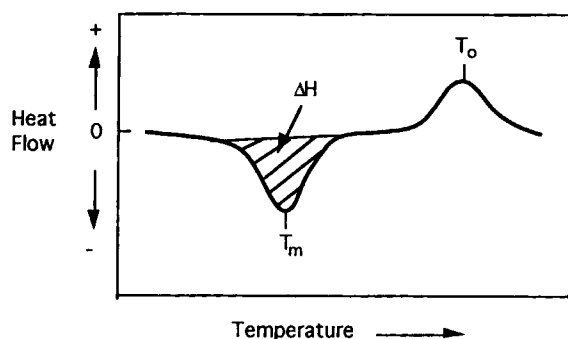
Figure 2 Graphical illustration of a DSC plot.

properties. A level of $p = 0.05$ was chosen to determine significance. The illustrated experimental data were given as mean ± standard deviation.

RESULTS AND DISCUSSION

Thermal Properties

DSC thermograms were used to study two events, melting and thermal oxidation, in terms of melting temperature (T_m) and oxidation temperature (T_o), which are illustrated graphically in Figure 2.

As shown in Figure 2, the heat of fusion (ΔH) was also obtained. Using the ΔH data, the percent crystallinity of the polyethylene was calculated by dividing ΔH, the heat of fusion measured by the DSC, by the heat of fusion of fully crystalline polyethylene, reported as 289.3 J/g.[22] The results are plotted in Figures 3–5. The days in the figures are the time elapsed after irradiation. It appears that the thermal properties of nonirradiated UHMW-PE seldom change in short-term storage but did change after long-time storage. The gas environments significantly affected the thermal properties of the polymer. Figure 3 shows that gamma irradiation increased the melting temperature of UHMW-PE in all four environments at 10, 130, 250, and 360 days postirradiation. This result is contradictory to the data reported in an early report,[23] where irradiation was conducted at 0 to 40 Mrad in vacuum and the melting temperature showed no change. Irradiation in an acetylene environment led to the highest increase of T_m ($\sim 5°C$), while the other three environments showed limited increases ($\sim 1°C$). This may indicate that radiation-induced molecular chain movement has taken place and resulted in recrystallization to more perfect crystals. This can also be associated with chain scission of the amorphous region, followed by recrystallization, which can be af-
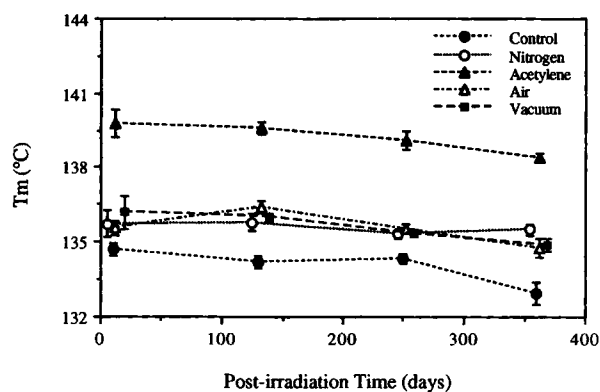

Figure 3 Effect of gamma irradiation on melting temperature of compression-molded UHMW-PE. Control = nonirradiated samples; vacuum, nitrogen, air, and acetylene = samples irradiated in vacuum, nitrogen, air, and acetylene, respectively.

fected further by crosslinking in the presence of acetylene. Such an effect is consistent with earlier studies where acetylene was reported to promote crosslinking,[19,20] which will, in turn, increase the T_m through a decreased entropy contribution. Statistical analysis also showed that T_m was significantly affected by postirradiation in all samples except those treated in a nitrogen environment. At 360 days postirradiation, T_m showed a drop, which reflects a long-time aging of the UHMW-PE, and may imply a long-term instability of both irradiated and nonirradiated polyethylene. It is interesting to note that T_m for the UHMW-PE irradiated in nitrogen showed no postirradiation effects. Figure 4 shows that all samples except those treated in acetylene environment experienced a significant decrease in T_o after gamma irradiation. There is no difference in T_o values for the control and samples irradiated in the
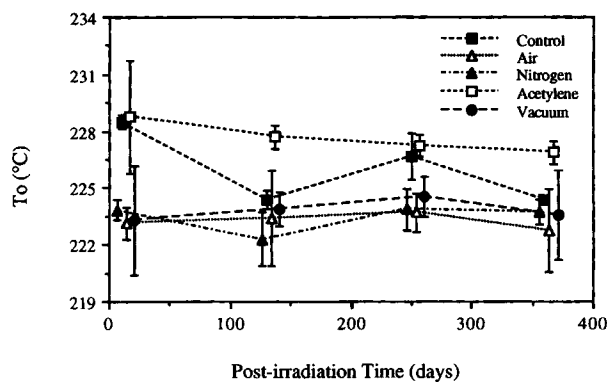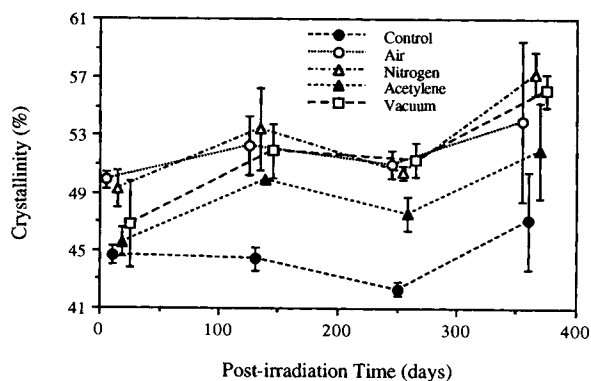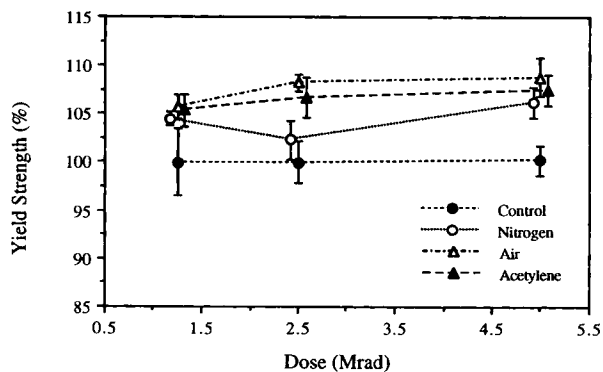

Figure 4 Effect of gamma irradiation on oxidation temperature of compression-molded UHMW-PE.

Figure 5 Effect of gamma irradiation on percent crystallinity of compression-molded UHMW-PE.

presence of acetylene. The results suggest that (1) irradiation causes oxidation degradation of polyethylene in an oxygen-containing environment and/or chain scission; (2) a C—C bond crosslinking of irradiated polyethylene occurs in the presence of an acetylene environment and raised T_o, which counterbalance any decrease of T_o due to polymer degradation. This may also explain why oxidation temperature changed slightly with time. Statistically, there is no postirradiation effect on T_o except for the nonirradiated UHMW-PE samples, which showed a decreased T_o only at longer times. Figure 5 shows the calculated crystallinity from the measured heat of fusion. Following gamma irradiation, the crystallinity of UHMW-PE increased, as shown in Figure 5. At 10 and 250 days, the crystallinity of samples irradiated in air and nitrogen were significantly greater than the control and the samples irradiated in acetylene. At 130 days and 360 days, the crystallinity of irradiated samples were significantly greater than the control. Among the four conditions, acetylene environment exhibited smallest increase

in crystallinity. The above results clearly reflect the postirradiation effect on crystallinity. Generally, the longer the postirradiation, the higher the crystallinity. This suggests that irradiated polyethylene continues to change with time, possibly due to trapped free radicals,[26] which caused a delayed chain rearrangement. So the same would be expected for UHMW-PE. The increase in crystallinity is consistent with density increase of irradiated UHMW-PE.[25] It was stated that the increase in crystallinity of irradiated polymers may be due to recrystallization of polymer chains at crystalline–amorphous interfaces onto the lamellae leading to an increase in their thickness,[24] and, hence, the observed increase in T_m. To summarize, the above results may suggest that gamma sterilization of UHMW-PE products in an acetylene environment is an excellent approach to achieve desirable thermal properties.

Tensile Properties

Tensile tests were run on UHMW-PE samples irradiated in air, nitrogen, and acetylene gas environments 2 weeks after gamma irradiation. As part of the tensile testing studies, the following parameters were determined: yield strength (σ_y), ultimate strength (σ_u), sample modulus (E), ultimate elongation (ϵ_u) and fracture energy (W_u). Figures 6–10 illustrate the results (percentage of parameter as compared with the control). For the control (not irradiated samples), $\sigma_y = 24.7 \pm 0.6$ MPa, $\sigma_u = 47.9 \pm 1.7$ MPa, $E = 578 \pm 13$ MPa, $\epsilon_u = 176 \pm 12\%$ and $W_u = 68.5 \pm 5.4$ lbs-in. It appears that both radiation dose and gas environment affect the tensile properties of UHMW-PE. Statistical analysis of the results indicates that (1) for a particular dose, the type of gas environment significantly changed σ_y,

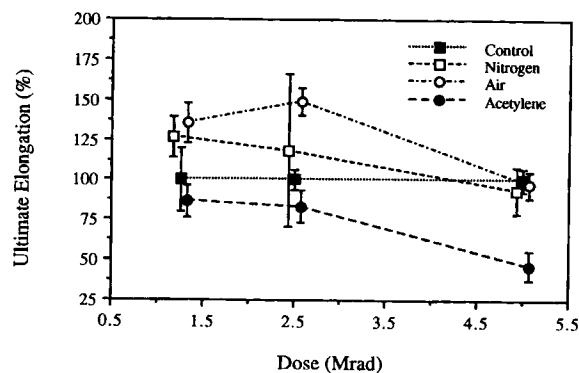**Figure 6** Effect of gamma irradiation on yield strength of compression-molded UHMW-PE.
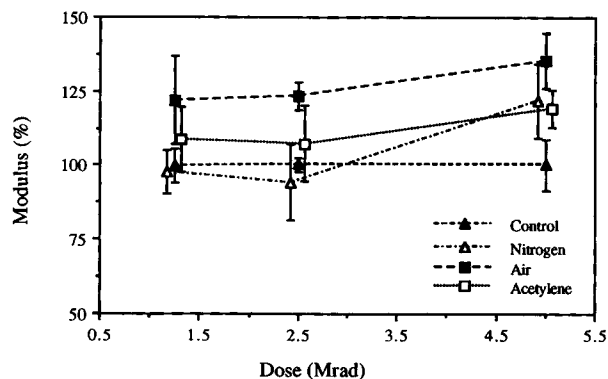
Figure 7 Effect of gamma irradiation on sample modulus of compression-molded UHMW-PE.
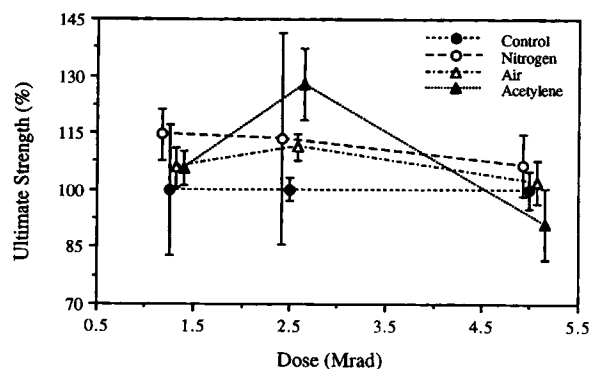
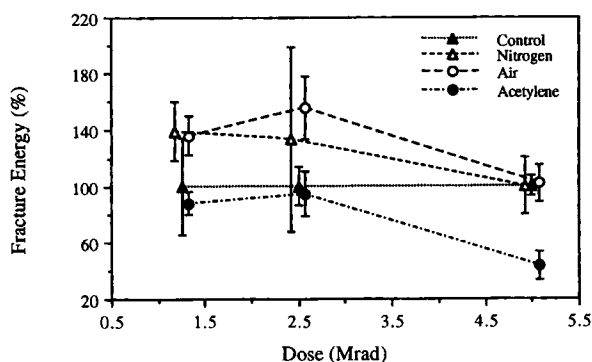**Figure 8** Effect of gamma irradiation on ultimate strength of compression-molded UHMW-PE.

Figure 10 Effect of gamma irradiation on fracture energy of compression-molded UHMW-PE.

E, and ϵ_u ($p < 0.025$); and (2) in any specific gas environment, the radiation dose significantly affected σ_y, σ_u, E, ϵ_u, and W_u ($p < 0.025$) except for nitrogen environment where σ_u, ϵ_u, and W_u were not significantly affected ($p > 0.2$). At doses of 1.25 and 2.5 Mrad, yield stress and sample modulus displayed higher increase in air and acetylene than in nitrogen. In fact, the sample modulus dropped in nitrogen. At these two doses, crosslinking appears to dominate in air and acetylene, while chain scission is a major event in nitrogen. The highest increase recorded for σ_y and E were 9 and 36%, respectively. At 5 Mrad, all three gas environments showed an increase in σ_y and E. And a decrease in ultimate elongation at 5 Mrad suggests that the crosslinking began to dominate at this dose. This can be explained in terms of irradiation-induced crosslinking network formation and a resulted increase in the number of molecules interconnecting lamella. This, in turn, restricts the deformability of UHMW-PE. High energy ionizing irradiation causes both chain scission and crosslinking, and the extent of which may de-

pend on the dose and/or environments. In the absence of oxygen, crosslinking is formed between carbon atoms of the amorphous phase. If oxygen is present, the crosslinking may also be associated with the formation of peroxide linkages, which are thermally and chemically labile, while crosslinking in the presence of acetylene can produce stable C—C bonds. Results of the present study showed that E decreased and ϵ_u increased (Fig. 11) when the samples irradiated in presence of air were incubated for 70 h at room temperature in presence of N,N-dimethyl aniline, a known catalyst for peroxide dissociation. Reduction in ultimate elongation of samples irradiated in acetylene increased as the dose increased, suggesting that the C—C crosslinking dominates in these samples, with acetylene participating as a promoter and/or a reactant. This was consistent with the recorded increase in specimen weight after irradiation at 2.5 Mrad (Fig. 17). At 5 Mrad, ultimate elongation reflected a general decrease, which is most noticeable for acetylene environment where more than 50% reduction was re-

Figure 9 Effect of gamma irradiation on ultimate elongation of compression-molded UHMW-PE.
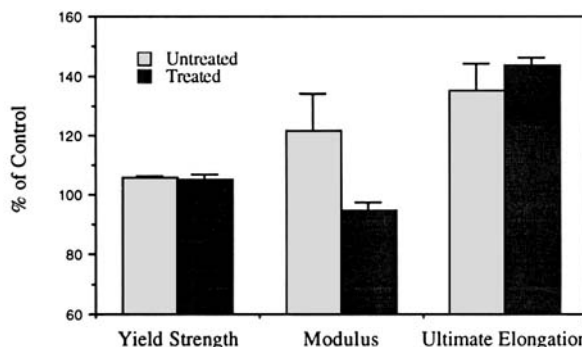
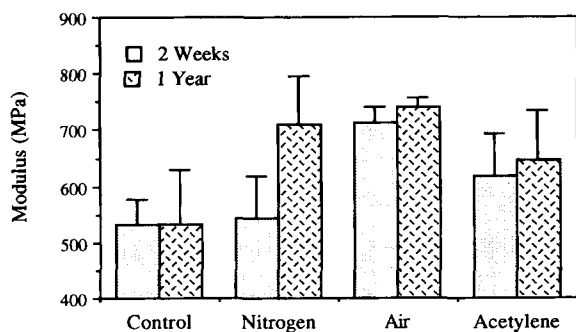**Figure 11** Effects of N,N-dimethyl aniline treatment on tensile properties of UHMW-PE samples irradiated at 1.25 Mrad in air environment.
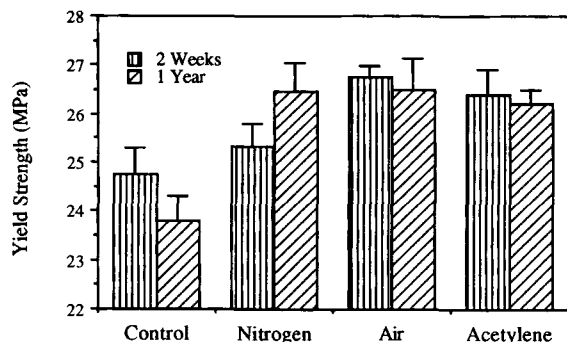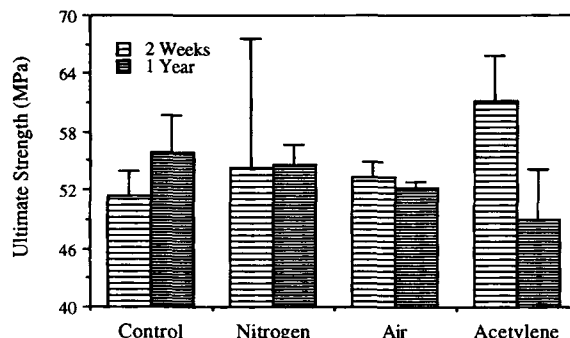
Figure 12 Effect of postirradiation aging on yield strength of UHMW-PE.

Figure 14 Effect of postirradiation aging on ultimate strength of UHMW-PE.

corded. It may be expected that higher dose will largely decrease the toughness of UHMW-PE and, thus, make the polymer brittle, an undesirable characteristic for orthopedic implants.

To examine the postirradiation aging effect on tensile properties, the tensile tests were run on the samples at 1 year postirradiation, and the data were compared with those at 2 weeks postirradiation. The results are graphically illustrated in Figures 12 to 16. Figure 12 shows that the yield strength of UHMW-PE slightly decreased for the control and the samples irradiated in air and acetylene environments at 1-year postirradiation, but it significantly increased for the samples irradiated in the nitrogen environment. Figure 13 shows a general increase in modulus upon postirradiation aging. This increase is mainly due to an increase in the crystallinity of UHMW-PE upon postirradiation aging. Figure 14 shows the ultimate strength of UHMW-PE. At 1 year postirradiation, it decreased for the samples irradiated in air and acetylene environments, but increased for the control. Finally, Figures 15 and 16 indicate that upon postirradiation aging the ultimate elongation and fracture energy were significantly

increased for the control and the samples irradiated in nitrogen and air environments, but decreased in acetylene environment. In summary, the postirradiation aging does affect the tensile mechanical properties of UHMW-PE.

Mass Change

Samples used for weight measurement had the same geometry as the tensile specimens (weighing about 1.2 g). Figure 17 illustrates the weight changes of UHMW-PE gamma-irradiated at 2.5 Mrad under different environments and the postirradiation aging effect. The results suggest that gamma irradiation can cause significant weight increases under all four conditions, with acetylene yielding the highest weight gain. The weight gain under subambient conditions is most likely due to the fact that the environment under vacuum was not free of oxygen; however, it did show the smallest weight gain. Irradiation in oxygen-containing environment produces peroxides, and can also lead to weight gain. The weight gain in nitrogen may be related to its reactivity with polyethylene in the presence of high-

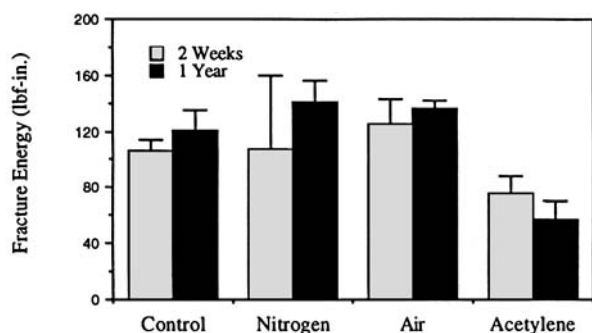**Figure 13** Effect of postirradiation aging on sample modulus of UHMW-PE.
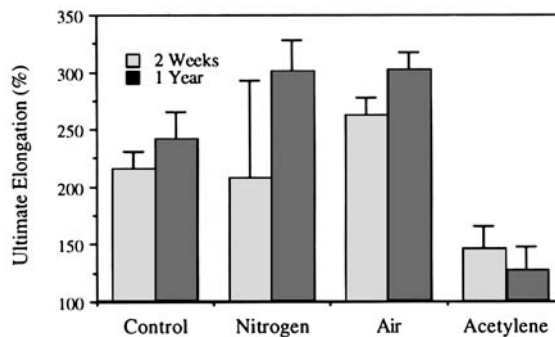
Figure 15 Effect of postirradiation aging on ultimate elongation of UHMW-PE.
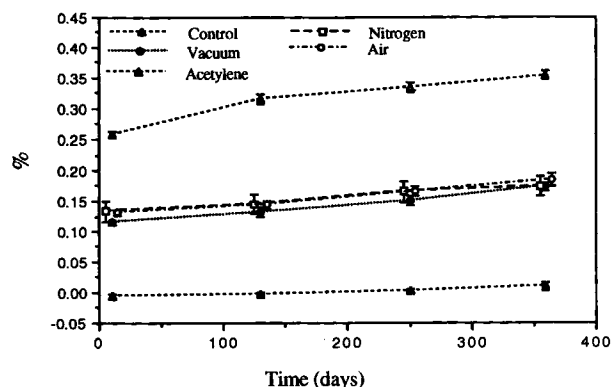
energy ionizing irradiation, but more likely to the existence of oxygen impurities in nitrogen gas. For low molecular weight polyethylene, the postirradiation oxidation was verified by the increase in the concentration of carbonyl groups,[26] which in turn, lead to the weight gain. The same has been shown in the present study. Figure 17 shows that although the sample weight continued to increase, the rate decreased with postirradiation time. It is likely that the weight gain was caused by existing free radicals that were rapidly consumed. It is interesting to note that the nonirradiated UHMW-PE samples (i.e., the control) showed significant weight increases with time, which may be related to the slow oxidation of UHMW-PE in an oxygen-containing environment. It is not reasonable to think that the weight increase in acetylene environment was due to the adsorption of acetylene molecules on the polyethylene surface because these samples exhibited the highest weight gain rate at 130, 250, and 360 days when the samples were exposed to air. Recorded changes in tensile properties at 1-year postirradiation do not support the hypotheses that acetylene and water adsorption are the main cause for weight gain of UHMW-PE.

CONCLUSIONS

The present study showed that gamma irradiation, types of irradiation environment, and postirradiation aging affect the thermal and tensile properties of compression-molded UHMW-PE. After gamma irradiation, the melting temperature increased more than 5°C in acetylene environment, but less than 2°C in air, nitrogen, and vacuum environments. Oxidation temperature decreased in all samples except those treated in the presence of acetylene. Following irradiation, crystallinity continuously changed. At 1.25 and 2.5 Mrad, air and acetylene environments

Figure 17 Weight change of UHMW-PE after gamma irradiation.

promote crosslinking and, thus, increase in yield stress and modulus. At 5 Mrad, all three gases showed increase in yield stress and modulus, but decrease in ultimate elongation. A fraction of the crosslinks formed due to oxygen can be viewed as being transient and may dissociate upon aging. Gamma irradiation in acetylene causes mainly crosslinking and at a low dose range it can be used as a means to improve the performance of UHMW-PE products. The postirradiation effects are likely to be caused by the macromolecular free radicals. UHMW-PE is slowly oxidized in air.

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Figure 16 Effect of postirradiation aging on fracture energy of UHMW-PE.

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