Effects of Gamma Irradiation, Irradiation Environment, and Postirradiation Aging on Thermal and Tensile Properties of Ultrahigh Molecular Weight Polyethylene Fibers

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SYNOPSIS

The effects of gamma irradiation in four types of irradiation environment on the thermal and tensile properties of gel-spun, ultrahigh molecular weight polyethylene fibers (Spectra™ 1000) have been investigated. The gamma irradiation was conducted at 2.5 Mrad and in air, nitrogen, acetylene, and vacuum to study the effects of irradiation media on the aforementioned properties. Thermal and tensile properties of virgin and irradiated fiber samples were examined using differential scanning calorimetry and an Instron tensile tester, respectively. The results indicate that both gamma irradiation and irradiation environment affected the properties of the polyethylene fibers, and substantial changes were observed for the oxygen-containing environment. The tensile-fractured surfaces of the fibers were examined by scanning electron microscopy. The properties of irradiated fibers were further evaluated at 160 days postirradiation and found to be affected, substantially. The postirradiation aging significantly decreased the tensile strength and elongation of the irradiated fibers, indicating that polyethylene fibers should not be exposed to gamma irradiation. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

In the early 1970s, work began on the drawing of melt-crystallized polyethylene to exceptionally high draw ratios in order to produce high-strength polyethylene fibers.[1] This was followed by a number of further developments; in particular, the gel spinning/drawing process of ultrahigh molecular weight polyethylene (UHMW-PE).[2,3] The gel-spun ultrahigh strength and modulus UHMW-PE fibers have been commercialized in 1985 in USA by Allied Signal Inc. as Spectra™ 900 and Spectra™ 1000. The Spectra™ fibers are among the strongest, lightest-weight fibers known. Due to their exceptionally high strength, high toughness, and low density, which gives even higher specific strength, UHMW-PE fibers have been rapidly introduced into the composite market, used, for example, as reinforcements for a myriad of products from ballistics to sports equipment. Meanwhile, a number of investigators have studied the reinforcing effects of polyethylene fibers in a few composite materials. Chang and co-workers used polyethylene fibers to reinforce epoxy resin, as high modulus thermoset composites.[4] Marais and Feillard reported a composite made of polyethylene fibers and high density polyethylene.[5] From the late 1980s, a lot of work has been carried out on the adhesion of polyethylene fibers to epoxy resins.[6-10] The goals of most of those researches were to introduce polar groups on the polyethylene fiber surface through chemical etching and plasma treatment, and thus to improve the interfacial bonding in polyethylene fiber-reinforced epoxy composites.

In a recent report, Shalaby and Deng described the formation and properties of UHMW-PE fiber reinforced UHMW-PE composites as load-bearing components for biomedical engineering applications.[11] Following sterilization with gamma radiation

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at 1 to 5 Mrad, this self-reinforced UHMW-PE composite exhibited a decrease of up to 20% in longitudinal tensile properties, but an increase of up to 10% in transverse properties, for unidirectional laminates and a fiber weight fraction of 5%.[12] On the other hand, it had previously been shown that low dose (1 to 5 Mrad) gamma irradiation increases the tensile strength and modulus of molded UHMW-PE.[13] The reduction in the longitudinal tensile properties of self-reinforced UHMW-PE composites following gamma irradiation was, therefore, speculated to be due primarily to changes in the properties of polyethylene fibers. In addition to gamma radiation sterilization, there are certain use conditions such as space applications where polyethylene fibers will be exposed to some types of high energy radiation which, in turn, may also affect their properties.

Klein and co-workers studied the effects of electron irradiation on the structure and mechanical properties of highly drawn polyethylene fibers.[14] The irradiation was performed in vacuum and acetylene and dose ranged from 0.07 to 52 Mrad. It was found that percent gel content increased with increasing dose for melt-spun fibers, but decreased for gel-spun fibers at doses of greater than 0.7 Mrad in acetylene. For melt-spun fibers, the creep rate at high stress for an acetylene treated sample was found to be less than that of a sample irradiated to a similar gel content in vacuum. Gel-spun fibers showed a much lower creep rate than melt-spun fibers at all stress. In their work, however, no postirradiation aging effects on polyethylene fibers were examined, although it has been recognized that latent free radicals causes continuous changes in UHMW-PE properties.[13]

The effects of gamma irradiation on UHMW-PE have been the subject of a number of earlier reports,[15–18] but similar studies on gel-spun UHMW-PE fibers are rare within the literature. Therefore, this led to the pursuit of the study subject of the present report, which is, to determine effects of gamma irradiation, irradiation environment, and postirradiation aging on thermal and tensile properties of gel-spun UHMW-PE fibers. The ultimate goal of the research is to define means to reduce radiation damage and thus improve the long-term stability of the products made with UHMW-PE fibers.

EXPERIMENTAL

Materials

Gel-spun ultrahigh strength and modulus UHMW-PE fibers (Spectra™ 1000) were obtained from the Fiber Division, Allied Signal Inc., VA. The fibers were wound on a spool and delivered in the yarns of 650 deniers, each containing 120 filaments. The diameter of a single filament, as determined by scanning electronic microscopy, is about 30 μm. The reported tensile strength of industrial grade Spectra™ 1000 fibers varies between 2 to 4 GPa. For the purpose of this study, five groups of yarns (each group having a length of about 20 meters) were taken from the as-received fiber spool and wound on a small spool with a diameter of about 20 mm, with careful handling to avoid any severe bending of the fibers. Such prepared samples were used for the gamma irradiation experiments.

Gamma Irradiation

Gamma irradiation was conducted on the UHMW-PE fiber samples at room temperature and at a nominal dose of 2.5 Mrad in three different gas environments; namely, air, nitrogen and acetylene, using a ^{60}Co source and 0.25 Mrad/h dose rate. The nitrogen and acetylene gas environments were created by repeatedly evacuating and applying 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. The irradiation experiment was also performed under vacuum condition for comparison, where the vessel was evacuated below 1 mmHg before sealing. The vessels were then sealed. When using an acetylene gas environment, the gas pressure inside the vessel before irradiation was 2.5 psi above atmospheric pressure. However, for the nitrogen environment, the pressure was atmospheric.

Thermal Analysis

Differential scanning calorimetry (DSC) was used to study the thermal properties of polyethylene fibers. A Du Pont TA Instruments 2000 thermal analyzer with a computer data system was used. The unit was calibrated using indium. Fiber samples weighing approximately 4 mg were cut using scissors, placed in a closed, two-part aluminum pan (but not airtight), and heated at 10°C/min from room temperature to 300°C in air, because it was assumed that the heat-aging performance (thermal oxidation) would be a particularly severe test of stability because of the inherent high surface-to-volume ratio of the fibers. An average of three samples were measured from each fiber group. The samples irra-

diated in vacuum, nitrogen, and acetylene environments were not exposed to air prior to their analysis by DSC.

Tensile Test

The polyethylene fibers were subjected to tensile mechanical testing following ASTM Standard D2256.[19] The tensile properties of the irradiated samples and the control (i.e., as-received virgin fibers) at room temperature were evaluated using an Instron universal mechanical tester (Model 1125), 1 week after gamma irradiation. The samples irradiated in vacuum, nitrogen, and acetylene environments were exposed to air 1 day before testing. A crosshead speed of 300 mm/min and a gage length of 254 mm were used. An average of 10 specimens from each group were tested. Three tensile parameters, maximum tenacity, maximum strain and initial modulus, were determined.

Scanning Electron Microscopy

Scanning electron microscopy (SEM) was used to examine the fracture surfaces of the tensile-tested polyethylene fibers 2 days after tensile tests were conducted. The samples were coated with gold in a Hummer X Sputter Coating instrument 1 day before SEM analysis. After coating, the samples were stored in a decicator, then subsequently viewed using a JEOL JSM-35 Scanning Electron Microscope using a 15 KEV beam.

Postirradiation Aging

Considering the long-term effects of gamma radiation, the postirradiation aging effects on the thermal and tensile properties of polyethylene fibers were examined at 160 days postirradiation. The samples were stored in glass bottles in a dark cabinet and at room temperature during aging. The glass bottles were occasionally opened to atmosphere to make necessary measurements.

Statistical Analysis

The experimental data were subjected to a statistical analysis assuming a general linear model between response and treatment.[20] Two factors (irradiation environment and postirradiation aging time) were statistically analyzed to determine their effects on the properties of UHMW-PE fibers. Using SAS software, the multiple comparison (Fisher's least significant difference) was conducted to compare the properties between any two subjects within the group. A level of $p = 0.05$ was chosen to determine significance, and the illustrated experimental data were given as mean ± 95% confidence interval, assuming a Student's t distribution.

RESULTS AND DISCUSSION

Thermal Properties

DSC thermograms were used to study two events, melting, and thermal oxidation, in terms of the peak melting temperature (T_m), peak oxidation temperature (T_o), and the heat of fusion (ΔH), as illustrated, graphically, in Figure 1.

From the measured ΔH data, the percent crystallinity of the polyethylene fiber was estimated by dividing the calculated ΔH by the heat of fusion of fully crystalline polyethylene, reported as 289.3 J/g.[21] The effects of irradiation on the general shape of DSC thermograms of polyethylene fibers are illustrated in Figure 2. Compared to the compression-molded UHMW-PE, the DSC analysis of UHMW-PE fibers showed a distinct feature, a major melting peak, and a minor one. Such melting behavior of gel-spun UHMW-PE fibers is a consequence of the unique morphology resulted from the gel-spinning technique and the subsequent high drawing. The two melting peaks may also suggest a core–skin structure for gel-spun UHMW-PE fibers. Generally, the widths of melting endotherms of DSC thermograms were enlarged after gamma irradiation, which may indicate a wider distribution of crystal size for irradiated fibers compared to the virgin fibers. This may result from chain scission, followed by recrystallization. Of the five groups of samples analyzed,

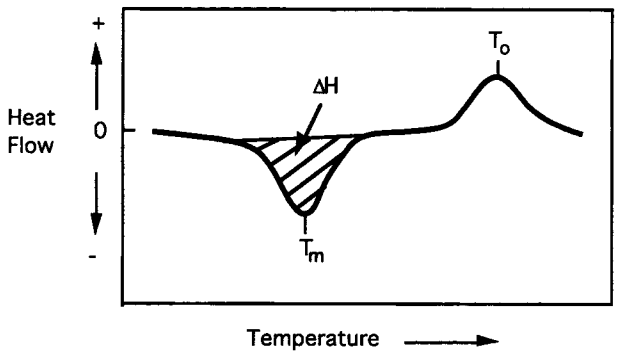


Figure 1 Graphical illustration of a typical DSC thermogram.

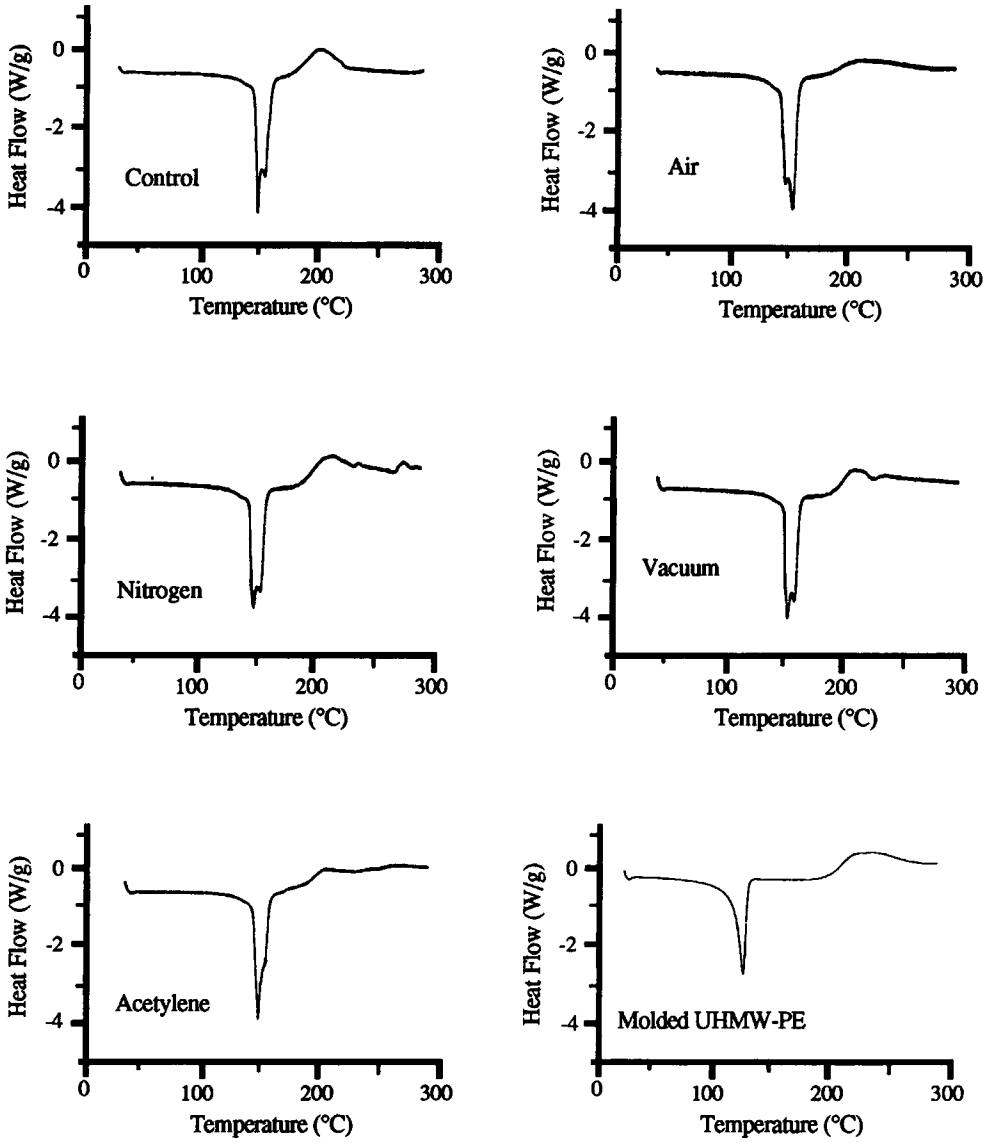


Figure 2 DSC thermograms of UHMW-PE systems; control = as-received virgin fiber sample; air, nitrogen, vacuum, and acetylene = fiber samples irradiated in air, nitrogen, vacuum, and acetylene, respectively; molded UHMW-PE = compression-molded UHMW-PE (GUR405 sample).

samples irradiated in the air and acetylene gas environments showed distinct differences as compared to the control (nonirradiated UHMW-PE fiber). In the air environment, irradiation resulted in reversal in orders of melting points associated with major and minor melting peeks; in the acetylene gas environment, the second melting peek almost disappeared. Those results may indicate that some molecular reorganization on microscopic level had taken place for the samples irradiated in air and acetylene, which may be due to oxidation and chain scission, and crosslinking, respectively. This, in turn, may lead to the relaxation of the chain orientation locked in during fiber formation. For the samples irradiated in nitrogen or vacuum, the changes in the shape of DSC thermograms were less distinct. These results strongly indicate the effects of irradiation environment on thermal properties of UHMW-PE fibers.

Numerical data on the effects of gamma irradiation and types of irradiation environment on the melting temperatures (T_{m1} corresponds to the first

Table I DSC Data of Polyethylene Fibers following Irradiation (Mean ± 95% Confidence Interval)

Samples	T_{m1} (°C)	T_{m2} (°C)	T_o (°C)	Crystallinity (%)
Control	147.2 ± 0.2	153.5 ± 2.6	209.8 ± 16.7	81.2 ± 3.4
Acetylene	146.7 ± 1.6	153.5 ± 0.3	207.8 ± 1.5	73.9 ± 2.8
Air	146.3 ± 0.6	152.5 ± 1.1	213.0 ± 8.6	84.2 ± 8.6
Nitrogen	147.3 ± 2.5	153.1 ± 0.1	217.9 ± 6.5	79.0 ± 1.5
Vacuum	146.4 ± 1.4	153.0 ± 0.5	205.5 ± 3.0	79.4 ± 4.5

melting peek, and T_{m2} the second melting peek), oxidation temperatures (T_o) and percent crystallinity are summarized in Table I. Statistical analysis of these data indicated that there were no significant differences in T_{m1} of all groups of polyethylene fibers, or the T_{m1} is not affected by gamma irradiation and irradiation environment. However, for the virgin samples (the control) and those irradiated in acetylene, their T_{m2}s were significantly higher than those irradiated in air, or the irradiation in air significantly decreased the T_{m2}, which indicates the detrimental effects of oxygen-containing environment on UHMW-PE fibers. Compared to the molded UHMW-PE where irradiation increases the melting temperature,[13] the irradiation will not raise the melting temperature of the gel-spun UHMW-PE fibers. Generally, UHMW-PE fibers have crystallinity of about 80%, compared to crystallinity of about 50% for molded UHMW-PE. Thus, only a small portion of amorphous phase in polyethylene fibers is expected to be affected by irradiation. As a result, chain scission, crosslinking, and recrystallization in amorphous phase of the fibers would be much more limited. Therefore, less crosslinking and recrystallization means less effects on the melting temperature. The oxidation temperature was much more influenced by irradiation compared to melting temperature. Samples irradiated in the nitrogen environment yielded significantly higher T_o than virgin samples and the samples irradiated in vacuum and acetylene. The use of the air environment led to a higher T_o as compared with the vacuum environment. In comparison with the molded UHMW-PE,[13] UHMW-PE fibers showed a significantly lower T_o, which may be due to the high surface-to-volume ratio of the fibers. This may indicate that oxidation is a diffusion-controlled process. After irradiation, crystallinity of polyethylene fibers irradiated in acetylene, nitrogen, and vacuum decreased as compared to a general increase for molded UHMW-PE. The reason for this may be that because the polyethylene fibers have a much higher crystallinity than the molded UHMW-PE, the breakdown of the crystals was more than the recrystallization following irradiation. This is also possibly due to the relaxation of the chain orientation for the fibers. The air environment produced significant higher crystallinity than acetylene, nitrogen, and vacuum; but it yielded no significant difference in crystallinity as compared to the control. The acetylene environment showed the largest reduction in its crystallinity, which is significantly different from the rest. The maximum observed change in crystallinity was less than 10%.

The results of postirradiation aging effects on thermal properties of UHMW-PE fibers are illustrated in Table II. The effects here are very obvious. First, T_{m1} seems to decrease upon postirradiation aging, particularly in acetylene environment where T_{m1} was significantly reduced. All of the irradiated samples exhibited a reduction in T_{m2}. Furthermore, T_{m2} totally disappeared for the

Table II DSC Data of Polyethylene Fibers at 160 Days Postirradiation (Mean ± 95% Confidence Interval)

Samples	T_{m1} (°C)	T_{m2} (°C)	T_o (°C)	Crystallinity (%)
Control	146.8 ± 2.6	153.0 ± 0.2	204.6 ± 16.2	81.6 ± 3.3
Acetylene	144.8 ± 0.6	150.7 ± 1.5	211.4 ± 2.5	80.6 ± 8.0
Air	146.4 ± 4.7	—	217.3 ± 11.4	87.4 ± 2.5
Nitrogen	145.8 ± 1.8	149.9 ± 0.8	217.8 ± 3.2	86.2 ± 2.9
Vacuum	145.2 ± 0.2	150.2 ± 1.7	228.5 ± 3.2	86.4 ± 2.1

Table III Tensile Results of Polyethylene Fibers following Irradiation (Mean ± 95% Confidence Interval)

Samples	Maximum Tenacity (g/den)	Maximum Strain (%)	Modulus (g/den)
Control	31.9 ± 2.1	3.3 ± 0.2	1200 ± 25
Acetylene	31.4 ± 0.9	3.0 ± 0.1	1204 ± 25
Air	25.6 ± 1.4	2.8 ± 0.1	1184 ± 37
Nitrogen	32.8 ± 1.0	3.5 ± 0.1	1160 ± 38
Vacuum	32.7 ± 1.1	3.4 ± 0.1	1219 ± 24

samples irradiated in air. Compared to the control, the crystallinity of irradiated samples showed a general increase upon postirradiation, which is in contrast to the data in Table I. And the samples irradiated in air, vacuum, and nitrogen showed significantly higher crystallinity than the control and samples irradiated in acetylene. However, the oxidation temperature of the irradiated samples were much higher than that of the control at 160 days postirradiation, which may be due to the fact that the increased crystallinity slows down the diffusion of oxygen into polyethylene fibers. These results clearly indicated the postirradiation aging effects on thermal properties of UHMW-PE fibers due to the latent radicals.

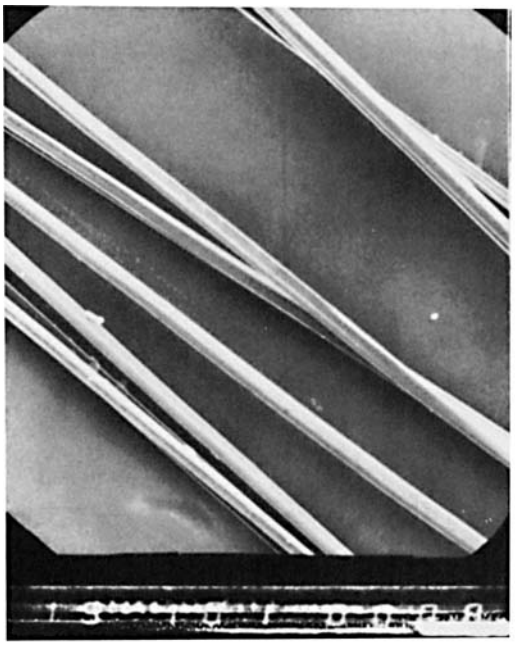
Tensile Properties

Unlike the compression-molded UHMW-PE, gel-spun UHMW-PE fibers show no yield point in tensile test, and the strain at break is generally less than 4%. The tensile testing results are presented in Table III. Statistical analysis of the data indicates that the samples irradiated in vacuum and nitrogen yielded significantly higher maximum tenacity than the samples irradiated in acetylene and air. Compared to the control, only the samples irradiated in air showed a significant decrease in maximum tenacity, which reflects the detrimental effects of the oxygen-containing environment on irradiated polyethylene fibers. For maximum strain, the samples irradiated in nitrogen and vacuum showed significantly higher values than the control or the samples irradiated in acetylene and air. Compared to the control, the maximum strain of samples irradiated in acetylene and air were reduced. Of all the groups, the samples irradiated in air exhibited the lowest maximum strain. Referring to the DSC data, it may be reasonable to suggest that the reduction observed in the maximum strain data for samples irradiated in air and acetylene are due to an increase in crystallinity and crosslinking, respectively. The increase observed in the maximum strain data for the samples irradiated in vacuum and nitrogen may possibly be due to chain scission, which renders the polymer more stretchable. The vacuum condition showed significantly higher modulus than the control, air, and nitrogen. The acetylene environment yielded significantly higher modulus than nitrogen, which may be due to the acetylene-related crosslinking.

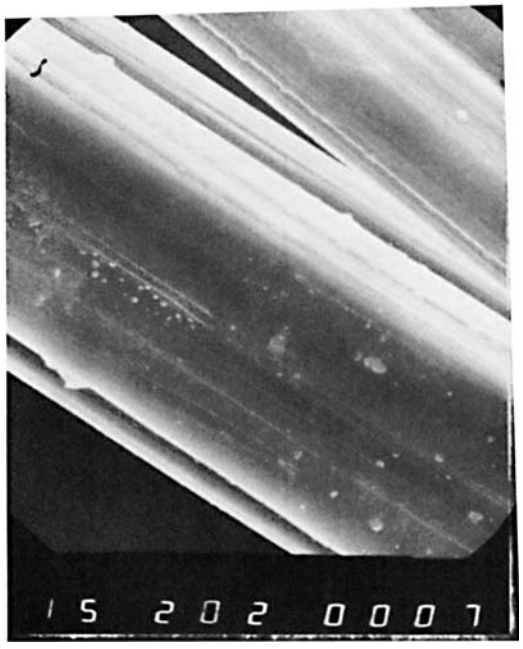
Table IV illustrates the postirradiation aging effects on the tensile properties of UHMW-PE fibers. It is obvious from this table that upon aging, all of the irradiated samples showed significant decrease in maximum tenacity and maximum strain as compared to the control. The reduction is above 20% for both maximum tenacity and maximum strain. Again, the largest decrease (about 30%) was for the samples irradiated in air. Comparing the data in Table IV with those in Table III indicates the further reduction in maximum tenacity and maximum strain for the samples irradiated in air. The decrease in maximum strain indicates that the materials became more brittle, which may have been caused by increases in crystallinity and crosslinking. The samples irradiated in acetylene and air had a higher modulus than the control and the samples irradiated in nitrogen and vacuum, which may possibly due mainly to recrystallization and crosslinking. Although crystallinity also increased for the samples irradiated in nitrogen and vacuum, the chain relaxation in these two cases may have contributed more to the modulus than the recrystallization. The above results clearly suggest that the tensile properties of UHMW-PE fibers are reduced upon exposure to gamma irradiation.

Table IV Tensile Results of Polyethylene Fibers at 160 Days Postirradiation (Mean ± 95% Confidence Interval)

Samples	Maximum Tenacity (g/den)	Maximum Strain (%)	Modulus (g/den)
Control	32.4 ± 1.3	3.4 ± 0.1	1174 ± 24
Acetylene	24.1 ± 0.5	2.6 ± 0.0	1204 ± 32
Air	22.6 ± 0.6	2.4 ± 0.0	1201 ± 27
Nitrogen	23.4 ± 0.5	2.6 ± 0.1	1159 ± 22
Vacuum	23.7 ± 0.6	2.6 ± 0.1	1179 ± 42



(a)

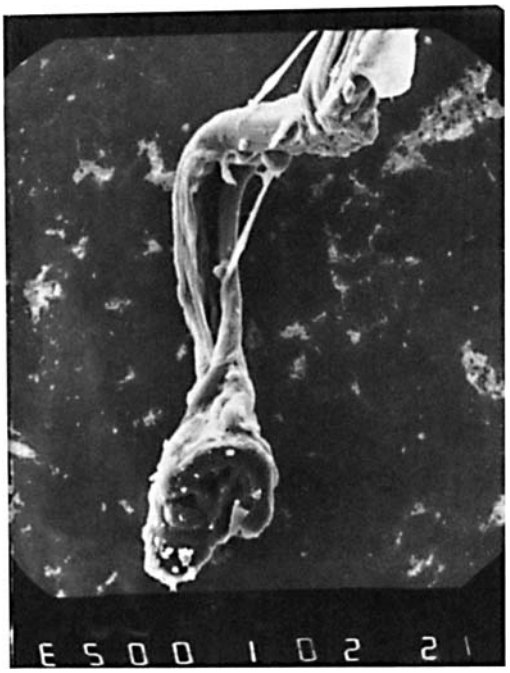


(b)

Figure 3 SEM micrographs of as-received polyethylene fibers.

Fracture Surfaces of UHMW-PE Fibers

SEM analysis of the fracture surfaces of tensile-loaded polyethylene fibers was pursued to determine any morphological effects of gamma irradiation and irradiation environments due to changes in the microfailure mechanisms. The fiber specimens were randomly selected from the samples tensile-tested following gamma irradiation, and viewed by SEM. The results are illustrated by the representative micrographs presented in Figures 3–8. Generally speaking, the fracture surfaces for



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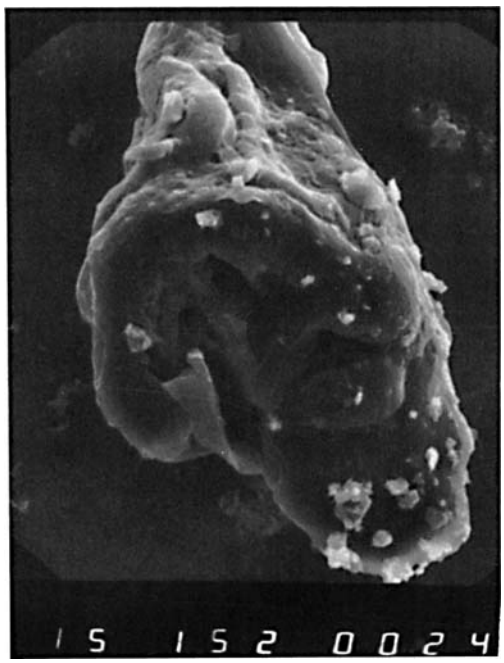
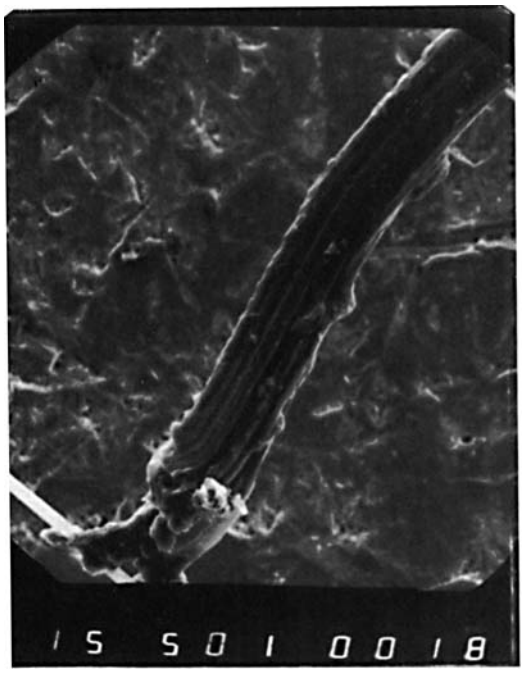


(b)

Figure 4 SEM micrographs of tensile fracture surface of a virgin polyethylene fiber.



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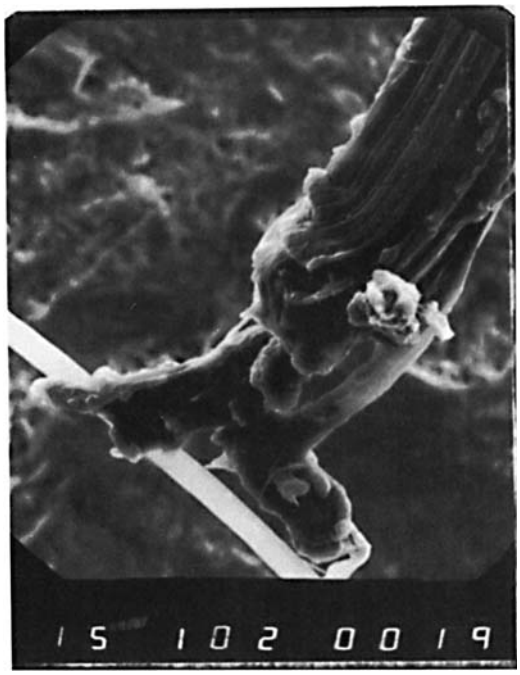
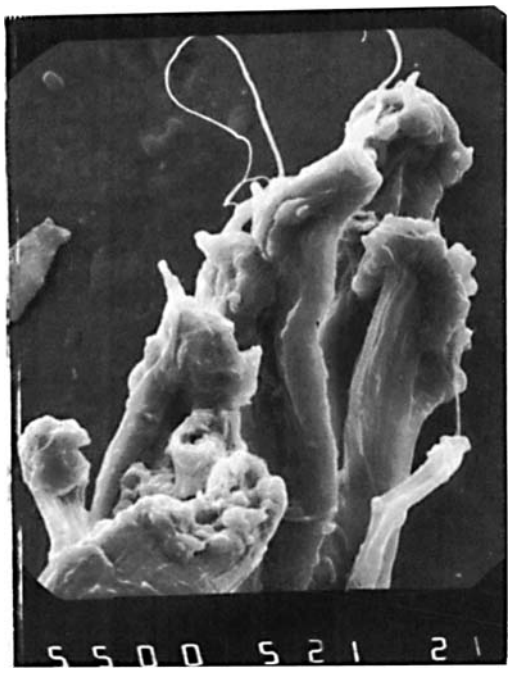


(b)

Figure 5 SEM micrographs of tensile fracture surface of a polyethylene fiber irradiated in nitrogen.

all groups showed different features. Compared to an unloaded specimen (Fig. 3), tensile-loaded polyethylene fibers all showed extended deformation, necking, and stretching bands. However, a limited plastic deformation was seen for the fractured polyethylene fibers, which may suggest that a highly extended chain conformation exists in polyethylene fibers and the chain slippage under tensile load is very limited.

(a)



(b)

Figure 6 SEM micrographs of tensile fracture surface of polyethylene fibers irradiated in air (note that there are two fiber ends).

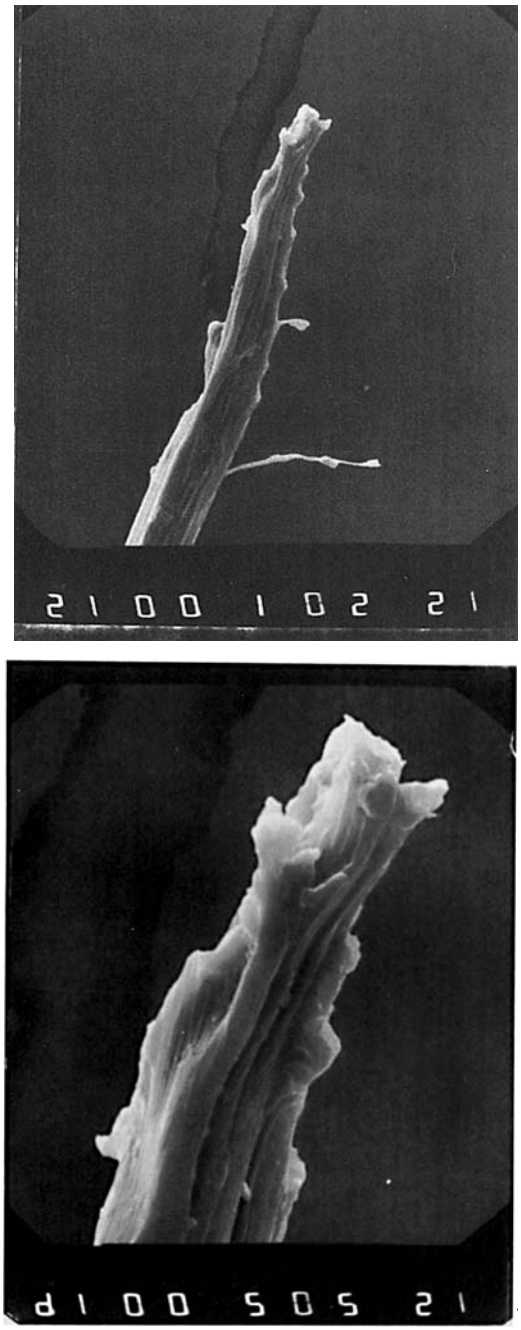


Figure 7 SEM micrographs of tensile fracture surface of a polyethylene fiber irradiated in acetylene.

CONCLUSIONS

The present study showed that gamma irradiation, irradiation environment, and postirradiation aging affect the thermal and tensile properties of gel-spun UHMW-PE fibers. Following gamma irradiation, the greatest change in properties was observed for the fibers irradiated in air. These results are similar to those from molded UHMW-PE. The detailed fracture surfaces of the tensile-loaded polyethylene fibers studied by scanning electron microscopy reflect clear effects of gamma irradiation and irradiation environment. It is hypothesized that the acet-

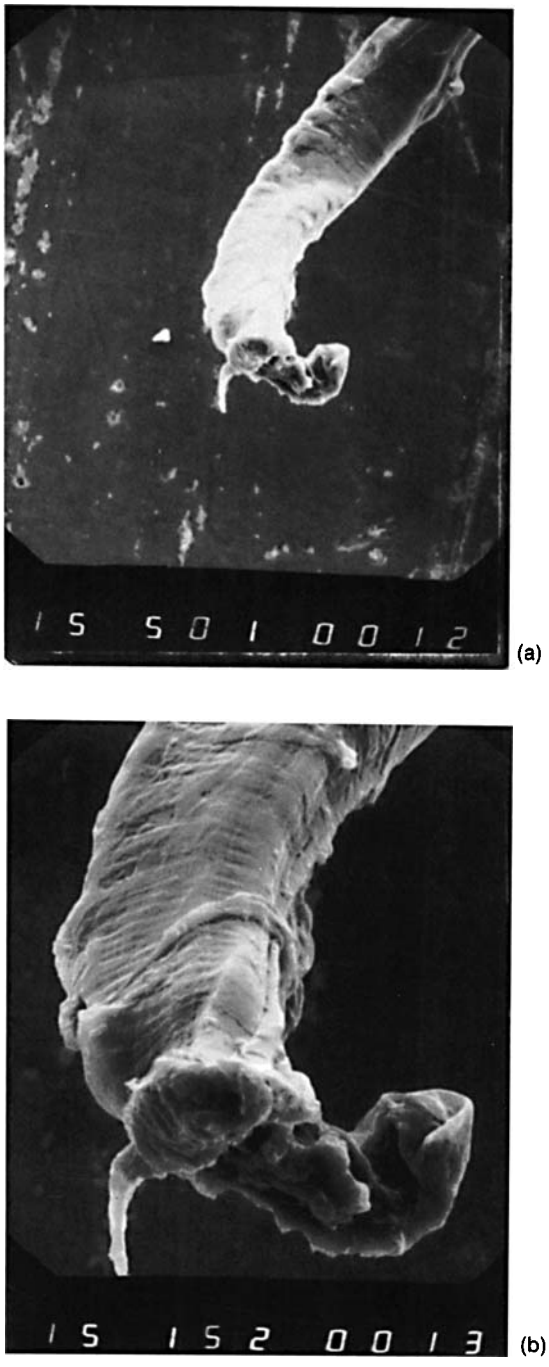


Figure 8 SEM micrographs of tensile fracture surface of a polyethylene fiber irradiated in vacuum.

ylene environment mainly introduced crosslinking, while chain scission was the major events for samples treated in the vacuum and nitrogen environments. The postirradiation aging study at 160 days indicates that upon postirradiation aging all of the irradiated samples showed decreases in melting temperature, maximum tenacity, and maximum strain, but increases in crystallinity and oxidation temperature. Those results suggest that UHMWPE fibers may not be suitable in a long-term application after they have been exposed to gamma irradiation.

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