Effect of electron beam irradiation on physical properties of ultrahigh molecular weight polyethylene

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ABSTRACT: If a large amount of polymer radicals remain trapped after the irradiation of ultrahigh molecular weight polyethylene (UHMWPE), the radicals may result in a significant alteration of its physical properties during long-term shelf storage and implantation. An electron spin resonance spectroscopic study was undertaken to investigate the remaining free radicals in UHMWPE after electron beam irradiation up to 500 kGy in air and an N_2 environment. Heat treatment was employed at 110 and 145°C for various periods of time to decay the free radicals. The free radicals were rapidly decayed for 1 h and gradually decayed as a function of time with the heat treatment. The decay of the free radicals was completed more rapidly with a heat treatment at 145°C than at 110°C. Therefore, a longer heat treatment time is required to scavenge all the free radicals formed in UHMWPE at 110°C. The oxidation profiles showed that the oxidation index of the heat-treated UHMWPE was lower than the oxidation index of the non-heat-treated UHMWPE. The heat treatment of irradiated UHMWPE can substantially reduce the concentration of free radicals; therefore, UHMWPE has resistance against long-term oxidative degradation. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 97: 103–116, 2005

Key words: polyethylene; ultrahigh molecular weight polyethylene; crosslinking; electron beam irradiation; electron spin resonance; differential scanning calorimetry; Fourier transform IR; heat treatment; oxidation

INTRODUCTION

Ultrahigh molecular weight polyethylene (UHMWPE) is routinely used for the manufacture of the acetabular cup for total hip replacement and the patellar components for total knee replacement. Irradiation is usually employed for the sterilizing and crosslinking of UHMWPE. However, occasional failures have been reported, within 6–8 years of implantation in active or obese patients. Most failures are attributed to the oxidative degradation of the PE molecules initiated by the reaction of free radicals, which are generated by irradiation, with oxygen during shelf storage and implantation.[1–6] Irradiation of polymeric materials may cause an increase in their molecular weight that is due to crosslinking and/or a decrease in their molecular weight that is due to chain scission simultaneously. Free radicals are formed in UHMWPE during irradiation. These polymer radicals transform into oxidized moieties if oxygen is present in the vicinity of the formed radicals or remains trapped in the polymer matrix for a certain period of time after irradiation.[7–11] In this study, we investigated the UHMWPE radicals remaining after electron beam (EB) irradiation as a function of the dose and examined how effective heat treatment of the irradiated UHMWPE was for decaying the free radicals by the changes of the electron spin resonance (ESR) spectra. The degree of crosslinking was estimated via the determination of the gel fraction. In addition, Fourier transform IR (FTIR) and differential scanning calorimetry (DSC) were employed to study the changes of the chemical and physical properties. The heat treatment took place either above or below the melt transition. Heat treatment below the melt transition is referred to as annealing and above the melt transition is referred to as remelting. The oxidation profiles were measured by FTIR.

EXPERIMENTAL

Heat treatment after EB irradiation

The samples in this experiment were prepared from 10-mm diameter ram-extruded UHMWPE cylindrical bar stock (GUR 4150, average molecular weight = ~9.3 million, density = 0.93 g/mL). EB irradiation was carried out at a dose rate of 7500 kGy/h using an ELV-4 accelerator (1-MeV energy, 2.5-mA current) in air and an N_2 environment. The conveyor speed was adjusted to a dose of 5 kGy during a single pass to prevent overheating of the specimen.[2,11–13] The irradiated specimens were heated in an N_2 environment to prevent oxidative degradation at 110 and 145°C for 7 and 2 h, respectively, at a heating rate of 2°C/min. The specimens were cooled to room temperature at a cooling rate of 1°C/min.

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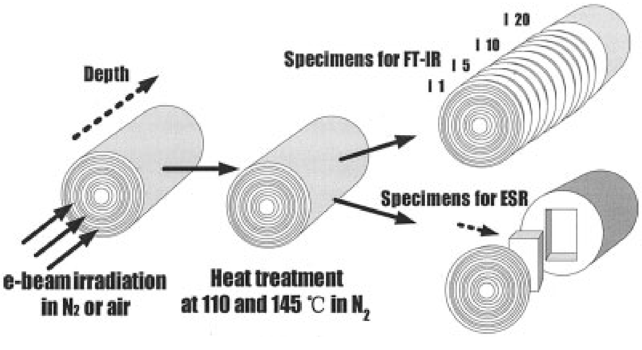


Figure 1 The schematic experimental method and preparation of the specimens.

ESR for free radicals

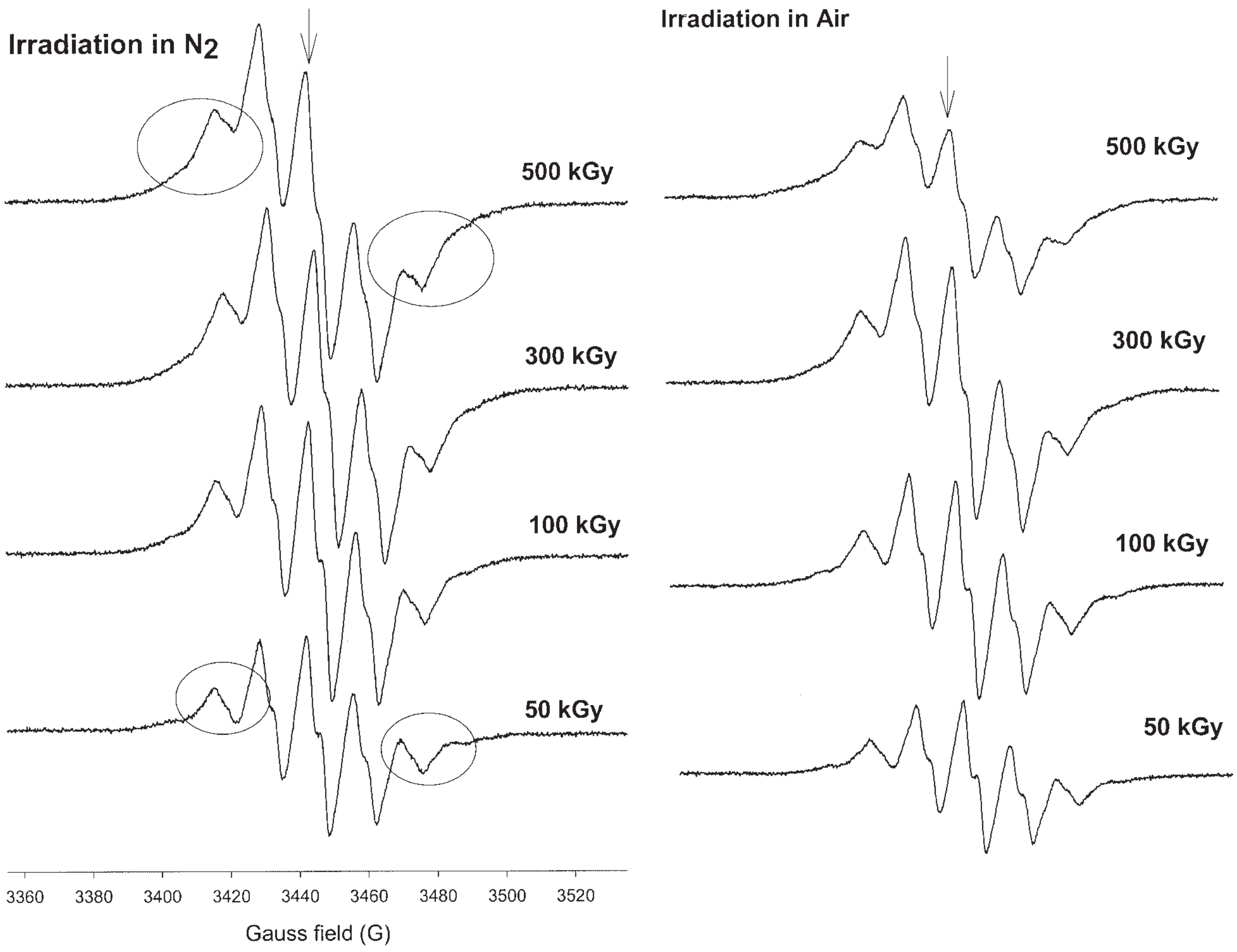
The specimens for the free-radical measurements were machined ($3 \times 5 \times 1.5$ mm^3) after cutting off 0.8 mm from the surface of the UHMWPE bar stock, as shown in Figure 1. An X-band ESR spectrometer (EPR EMX, Bruker) was used, which operated at 9.648-GHz microwave and 100-kHz magnetic field modulation frequencies. The microwave power was maintained at 20.12 mW, and the modulation amplitudes were 1 and 5 G. The double integration method was used to determine the relative free-radical concentration.[7–9]

FTIR spectroscopy

FTIR specimens were microtomed into 200 μm thick slices from the surface of the specimen, as shown in Figure 1. The oxidation-depth profiles were obtained with an FTIR apparatus (Tensor 37, Bruker) using 64 scans at a resolution of 16 cm^{-1}. The oxidation index (OI) was calculated by the ratio of the peak area of the ketone (C=O) group absorption band at 1717 cm^{-1} to the area of the methylene group reference band at 1370 cm^{-1}.[1–3]

$$\text{oxidation index} = \frac{\text{absorption area}_{1717}}{\text{absorption area}_{1370}}$$

The *trans*-vinylene (—C=C—) index was also calculated by the ratio of the peak area of the *trans*-vinylene



(a)

(b)

Figure 2 The change of the ESR spectrum of the UHMWPE irradiated (A) in N_2 and (B) in air as a function of absorbed irradiation dose.

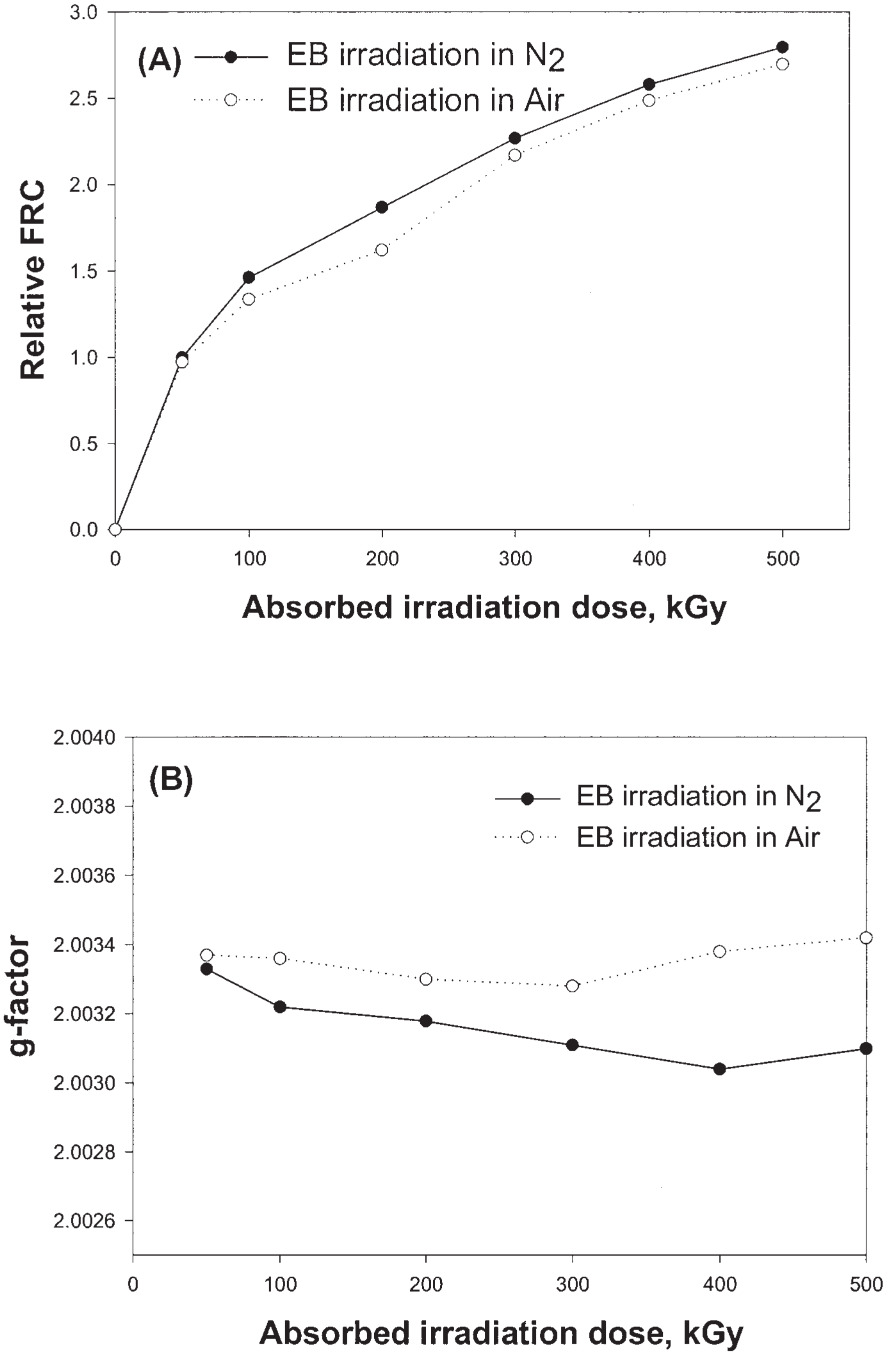


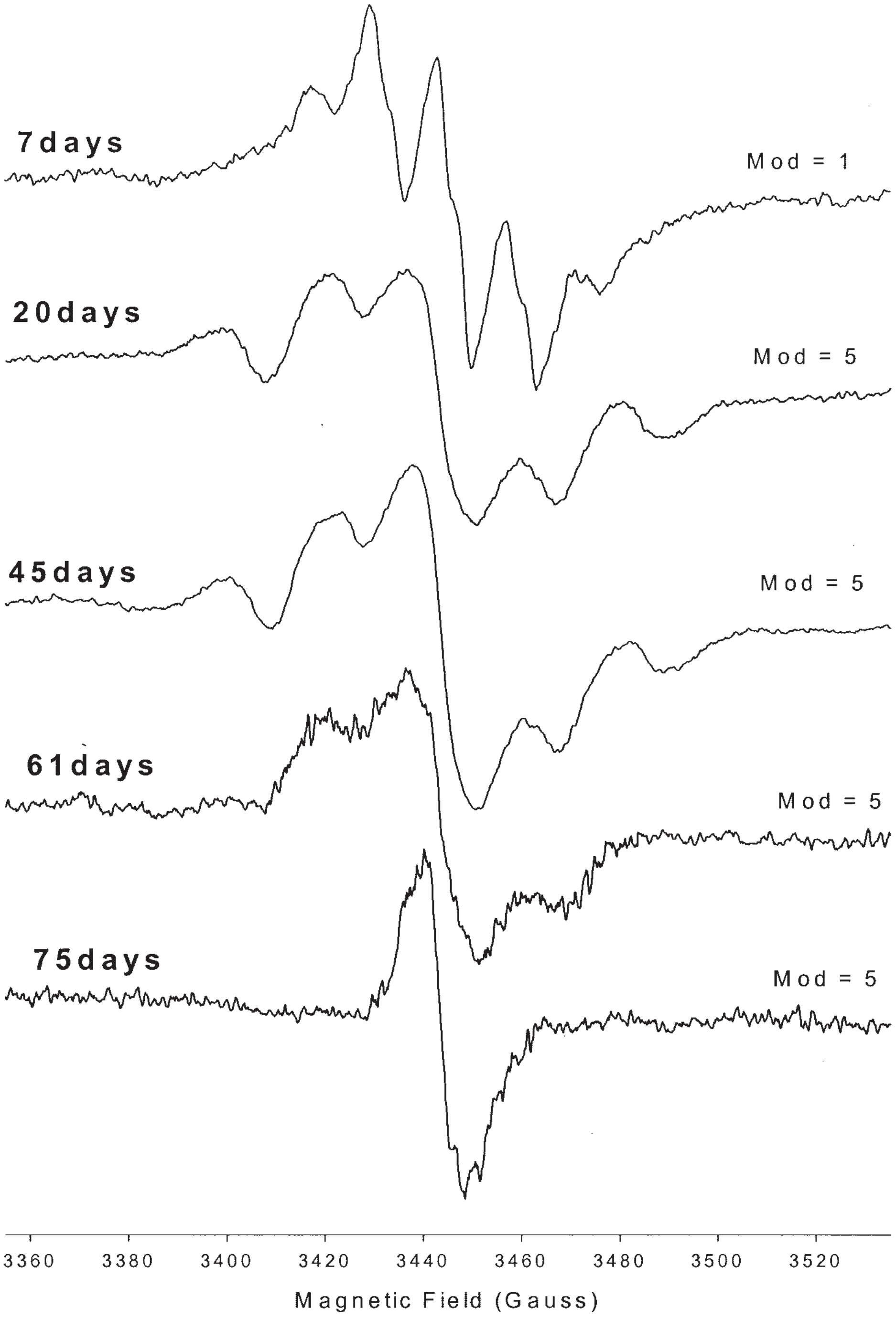
Figure 3 The change of (A) the relative free-radical concentration (FRC) and (B) the *g*-factor of UHMWPE irradiated in air and in N_2 with the increase of the absorbed irradiation dose.

band at 965 cm^{-1} to the area of the methylene group reference band at 1370 cm^{-1}.[14]

$$\textit{trans}\text{-vinylene index} = \frac{\text{absorption area}_{965}}{\text{absorption area}_{1370}}$$

Gel fraction measurement

The gel fraction of each sample was analyzed as a function of the absorbed irradiation dose. All the specimens were collected after cutting off 0.2 mm from the surface of the irradiated UHMWPE. Extraction of the sol fraction for the investigated samples was performed by boiling in xylene for 48 h, with 0.5 wt % of an antioxidant (2,6-di-*t*-butyl-4-methyl phenol). After extraction, the specimens were dried at 80°C in a vacuum oven to constant weight.[4,13] The gel fraction was determined from the ratio of the weight of the dried extracted specimen (W_d) to the initial weight of the specimens (W_i).



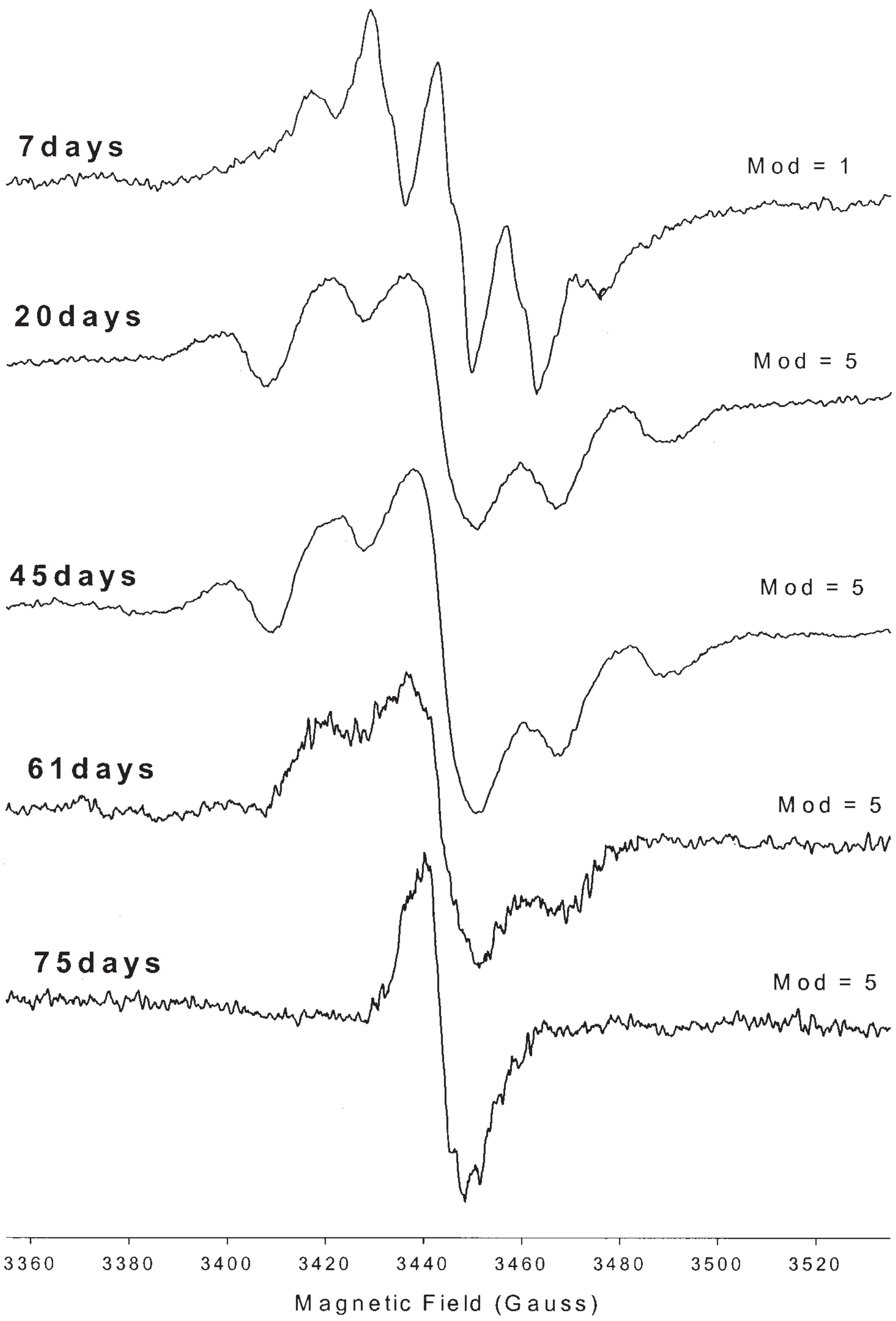
(a)

Figure 4 The change of the ESR spectrum of 300-kGy irradiated UHMWPE (A) in N_2 and (B) in air as a function of the storage time at 25°C.

$$\text{gel fraction (\%)} = \frac{W_d}{W_i} \times 100$$

DSC for crystallinity

For the DSC measurements, the weight of the specimens was 4.9–5.6 mg. Specimens were heated from 40 to 200°C with a heating rate of 10°C/min in a continuous nitrogen purge (Perkin–Elmer DSC-7). The melting temperature was identified from the peak of the melting endotherm. Indium was used for the calibration of the temperature and heat of the fusion. The mass fraction of the crystalline regions (termed crystallinity henceforth) in the specimens was calculated using the following expression[10]:



(b)

Figure 4 (*Continued from the previous page*)

$$\text{crystallinity (\%)} = \frac{E}{m \cdot \Delta H} \times 100$$

where E is the heat absorbed by the sample in the melting (J), m is the mass of the specimen (g), and ΔH is the heat of melting of the PE crystals (ΔH = 291 J/g).[10]

RESULTS AND DISCUSSION

Relative free-radical concentration

The ESR spectra of the UHMWPE irradiated in an N_2 and in an air environment for the absorbed irradiation dose are shown in Figure 2. Any significant difference between the irradiation in N_2 and in air was not shown in the ESR spectra. The maximum

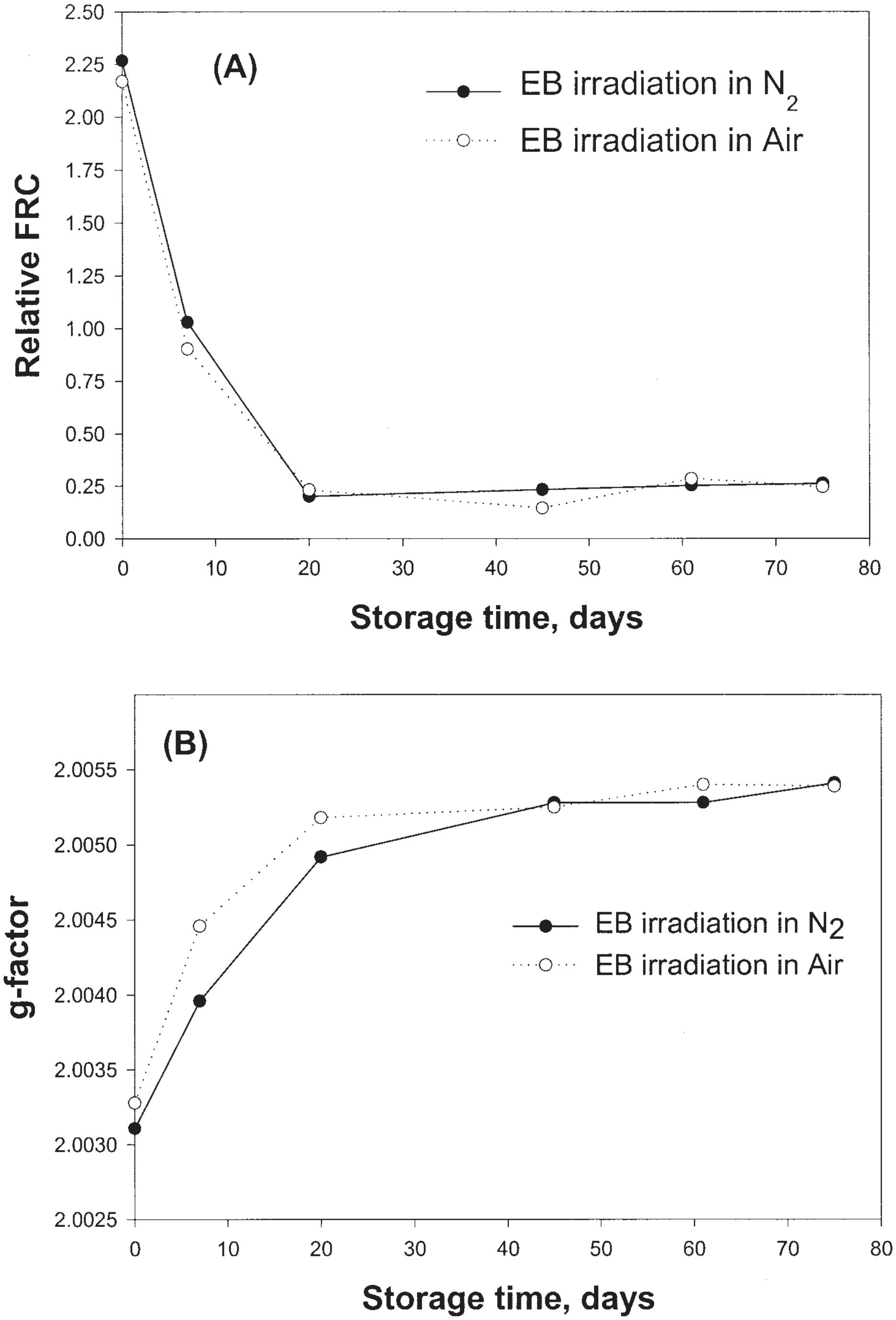


Figure 5 The change of (A) the relative free-radical concentration and (B) the *g*-factor of the 300-kGy irradiated UHMWPE in air and in N_2 as a function of the storage time at 25°C.

intensity increased with the irradiation but the central line in the spectra (arrow) decreased comparatively, indicating the growth of oxygen-induced radicals.[7–9]

The relative free-radical concentration was calculated by a double integration of these ESR spectra, assuming that the peak area of the UHMWPE irradiated to 50 kGy in N_2 was unity. The free-radical concentrations of the specimens irradiated in air and in N_2 are given in Figure 3(A). Note that the free-radical concentration gradually increases with the irradiation dose and the free-radical concentration of the irradiation in N_2 is slightly higher than the irradiation in air, but not significantly. To examine the transformation of the PE radical species, the *g*-factor was evaluated from the ESR spectra. ESR is a forum for microwave absorption spectroscopy for the transitions induced between the Zeeman energy levels arising from the interaction

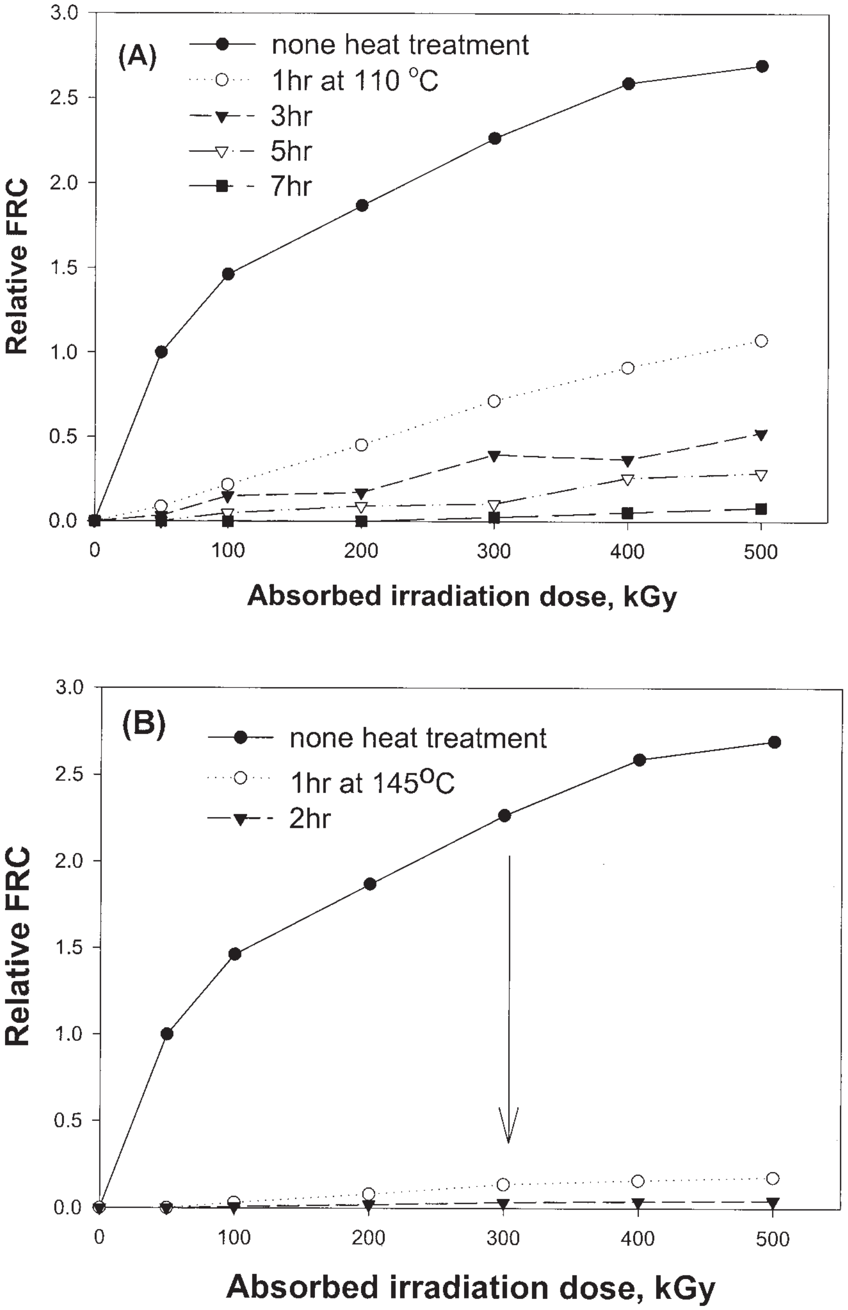


Figure 6 The change in the relative free-radical concentration (FRC) as a function of the heat treatment time at (A) 110 and (B) 145°C in N_2.

of an assemblage of the paramagnetic electrons with an externally applied magnetic field (H). The energy difference (E) between the Zeeman levels is associated with a characteristic absorption frequency (ν), which is given by the Einstein Planck relation,

$$E = h\nu = g\beta H$$

where h is Planck's constant; β is the Bohr magneton; and g is the spectroscopic splitting factor, which is defined by $h\nu = g\beta H$. The position center of the spectrum gives the H at which the resonance occurs, and it can be used to calculate the g value. A free electron spin is expected to have a value of $g = 2.0$. In real materials, g may differ from this value, depending on the variations in the coupling between the spin and orbital angular momentum. The g values of some organic radicals are as follows:

$CH_3—\dot{C}H—CH_3 : 2.0027$ $CH_2{=}CH—\dot{C}H_2 : 2.0026$

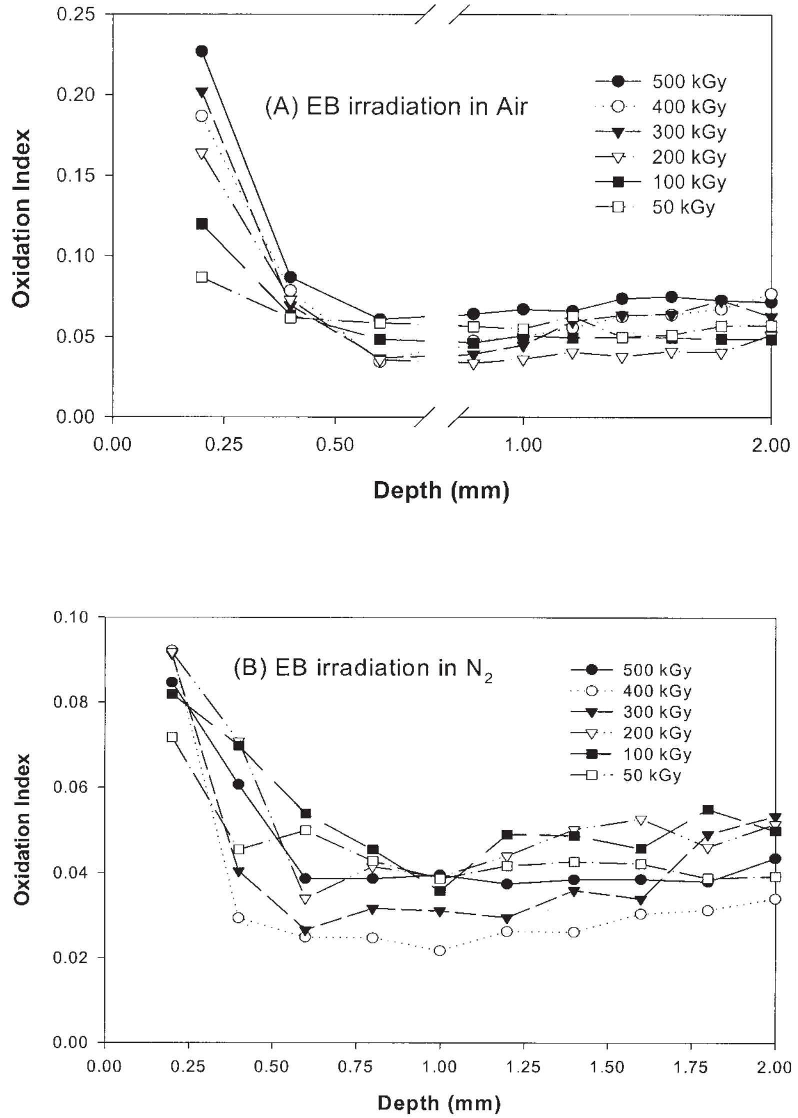
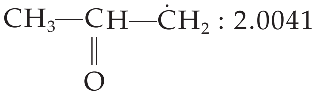
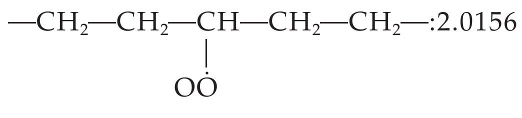


Figure 7 The oxidation-depth profiles of the UHMWPE after irradiation (A) in air and (B) in N_2 with different absorbed irradiation doses (50–500 kGy).



$CH_3—\underset{\underset{O}{\|}}{C}H—\dot{C}H_2$: 2.0041



$—CH_2—CH_2—\underset{\underset{O\dot{O}}{|}}{C}H—CH_2—CH_2—$:2.0156

If oxygen is present, the PE radicals will be oxidized to form oxygen-containing radicals that have higher *g*-factors than the PE radicals without any attached oxygen atoms.[8]

The changes of the *g*-factor of the UHMWPE irradiated in air and in N_2 are shown in Figure 3(B). It is accepted that the irradiation of UHMWPE produces alkyl radicals (— · CH—CH_2—), which gradually transform to more stable allyl radicals (— · CH—CH=CH—) with an increase of the dose.[12,15] However, the *g*-factor of the UHMWPE irradiated in air increases for a higher dose because of the oxygen diffusion into the UHMWPE matrix, which leads to the formation of a peroxy radical. As shown in Figure 3, the *g*-factor changes between the values of 2.0032 and 2.0036.

Figure 4 shows the change of the ESR spectra of the UHMWPE that was irradiated to 300 kGy in N_2 and in air and then stored in air at 25°C. The number of spectra peaks decreases with an increase in the storage time, approaching a single peak spectrum, irrespective of the irradiation environment.

Figure 5(A) shows the changes of the relative free-radical concentration for the 300-kGy irradiation as a function of the storage time at 25°C. The relative free-

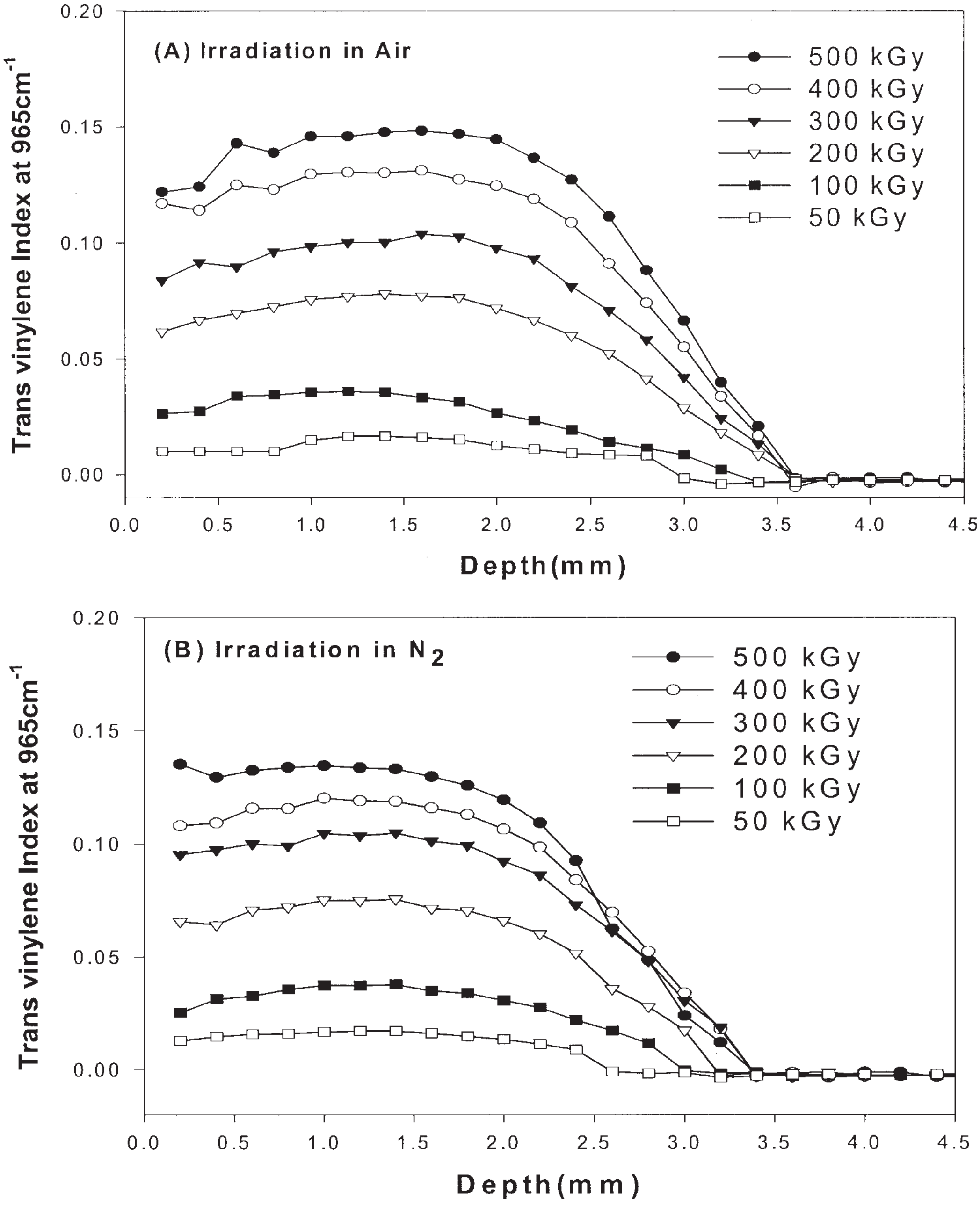


Figure 8 The *trans*-vinylene index depth profiles of the UHMWPE after irradiation (A) in air and (B) in N_2.

radical concentration decreases during storage until 20 days, although they do not disappear completely after a period of storage. In Figure 5(B), the changes of the *g*-factor for the 300-kGy irradiation are shown as a function of the storage time at 25°C. The *g*-factor also increased steeply until about 20 days and became almost stable. This indicates that the alkyl and allyl PE radicals are transformed into oxidized species during 20- (irradiation in air) and 30-day (irradiation in N_2) storage time.

Figure 6 shows the decrease of the relative free-radical concentration by heat treatment in N_2 at 110 and 145°C (above the melting temperature). As can be seen, the relative free-radical concentration was rapidly decreased for 1 h and gradually decreased as a function of the heat treatment time. The decay of the free radicals was completed more rapidly with a 145°C heat treatment. Therefore, a longer heat treatment time was required to scavenge all the free radicals formed on the UHMWPE at 110°C than at 145°C.

Oxidation of UHMWPE

The FTIR spectra were obtained immediately after EB irradiation. Figure 7 presents the oxidation-depth pro-

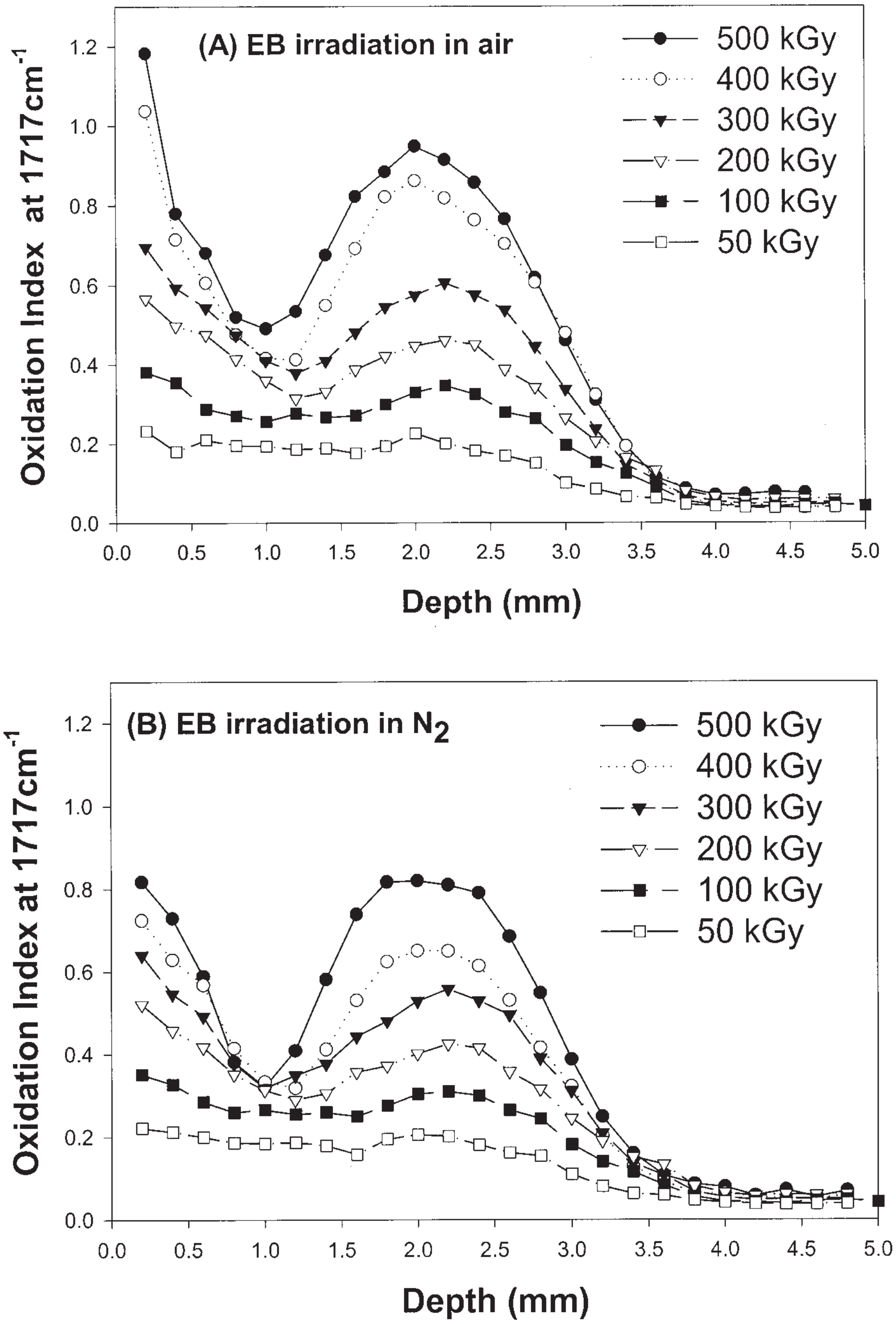


Figure 9 The oxidation-depth profiles of the UHMWPE for irradiation (A) in air, (B) in N_2, (C) with a 7-h heat treatment at 110°C, and (D) with a 2-h heat treatment at 145°C after irradiation in N_2 with 45-day actual shelf aging time (1 atm air at 25°C).

files of the UHMWPE irradiated in air and in N_2. The OIs were almost liner with the absorbed dose in air and decreased steeply until a 0.8-mm depth from the surface, as shown in the figure. These trends are indicative of the oxygen diffusion into the UHMWPE matrix. Moreover, especially on the surface, the OIs of the UHMWPEs irradiated in nitrogen were low, compared to those irradiated in oxygen.

The penetration of EB radiation depends on the energy of the electrons used and the density of the material. For instance, with UHMWPE (density $= \sim 0.93$ g/cm^3), the penetration of a 1-MeV EB is about 3.58 mm and the maximum dose occurs at about 1.7 mm from the surface, theoretically.[1,13] One of the radiolytic events that occurs during the irradiation of PE is the formation of the *trans*-vinylene unsaturations. *trans*-Vinylene can be quantified using FTIR spectroscopy by the observation of the absorbance band at 965 cm^{-1}. Figure 8 shows the variation of the *trans*-vinylene index as a function of the depth from

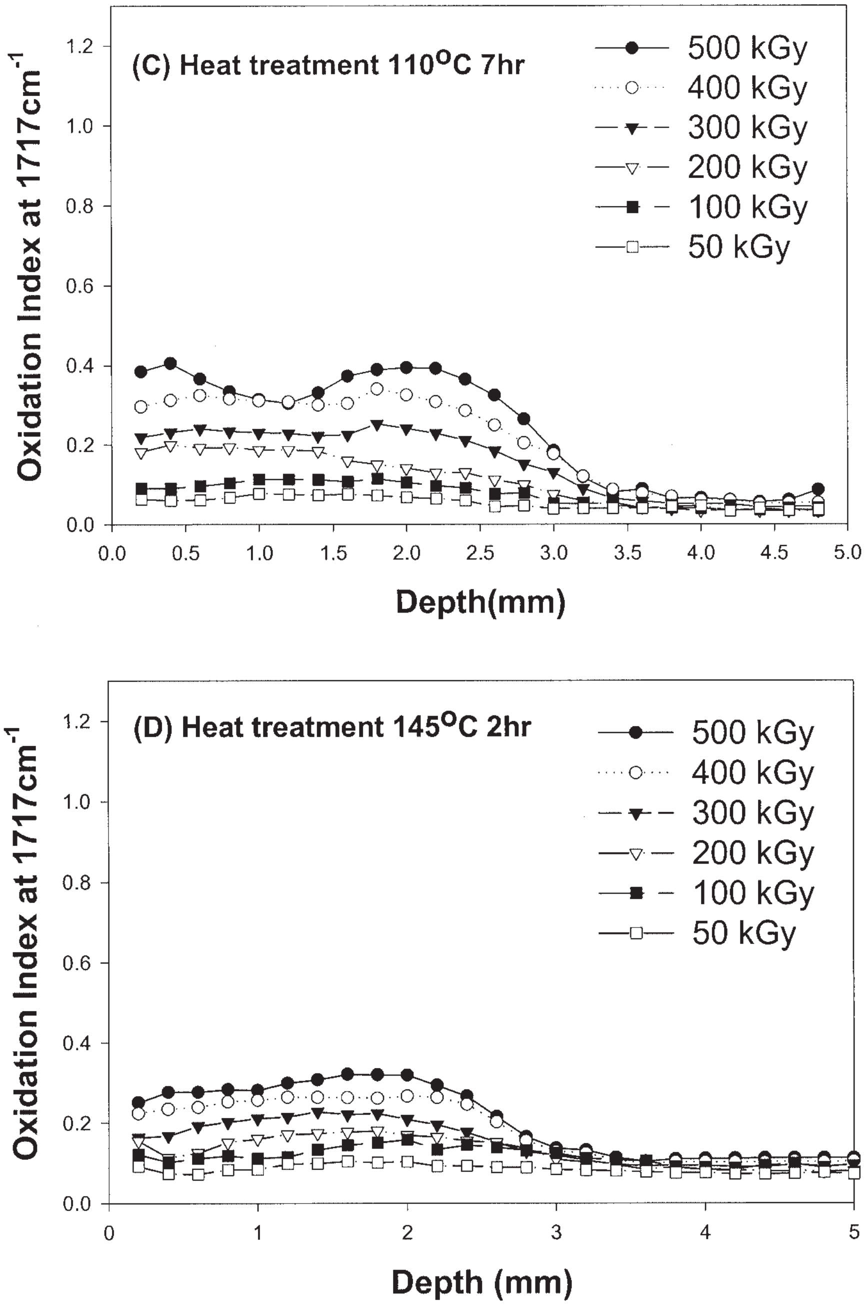


Figure 9 (*Continued from the previous page*)

the EB incidence surface for each irradiation dose. The *trans*-vinylene index gradually increases with the absorbed irradiation dose in both the air and the N_2 environments, and the level of the *trans*-vinylene index of the UHMWPE irradiated in air was higher than that for samples irradiated in N_2. The *trans*-vinylene index of irradiated samples in air slightly increased until about a 1.8-mm depth for a higher irradiation dose (above 200 kGy) and at a 1.3-mm depth for a lower irradiation dose. In contrast, the depth profile for irradiated samples in N_2 appear at 1.2 and 1.4 mm for higher and lower irradiation doses, respectively (see Fig. 8). Beyond the depth of about 3.6 mm, any change of the *trans*-vinylene index was not observed.

In Figure 9(A,B), the OI of UHMWPE in air was higher in comparison with irradiated samples in N_2, and there is no significant difference in the oxidation-depth profiles of the UHMWPE irradiated in air and in the N_2 environments without heat treatment for an actual 45-day shelf aging time (1 atm air at 25°C). The OI of the UHMWPE irradiated in air was higher, but there is no significant difference of the OI beyond the 4-mm depth from the UHMWPE surface for all the absorbed irradiation doses. The OI increased with the

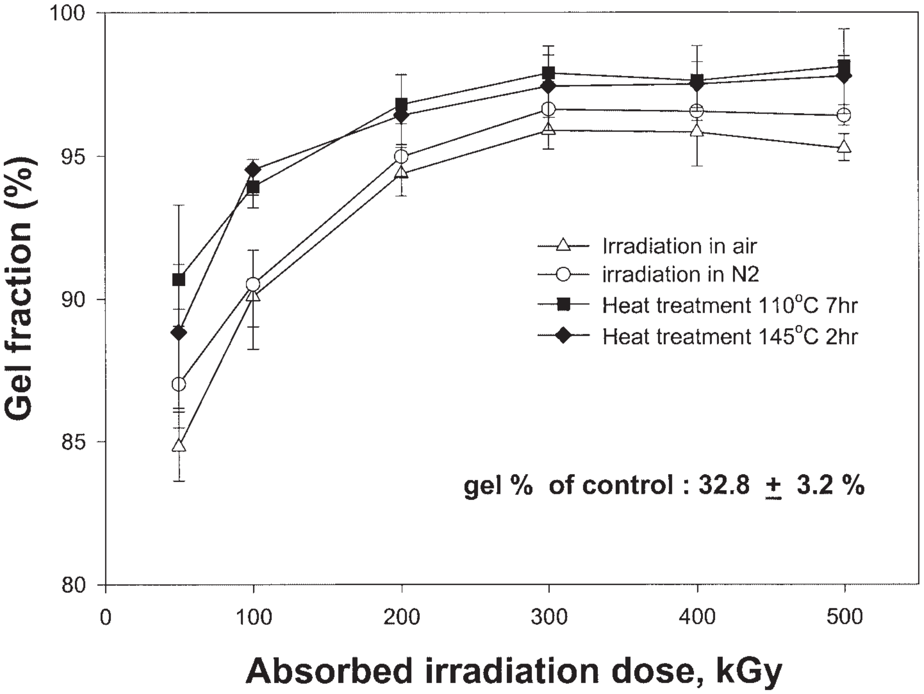


Figure 10 The change of the gel fraction of the irradiated UHMWPE as a function of the irradiation dose and heat treatment temperature.

increase of the absorbed irradiation dose, and its maximum occurred at the EB incidence surface for each absorbed irradiation dose. The OI increased with an increasing irradiation dose. However, the OI decreased until a 1.0-mm depth, increased until it reached the maximum value at about a 2.0-mm depth, and then decreased again even for an absorbed irradiation dose. This tendency was not significant for a lower absorbed irradiation dose. We consider that the factors of polymer degradation are the oxygen diffusion and the free radicals generated during irradiation. We can assume that the main oxidation effect of the UHMWPE is the oxygen diffusion within about a 0.8-mm depth and the main effect of the oxidation is the free-radical concentration beyond the 0.8-mm depth.

Figure 9(C,D) shows the oxidation-depth profiles for an actual 45-day shelf aging time after the UHMWPE was irradiated in an N_2 environment and heat treated at 110 and 145°C. It can be seen that the OI of the heat-treated UHMWPE was lower than the non-heat-treated UHMWPE. At the same irradiation dose, the OI is higher in the highly irradiated region (more accurately, theoretical peak dose = 1.7-mm depth). As shown in the oxidation profiles, the free radicals decay by the heat treatment can inhibit the oxidative degradation of UHMWPE irradiated during a long period of time.

Gel fraction

Figure 10 shows the relationship between the irradiation dose and the gel fraction of the UHMWPE irradiated in air and in N_2. In both cases, the gel fraction was increased with an increasing irradiation dose, reaching about 95.8% at 300 kGy for irradiation in air and about 96.6% at 300 kGy for irradiation in N_2. In addition, the gel fraction was increased by the heat treatment in N_2 for 7 h at 110°C or for 2 h at 145°C. As the irradiation dose increases, the concentration of the free radicals increases and, as a consequence, the crosslinking increases. The crosslinking and chain scission of the UHMWPE during irradiation occurs simultaneously. In highly irradiated samples, the radical concentration is high; a greater chain scission reaction is induced and can continue for some time after irradiation. Therefore, there was no further increase in the gel fraction over a 300-kGy irradiation dose.

DSC

The changes of the crystallinity as a function of the absorbed irradiation dose and heat treatment are shown in Figure 11(A). The crystallinity gradually increases with the increase of absorbed irradiation dose up to 200 kGy and thereafter levels off. Interestingly, the change in the level of crystallinity for irradiated samples in N_2 at a higher temperature heat treatment (145°C) is lower than that for irradiated samples in air at a lower temperature heat treatment (110°C). The crystallinity was increased by the 110°C heat treatment, but it was decreased by the 145°C heat treatment. The melting temperature was determined

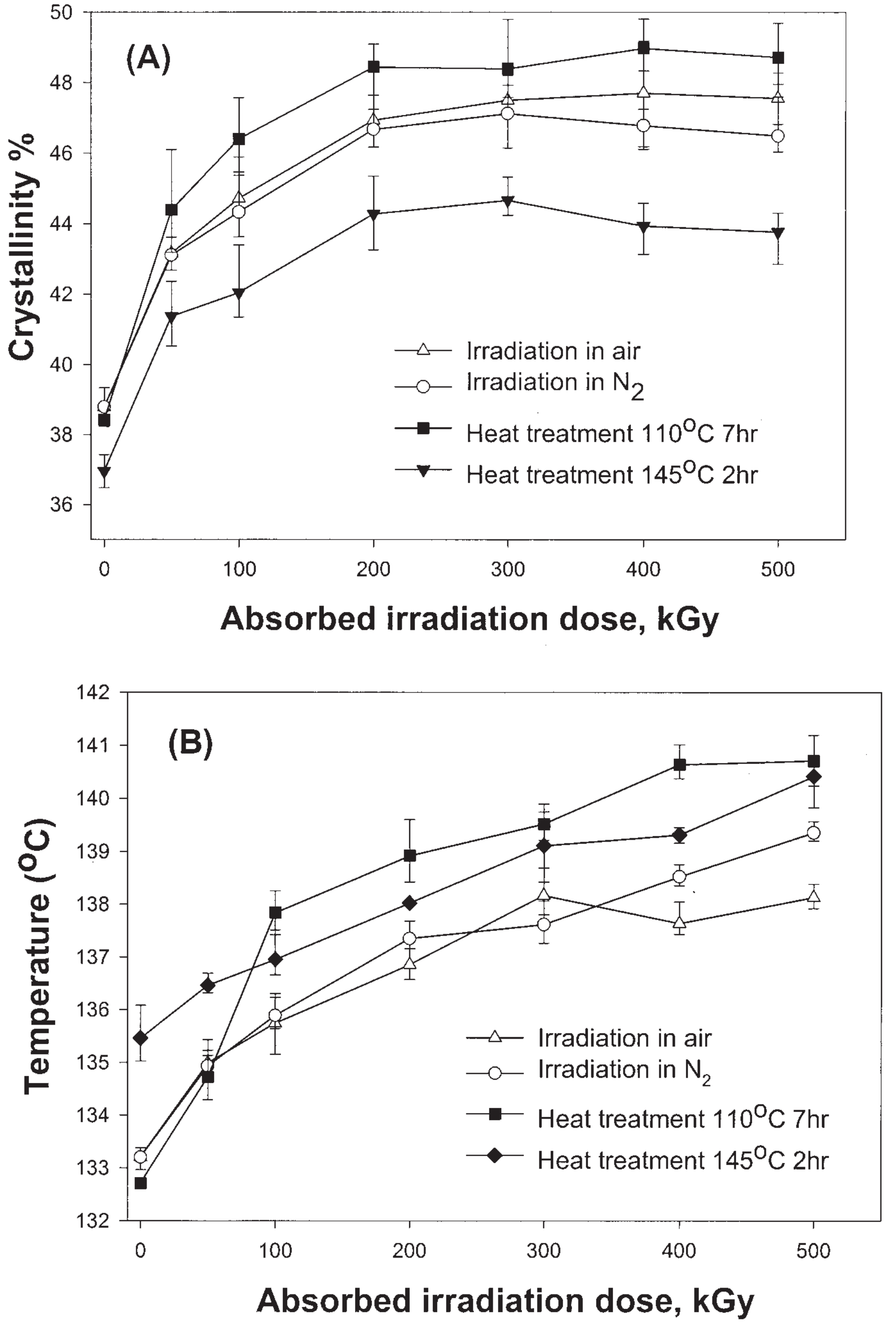


Figure 11 The change of (A) the crystallinity and (B) melting temperature of the irradiated UHMWPE as a function of the irradiation dose and heat treatment temperature.

from the main endotherm peak of the DSC curves. It also increased with an increase of the irradiation dose, as shown in Figure 11(B). The heat treatment increased the melting temperature. In addition, note that there is a slight change in the melting temperature because of the irradiation in air and in N_2 environments. Moreover, it was found that the heat treatment increases the melting temperature of the investigated samples and also exhibits higher melting temperature values in comparison with the non-heat-treated samples. The increase of the crystallinity during irradiation is caused by the formation of a new crystal from the radiation-induced backbone chain scission in the lamella or at the crystal–amorphous interface. The high peak melting temperatures in the irradiated sample suggest that the melting process is being kinetically arrested by the crosslinking, thus producing higher melting temperatures at the relatively fast heating rate of 10°C/min. The heat treatment below the melting temperature helps to form the new crystals and crosslinking after the irradiation of the UHMWPE. Therefore, the crystallinity was increased. For heat treatment above the melting temperature, the formation of crystals is inhibited as the crosslinking interrupts the recrystallization of the melted UHMWPE. Therefore, the crystallinity was comparatively low.

CONCLUSIONS

The free radicals in the UHMWPE during irradiation transform into oxidized moieties if oxygen is present in the vicinity of the formed radicals or remains trapped in the polymer matrix for a certain period of time after irradiation. In this study, we investigated the UHMWPE radicals remaining after EB irradiation as a function of the dose and examined how effective the heat treatment of the irradiated UHMWPE was for scavenging the free radicals by the changes of the ESR spectra.

The scavenging of free radicals was completed more rapidly with a heat treatment at 145°C than at 110°C. Therefore, a longer heat treatment time is required to scavenge all the free radicals formed in the UHMWPE at 110°C. The oxidation profiles showed that the OI of heat-treated UHMWPE was lower than the OI of non-heat-treated UHMWPE. The heat treatment of irradiated UHMWPE can substantially reduce the concentration of free radicals; therefore, UHMWPE has resistance against long-term oxidative degradation.

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