Polymer Vol. 39 No. 24 pp. 6115–6120, 1998
0032-3861/98/$ – see front matter

PII: S0032-3861(98)00075-5

Surface crosslinking of polyethylene by electron beam irradiation in air

Oleg N. Tretinnikov[a,b], Sakae Ogata[a] and Yoshito Ikada[a,*]
[a]Research Center for Biomedical Engineering, Kyoto University, 53 Kawahara-cho, Shogoin, Sakyo-ku, Kyoto 606, Japan
[b]B. I. Stepanov Institute of Physics, Academy of Sciences of Belarus, 70 Prospekt F. Skariny, Minsk 220072, Belarus
(Received 16 December 1997; accepted 20 January 1998)

Ultra-high molecular weight polyethylene (UHMWPE) was irradiated by electron beams to a dose of 100 kGy at a dose rate of 20 kGy min^{-1} and the near-surface region of the irradiated polymer was characterized by means of attenuated total reflection Fourier-transform infra-red (ATR *FT*i.r.) spectroscopy and micro-hardness measurement. The results obtained strongly suggest that irradiation in air introduced hydroperoxide groups into the polymer without formation of any other oxygen-containing groups. The generated hydroperoxides could be decomposed further by subsequent heat treatment of the irradiated polymer, resulting in crosslinking of UHMWPE chains in the near-surface region of the material. As a result of this surface modification, the surface hardness of UHMWPE substantially increased. © 1998 Elsevier Science Ltd. All rights reserved.

(Keywords: ultra-high molecular weight polyethylene; electron beam irradiation; crosslinking)

INTRODUCTION

Ultra-high molecular weight polyethylene (UHMWPE) is a linear polyethylene with an average molecular weight greater than $2 \times 10^6\,\mathrm{g\,mol}^{-1}$. In view of its excellent engineering properties, such as resistance to chemicals and physical abrasion, low friction coefficient, and high impact strength, UHMWPE has found a wide spectrum of applications, particularly as a material for prostheses in orthopaedics[1].

When UHMWPE is irradiated with gamma rays or electron beams in an oxygen-free environment, the major effects observed are formation of crosslinks and unsaturation. Crosslinking results in formation of a three-dimensional chemical network and, consequently, alters the mechanical properties of the polymer. The radiation-induced crosslinking has been shown to be particularly valuable in improving the wear resistance and creep performance of UHMWPE[2,3].

In addition, it has been well established that irradiation of UHMWPE in the presence of oxygen or air leads to oxidation of the polymer and, as a result, to a loss of its superior mechanical properties[4]. Oxygen reacts readily with alkyl radicals and forms species such as hydroperoxides, alcohols, acids, ketones, etc. The extent of radiation-induced oxidation increases with radiation dose and, in addition, with exposure time[5]. In the case of irradiation with ^{60}Co gamma-rays, the radiation intensity is usually very low and the time needed to reach a certain dose is protracted (typically, more than 5 h for a dose of 25 kGy). On the contrary, very high radiation intensities are characteristic of electron irradiation and, consequently, very high irradiation doses may be obtained with irradiation times less than 10 min. As a result, the extent of oxidation of gamma-irradiated samples is much higher than that of polymers irradiated to the same dose with high-energy electrons. In addition, electron irradiation localizes the oxidation process in a thin surface layer (10–$10^2\,\mu$m, depending on the conditions of irradiation), while deeper layers of the material undergo damage with gamma rays at the same dose[6]. This different effect on polymer oxidation may be due to slow diffusion of oxygen into the irradiated polymer bulk phase from the outer atmosphere.

It is then apparent that the extent of oxidation of UHMWPE may be reduced by shortening the exposure time. This can be achieved by raising the dose rate, but, to the best of our knowledge, there have been no reports on the oxidation behaviour of UHMWPE irradiated at very high dose rates, such as those higher than 5 kGy min^{-1}. In this paper we report the results of surface characterization and crosslinking of UHMWPE irradiated by electron beams to a dose of 100 kGy at a dose rate of 20 kGy min^{-1}.

EXPERIMENTAL

The specimens used were 2 mm-thick blocks ($20 \times 10\,\mathrm{mm}^2$ cross-section) machined from an extruded bar of UHMWPE, GUR 415 ($M_\mathrm{w} = 7 \times 10^6$, Hoechst, Germany). They were purified by soaking in methanol at room temperature under continuous stirring for 24 h, blotted with filter paper, and vacuum dried for 3 h. For irradiation and subsequent heat treatment in air, the blocks were placed in a polyethylene bag without sealing. For irradiation and post-treatment in vacuum, the blocks were placed in an aluminum foil-polyethylene laminate package and the package was heat-sealed in a 10^{-3} Torr vacuum. All specimens were irradiated to a dose of 100 kGy at a dose rate of 20 kGy min^{-1} with 9000 keV electron beams. The electron beam source used was a 10000 keV linear accelerator (linac) (High Voltage Engineering Corporation,

---

* To whom correspondence should be addressed. Fax: +81 75 7514144; E-mail: yyikada@medeng.kyoto-u.ac.jp

Burlington, MA, USA). The irradiated samples were heat-treated at 120°C for time periods up to 3 h. The surface characterization of the target side of the irradiated samples was carried out before and after heat treatment.

The physical structure and chemical composition of the subsurface region of UHMWPE specimens were examined by the attenuated total reflection Fourier-transform infrared (ATR *FT*i.r.) method. The spectra were recorded on a Shimadzu *FT*i.r.-8100 spectrophotometer (Shimadzu Corp., Kyoto, Japan) equipped with a Shimadzu 8000 ATR attachment. The internal reflection element (IRE) was a KRS-5 prism with a face angle of 45°. Each spectrum was obtained after at least 1000 scans were signal-averaged at a resolution of 4 cm^{-1}. The calculated probing depth of the ATR measurements was 1/5 the wavelength or 2 μm at 1000 cm^{-1}.

The micro-hardness of the UHMWPE surface was measured using a Shimadzu DUH-200 dynamic ultramicro-hardness tester. The dynamic hardness (H) was obtained from a load (P) applied to the test piece through an indenter and the resulting indentation depth (D) by the formula $H = P/\alpha D$, where α is a constant based on the indenter shape and αD represents the projected contact area of the indenter under the load P. By measuring at various test loads, the hardness could be obtained as a function of indentation depth. A triangular indenter with an apex angle of 115° was used in the hardness measurements. All values reported here are the average of at least eight readings measured at different locations on the polymer surface.

RESULTS AND DISCUSSION

ATR FT*i.r. study*

Identification of oxidation products and double bonds. The major products of radiation-induced chemical changes of polyethylene have characteristic infra-red absorption bands[7–9]. These corresponds to the following species:

A. Hydrogen-bonded OH species (alcohols at 3420–3450 cm^{-1}, hydroperoxides at 3380–3400 cm^{-1}, carboxylic acids at 3100–3200 cm^{-1}), and non-hydrogen-bonded (free) OH species (alcohols at 3600 cm^{-1}, hydroperoxides at 3550 cm^{-1});
B. Carbonyl species (ketones, acids, esters, etc.) at 1700–1800 cm^{-1};
C. C–O–X species at 1150–1250 cm^{-1};
D. Unsaturated products (C=C bonds) at 1640 and 850–1000 cm^{-1}.

Figure 1a–d shows the above four regions A, B, C, and D of ATR *FT*i.r. spectra for the UHMWPE sample before and after irradiation by electron beams in air, as well as after subsequent heat treatment for 20 and 180 min. In order to eliminate apparent differences in the i.r. band intensities between the as-measured ATR *FT*i.r. spectra, arising from the sample-to-sample variation in the sample/IRE contact, the spectra were normalized with respect to the intensity of PE peak at 2916 cm^{-1}. A very weak broad OH band between 3100 and 3600 cm^{-1} and a weak carbonyl peak at about 1735 cm^{-1} were observed in the spectrum of the unirradiated sample, indicating the occurrence of some oxidation during processing. The initial absorption at 1735 cm^{-1} did practically not alter upon irradiation and subsequent heat treatment, indicating that the content of carbonyl groups remained unchanged. In the OH region, the spectrum of the irradiated sample was characterized by two well-defined peaks, one at 3390 cm^{-1} and the other at 3190 cm^{-1}. These peaks disappeared upon subsequent heat treatment, and the ATR *FT*i.r. spectrum in this region became virtually identical to that of the unirradiated sample. Electron beam irradiation also gave a relatively strong C=C stretching band at 1645 cm^{-1} and a very weak *trans*-vinylene band at 965 cm^{-1}. The absorption at 1645 cm^{-1} decreased substantially by heat treatment of the irradiated sample for 20 min and disappeared when the treatment was continued for 180 min. No appreciable difference was observed between the spectra of the unirradiated, irradiated, and heat-treated samples in the 1150–1250 cm^{-1} region, suggesting that the concentration of COX species remained unchanged.

The above ATR *FT*i.r. results suggest that the sole outcome of radiation-induced surface oxidation of UHMWPE is formation of OH species absorbing at 3390 and 3190 cm^{-1} under the irradiation and heat-treatment conditions employed here. The absorption at 3390 cm^{-1} can unambiguously be ascribed to a hydrogen-bonded hydroperoxide[7,9,10]. The frequency of the second OH peak (3190 cm^{-1}) falls well into the OH stretch region characteristic of the cyclic dimer of carboxylic acids[11]. However, the absorbance at 3190 cm^{-1} observed for the irradiated polymer could not result from carboxylic acid species, because irradiation did not bring about any increase in the content of carbonyl-containing species in the polymer, when judged from the unchanged intensity of the carbonyl peak at 1735 cm^{-1}. Therefore, the peak at 3190 cm^{-1} should be assigned solely to hydroperoxides. Substantial red shift of this peak relative to the hydroperoxide band at 3390 cm^{-1} suggests that the respective OH groups are strongly hydrogen-bonded. We believe that the peak at 3190 cm^{-1} arises from cyclic dimers of hydrogen-bonded hydroperoxides. On the other hand, the hydroperoxide peak at 3390 cm^{-1} could probably originate from OH groups engaging in hydrogen bonding of lower strength, such as linear open chain oligomers[10].

The assignment of OH bands at 3390 and 3190 cm^{-1} in the ATR *FT*i.r. spectrum of irradiated UHMWPE to hydroperoxide groups is supported further by the observation that these bands disappeared upon heat treatment. This observation is in good accordance with the fact that organic hydroperoxides are relatively unstable and are hence readily decomposed by heat[12]. It has been well documented that thermal decomposition of hydroperoxides in polyolefins leads predominantly to oxidation, which is manifested in the formation of oxidized structures within the polymer, such as ketone, alcohol, and carboxylic acid functionalities[13,14]. One of the most striking findings of the present study is that thermal decomposition of the UHMWPE hydroperoxides formed by irradiation of the polymer at a dose rate of 20 kGy min^{-1} did not induce any formation of new oxygen-containing species. In other words, decomposition of the hydroperoxides proceeded via non-oxidative routes. The only way to understand this phenomenon is to suppose cleavage of the R–OOH bond followed by formation of crosslinks ($R\cdot + R\cdot \rightarrow R\text{–}R$; $R\cdot + RO\cdot \rightarrow R\text{–}O\text{–}R$) and evolution of O_2 and H_2O. Since heat treatment did not cause any appreciable increase in the i.r. absorbance due to C–O–C species in the irradiated polymer, the direct carbon–carbon crosslinking might probably dominate over the crosslinking through intermediate oxygen atoms. Additional evidence of UHMWPE crosslinking by decomposition of the hydroperoxides will be presented later in connection with micro-hardness measurements.

Finally, it is interesting to note that, as expected, no signs

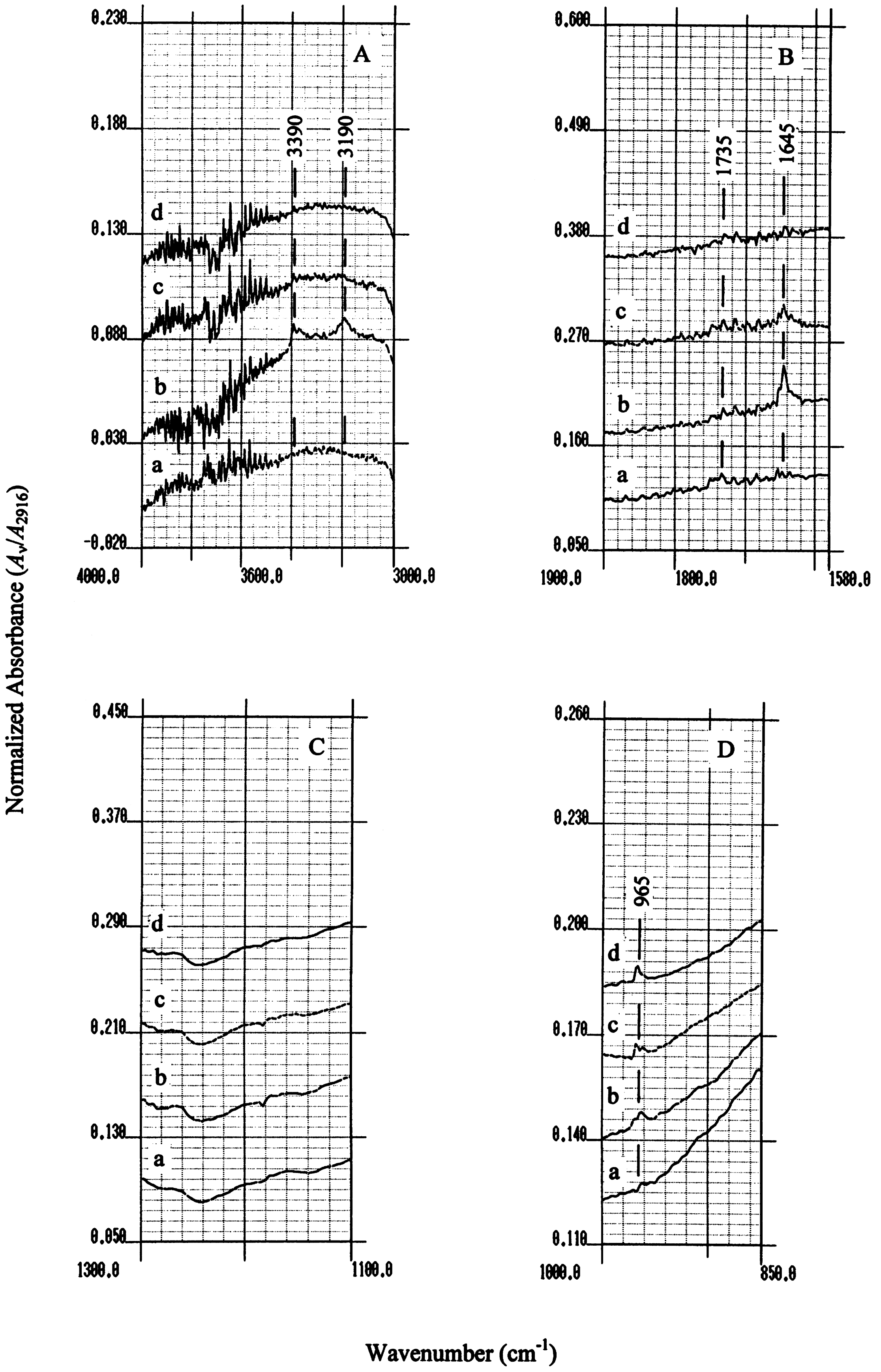

Figure 1 ATR *FT*i.r. spectra of UHMWPE in the regions (A, B, C, D) of infra-red absorption bands characteristic to radiation-induced chemical changes: (a) before irradiation; (b) after irradiation in air (100 kGy at 20 kGy min^{-1}); and (c) after subsequent annealing at 120°C for 20 min; and (d) 180 min

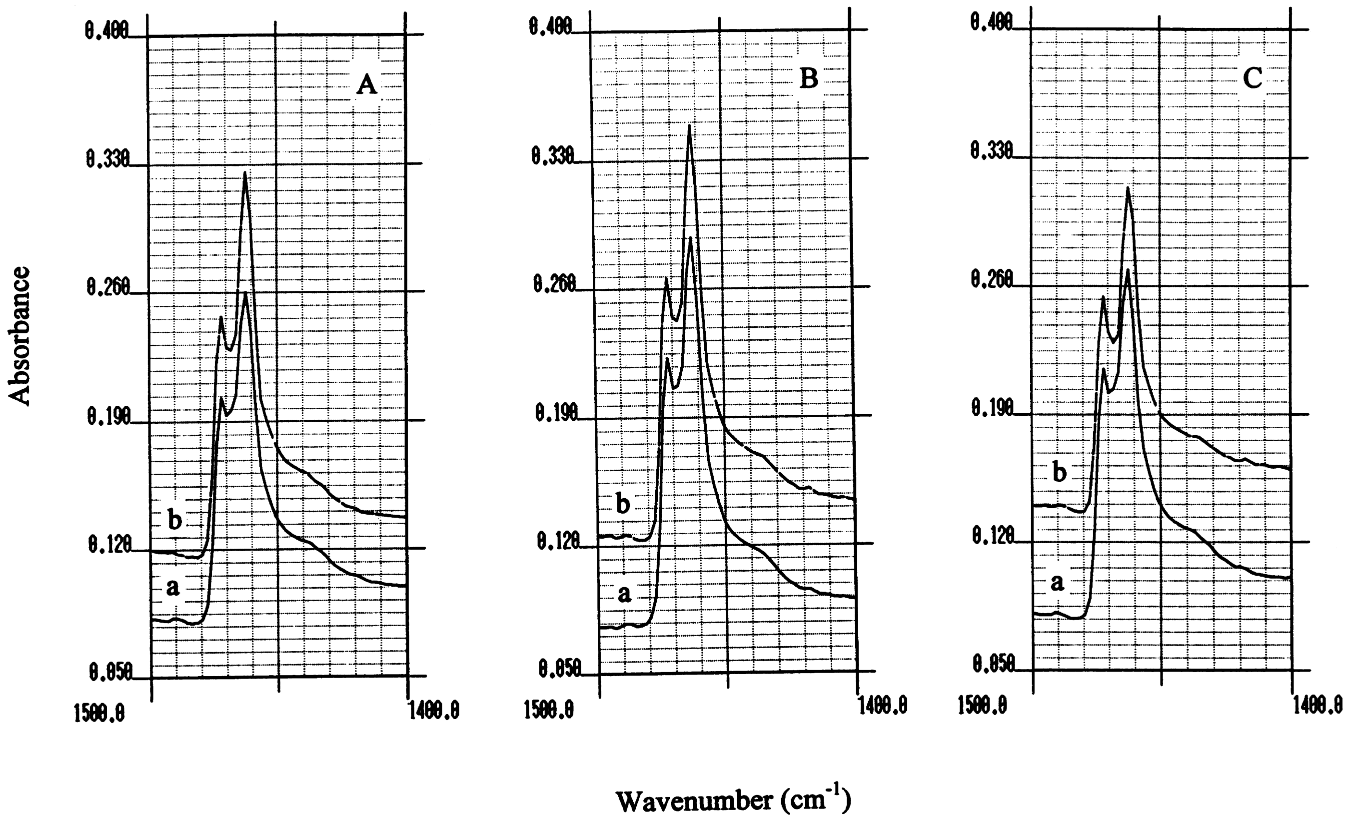

Figure 2 ATR *FT*i.r. spectra of UHMWPE in the CH_2-bending region for the original (A); irradiated-in-air (B); and irradiated-in-vacuum UHMWPE sample (C); and measured before (a); and after annealing at 120°C for 180 min (b)

of UHMWPE oxidation could be found in the ATR *FT*i.r. spectra of polyethylene irradiated and then heat-treated in vacuum.

Determination of crystallinity. The spectroscopic determination of PE crystallinity has been usually carried out by i.r. transmission spectroscopy, using the intensity ratio of the ''crystalline'' band at 1894 cm^{-1} and the ''amorphous'' band at 1303 cm^{-1}(15,16). However, in the ATR i.r. spectrum of PE, these bands are too weak to be used for quantitative analysis. Recently, Zerby *et al.* proposed that the strong doublet at 1473/1463 cm^{-1} assigned to the CH_2-bending vibration can be employed for the quantitative ATR *FT*i.r. evaluation of the crystalline *versus* amorphous content in the polymer[17]. The band at 1473 cm^{-1} is due to the crystalline phase only, whereas the band at 1463 cm^{-1} originates from both crystalline and amorphous phases. *Figure 2a–c* shows the ATR *FT*i.r. spectra in the CH_2-bending region for the original, irradiated-in-air, and irradiated-in-vacuum UHMWPE samples, measured before and after heat treatment at 120°C for 180 min. It can be seen that irradiation to 100 kGy caused a slight increase in the intensity of the 1473 cm^{-1} band, for both irradiation in air and in vacuum. The band intensity was increased further by the subsequent heat treatment. An increase in the absorption intensity at 1473 cm^{-1} was also observed when the original (unirradiated) sample was heat-treated. Since the band at 1473 cm^{-1} is purely due to the crystalline phase, the above spectral changes should be ascribed to an increase in the crystalline content. In order to quantitatively compare the crystallinity of the samples under consideration, we calculated the degree of crystallinity (α) using the empirical relationship obtained by Zerby *et al.*[17]

$$\alpha = \left(1 - \frac{I_a - I_b/1.233}{I_a + I_b}\right) \times 100$$

where I_a and I_b are the intensities of the 1473 and 1463 cm^{-1} bands, respectively. The crystallinity determined for the unirradiated UHMWPE from the ATR *FT*i.r. data was 48%. This spectroscopic result seems to be reasonable, as the literature suggests the α value of UHMWPE to be in the range of 42–50%. The crystallinities of irradiated samples were only slightly higher than that of the unirradiated polymer, i.e., 50 and 51% for the UHMWPE irradiation in air and vacuum, respectively. However, following the subsequent heat treatment, the crystallinity increased to 61% (air) and 59% (vacuum). Annealing of the unirradiated polymer also caused an increase in crystallinity, but the resulting α value (56%) was lower than the corresponding values observed for irradiated samples. It should be noted that the heat-induced crystallinity change occurred mainly over the first 30–60 min of annealing time for all three UHMWPE samples. The crystallinity data for 180-min annealing time exhibit maximum α values attainable by annealing at 120°C. Therefore, the observed difference in crystallinity between the annealed specimens of unirradiated and irradiated UHMWPE could not be due simply to the difference in the rate of heat-induced crystal growth, but should be ascribed to more subtle structural modification induced in UHMWPE by irradiation.

An increase in the degree of UHMWPE crystallinity, both immediately after irradiation and also on subsequent ageing at ambient or elevated temperatures, has been reported by several authors[18,19]. The phenomenon was attributed to the radiation-induced scission of tie molecules in UHMWPE

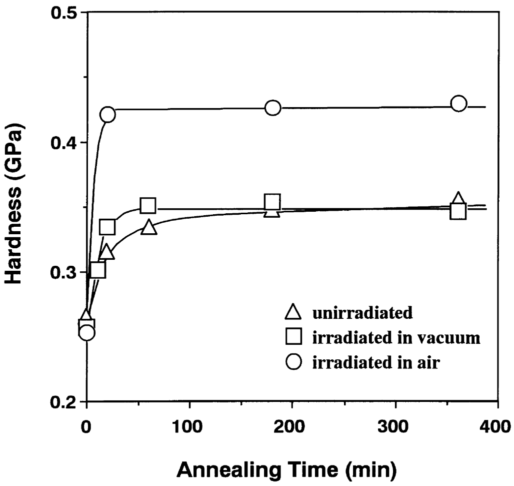

Figure 3 Effect of the annealing time at 120°C on the micro-hardness of UHMWPE; unirradiated UHMWPE (△), UHMWPE irradiated to 100 kGy at 20 kGy min^{-1} in vacuum (□) and in air (○)

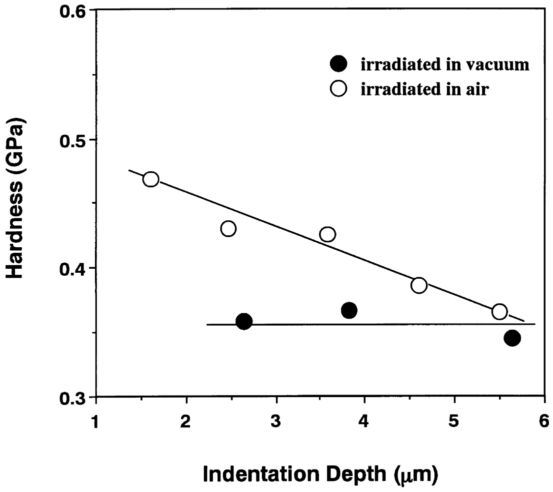

Figure 4 Micro-hardness *versus* indentation depth for UHMWPE irradiated to 100 kGy at 20 kGy min^{-1} and subsequently heat-treated at 120°C for 180 min; open and closed circles are for irradiation in air and vacuum, respectively

Table 1 Surface crystallinity (α) and micro-hardness (H) of UHMWPE samples

	Before annealing		After annealing (180 min, 120°C)	
Sample	α (%)	H (GPa)	α (%)	H (GPa)
Unirradiated	48	0.27	56	0.35
100 kGy in vacuum	51	0.26	59	0.35
100 kGy in air	50	0.25	61	0.43

with the consequent relaxation of local stresses, followed by the slow growth of new crystal lamellae. This mechanism could probably also be operative under the irradiation and heat-treatment conditions employed in our study.

Micro-hardness study

Most of the micro-hardness data reported here were obtained at a test load of 5 mN and a loading speed of 0.1 mN s^{-1}. Under this load, the indentation depth was in the range 2.5–3.2 μm. The micro-hardness values (H) of the UHMWPE measured before annealing were 0.25 and 0.26 GPa for irradiation in air and vacuum, respectively, which were essentially the same as that of the unirradiated polymer ($H = 0.27$ GPa). On annealing at 120°C, both the unirradiated and irradiated specimens showed a substantial increase in H values (*Figure 3*). The micro-hardness increased rapidly over the first 20 min. When annealing was continued further, H increased slowly and finally leveled off after 30 and 90 min of annealing time for the irradiated and unirradiated UHMWPE, respectively. The levelling off H value of UHMWPE irradiated in vacuum was equal to that of the annealed original polymer (0.35 GPa). However, the hardness of the annealed sample of UHMWPE irradiated in air was found to be 0.43 GPa, which was 23% higher than that of the above two specimens.

In general, hardness is directly related to both the crosslink density and the degree of crystallinity[20,21]. The crystallinity and hardness observed for the original and irradiated UHMWPE before and after annealing are presented in *Table 1*. It can be seen that the increase in crystallinity by irradiation in air and vacuum did not cause any increase in the micro-hardness of UHMWPE. This phenomenon may be explained by the fact that radiation-induced crosslinking occurs concurrently with chain scission. The former causes a rise in micro-hardness, while the latter decreases it. Subsequent annealing of the irradiated polymer led to an increase in both the crystallinity and micro-hardness. A similar trend was observed for the unirradiated specimen. Although the crystallinity of the UHMWPE irradiated in vacuum was found to be higher than that of the annealed original sample, the micro-hardness of both polymers was the same. This result is rather surprising, because one might have expected that the heat-induced crystallinity increase, as well as possible crosslinking by recombination of trapped radicals would make the hardness of the irradiated polymer higher than that of the unirradiated one. Since this was not the case for the sample under consideration, we conclude that the overall effect of the heat-induced increase in crystallinity and crosslink density was not high enough to overshadow the effect of radiation-induced bond scission. Interestingly, annealing of the UHMWPE irradiated in air enhanced the micro-hardness by 23% of that of the above two specimens. Since the α value observed for the UHMWPE treated in air differs only slightly from that of the UHMWPE treated in vacuum, the substantial difference in the micro-hardness between the two samples cannot be ascribed to the crystallinity effect. The most likely factor in addition to the crystallinity change, which could increase the micro-hardness, is crosslinking. Furthermore, ATR *FT*i.r. data reveal that the only difference in the surface chemical composition between the UHMWPE samples irradiated in air and vacuum was the presence of a hydroperoxide group in the former. Therefore, a plausible explanation for the hardness enhancement is that the surface crosslink density of the UHMWPE irradiated in air was markedly increased by heat treatment as a consequence of the thermal decomposition of the hydroperoxides generated.

If it is valid to conclude that the surface crosslinking of UHMWPE is increased by the thermal decomposition of hydroperoxides formed upon irradiation in air, the hardness of the near-surface region of the treated polymer must be higher than that of the polymer bulk. To check this, we measured the hardness of UHMWPE samples as a function of indentation depth by applying various test loads (2.5–20 mN). The data obtained for the UHMWPE annealed at 120°C for 180 min following irradiation in air and vacuum are presented in *Figure 4*. It can be seen that the hardness of the UHMWPE irradiated in vacuum was independent of the indentation depth with a value of 0.35–0.36 GPa over the whole range of indentation depth employed (2–6 μm). On the other hand, the hardness of the UHMWPE irradiated in air was found to be 0.47 GPa at the lowest attainable depth of 1.6 μm, which is 30% higher than that of the UHMWPE irradiated in vacuum. Hardness decreased gradually with the increasing indentation depth and reached a value equal to that of the sample irradiated in vacuum at an indentation depth of 5.6 μm.

CONCLUSIONS

In this paper we investigated the effect of high-energy electron-beam irradiation on the surface property change of UMWPE. The polymer was irradiated to a dose of 100 kGy at a dose rate of 20 kGy min^{-1} and the near-surface region of the irradiated polymer was characterized by means of ATR *FT* i.r. spectroscopy and micro-hardness measurements. The results obtained strongly suggest that irradiation in air introduced hydroperoxides into the polymer. It is interesting to note that no other oxygen-containing products were formed. The hydroperoxides generated could be decomposed further by subsequent heat treatment of the irradiated polymer, resulting in crosslinking of UHMWPE chains in the near-surface region of the material. This surface modification made the surface hardness of UHMWPE substantially higher.

ACKNOWLEDGEMENTS

The authors thank Prof. Sen-Ichi Fujita (Research Institute for Advanced Science and Technology, Osaka Prefecture University) for his kind help with electron beam irradiation as well as for helpful discussions. This research was funded by the Japan Society for the Promotion of Science Grant JSPS-(RFTF 96I00203 ("Research for the Future" Program) and supported in part by Johnson and Johnson.

REFERENCES

1. Willert, H. G., Buchhorn, G. H. and Eyerer, P. (Eds), *Ultra-High Molecular Weight Polyethylene as Biomaterial in Orthopedic Surgery*. Hogrefe and Huber, New York, 1991.
2. Oonishi, H., Takayama, Y. and Tsuji, E., *Int. J. Radiat. Appl. Instrum., Part C*, 1992, **39**, 495.
3. Sun, D. C., Wang, A., Stark, C. and Dumbleton, J. H., in 5th World Biomaterials Congress, Arlington, Canada, May 1996, p. 195.
4. Streicher, R. M., *Radiat. Phys. Chem.*, 1995, **46**, 893.
5. Charlesby, A., Atomic Radiation and Polymers. Pergamon, New York, 1960, chap. 13, pp. 235–239.
6. Kurth, M. and Eyerer, P., in *Ultra-High Molecular Weight Polyethylene as Biomaterial in Orthopedic Surgery* ed. H. G. Willert, G. H. Buchhorn and P. Eyerer. Hogrefe and Huber, New York, 1991, pp. 82–87.
7. Ginhac, J. M., Gardette, J. L., Arnaud, R. and Lemaire, J., *Makromol. Chem.*, 1981, **182**, 1017.
8. Lacoste, J. and Carlsson, D. J., *J. Polym. Sci. Part A: Polym. Chem.*, 1992, **30**, 493.
9. Albert, C. F. and Busfield, W. K., *J. Polym. Sci. Part A: Polym. Chem.*, 1997, **35**, 1549.
10. Minkoff, C. J., *Proc. Roy. Soc. A*, 1954, **224**, 1137.
11. Marechel, Y., in *Vibrational Spectra and Structure*, ed. J. R. Durig. Elsevier, Amsterdam, 1987, Vol. 16, Chapter 5.
12. Tobolsky, A. V. and Mesrobian, R. B., *Organic Peroxides*. Wiley Interscience, New York, 1954.
13. Chien, J. C. W., *J. Polym. Sci. Part A1*, 1968, **6**, 375.
14. Chien, J. C. W. and Jabloner, H., *J. Polym. Sci. Part A1*, 1968, **6**, 393.
15. Nikitin, V. N. and Pokrovskii, E. I., *Doklady Akad. Nauk SSSR*, 1954, **95**, 109.
16. Okada, T. and Mandelkern, L., *J. Polym. Sci. Polym. Phys. Ed.*, 1967, **5**, 239.
17. Zerby, G., Gallino, G., Fanty, N. D. and Baini, L., *Polymer*, 1989, **30**, 2324.
18. Bhateja, S. K., Andrews, E. H. and Young, R. J., *J. Polym. Sci. Polym. Phys. Ed.*, 1983, **21**, 523.
19. Shinde, A. and Salovey, R., *J. Polym. Sci. Polym. Phys. Ed.*, 1985, **23**, 1681.
20. Lee, E. H., Rao, G. R. and Mansur, L. K., *TRIP*, 1996, **4**, 229.
21. Rueda, D. R., Vilksne, A., Malers, L. and Balta Calleja, F., *J. Macromol. Chem. Phys.*, 1994, **195**, 3869.