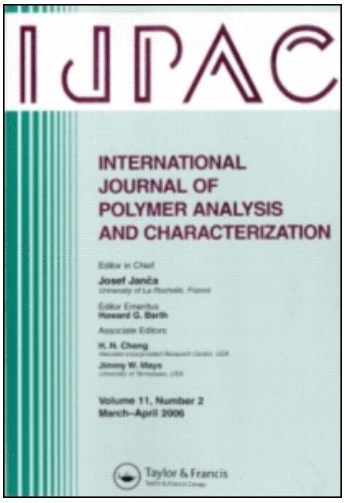

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Change in Structure of Ultrahigh Molecular Weight Polyethylene Due to Irradiation in Air and in Nitrogen

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Abstract: The change in the structure and properties of ultrahigh molecular weight polyethylene (UHMWPE) due to gamma irradiation has been studied in air and in a nitrogen atmosphere at different doses up to 400 kGy. Thermal analysis using differential scanning calorimetry (DSC) and swelling were used to monitor changes in crystallinity and cross-linking. New crystallites with different lamellae thicknesses were formed in samples irradiated in air. The samples irradiated in nitrogen did not show new crystallites unless irradiated at more than 200 kGy. Gel percentage and the Charlesby-Pinner equation were used to confirm the increase in cross-linking in the absence of oxygen.

Characterization by all the techniques used indicated that irradiation in air causes the production of new crystallites due to oxidation, by which shorter molecular chains are formed and lamellar thickness increases. A lower degree of oxidation and scission occur in nitrogen, as confirmed by scanning electron microscopy (SEM) analysis, which allowed the determination of fracture shape and morphology. Fewer micro-voids and less brittleness were noticed in an oxygen-free environment. To gain more cross-linking, less production of crystalline regions, and more ductility, it is recommended that UHMWPE be irradiated in the absence of oxygen.

Keywords: Ultrahigh molecular weight polyethylene; Crystallinity; Cross-linking

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INTRODUCTION

Ultrahigh molecular weight polyethylene (UHMWPE) is a semicrystalline polymer with crystalline regions in amorphous surrounding. Understanding the structure of its molecular chains, crystallinity, and type of the arrangements can explain physical and mechanical properties.[1–4]

An artificial hip joint consists of a ball made of metal or ceramics and a socket made of UHMWPE; it is designed to bear the mass of the body, as well as to facilitate movement in many directions. This type of polymer has been chosen for its biocompatibility, high melting point, high wear resistance, and high tensile strength.

To improve the properties of this polymer, tests were undertaken using a composite of UHMWPE-alumina ceramic[5] or blending it with polypropylene[6] or calcium stearate.[7] In vitro studies of changes in UHMWPE were also carried out.[8]

Despite the success of using this polymer in vivo, a high friction coefficient and high value of wear rate of the material cause many fundamental problems such as the generation of debris from the articulating surface, which causes loosening of implants.[9] Some possibilities for improving this polymer's properties were tested either by changing its bulk properties by irradiation or changing its surface properties by ion implantation.[10–12]

Improvement in mechanical properties of polymers can be achieved by irradiation.[3,4] Kurtz et al. reviewed the processing, sterilization, and cross-linking of UHMWPE for total joint arthroplasty.[13] The impact of ionizing irradiation by gamma and electron beams on the performance of UHMWPE was also reviewed.[14]

Irradiation is used also for the sterilization of the heat-sensitive polymer to kill microorganisms that might react in vivo. Irradiation causes the photons to penetrate the material, breaking the polymer chains, and creating free radicals, which in an air environment combine with oxygen causing oxidative degradation of the polymer. Free radicals can also combine to create cross-links between adjacent molecules. Cross-linked material improves the long-term performance and wear resistance but changes the ductility and fracture resistance.[4]

Irradiation changes polymer properties, causing cross-linking and scission. These two processes are simultaneous, but one of them predominates depending on the molecular structure, type of irradiation, and the dose. Changes in properties continue due to shelf aging and in vivo use. Storage conditions of UHMWPE will strongly affect its structure and change its properties.[15] Storage in the air modifies different properties[4,5,16] and causes an increase in crystallinity and oxidation.[17]

The aim of this article is to study the changes in structure, crystallinity, and cross-linking of UHMWPE due to the effect of gamma

irradiation in air and in an oxygen-free environment (nitrogen gas). Changes in structure cause changes in physical and mechanical properties that determine the longevity of this polymer in the body.

EXPERIMENTAL SECTION

Rectangular-shape UHMWPE samples supplied from Goodfellows Company, 1 mm thick, were irradiated by gamma rays at room temperature to total doses of 5, 25, 50, 100, 200, and 400 kGy using ^{60}Co gamma cell manufactured by Atomic Energy of Canada Co. Ltd., in two different environments, air and nitrogen.

DSC Measurements

The calorimetric investigations of the samples were performed with a Perkin Elmer model DSC7 differential scanning calorimeter. The heating rate was 10°C/min. The weight of the samples was between 5 and 10 mg. Calorimetric measurements were carried out as first heating-cooling and second heating-cooling sequences under N_2 atmosphere. The estimation of lamellar thickness, L_c, was obtained from DSC data using the Thomson-Gibbs equation:

$$T_m = T_{m0}\left(\frac{1-2\delta}{L_c\rho_c\Delta H_m^0}\right) \tag{1}$$

where T_m is the melting temperature (the maximum of the endothermic melting peak); T_{m0} is the equilibrium melting point of a perfect crystalline polyethylene = 145.8°C;[18] ρ_c is the crystalline phase density = 1.005 g/cm^3; δ is the fold surface energy = 93×10^{-7} J/cm^2;[19] and ΔH_m^0 is the enthalpy of melting of a perfect crystalline polyethylene = 288.84 J/g.[20]

Cross-linking Measurements

Measurement of the degree of cross-linking was performed by using ASTM2765-01 (method C). Duplicate tests were carried out for each dose. Irradiated samples of 1 cm^3 were placed in boiling xylene for 12 hours. The solutes were filtered through 150 μm sieves and the obtained insoluble gel was dried. Gel percentage was defined as:

$$\text{Gel (insoluble part)} = \left(\frac{W_d}{W_o}\right) \times 100\%$$

where W_o is the original weight of the samples and W_d the weight of dried gel.

Scanning Electron Microscopy (SEM)

To study the morphology of the fracture surface, a Philips Model XL30 SEM was used. Samples were immersed in liquid nitrogen and fractured, then the fractured surface was sputter-coated with gold in a vacuum chamber. The pictures of surface fractures were taken at different magnifications.

RESULTS

DSC Analysis

Figure 1 shows DSC curves for pristine UHMWPE in the initial and second heating and cooling. In the initial heating of the pristine sample, only one endothermic peak is present, and a second one exists for exothermic peak at cooling. Second heating does not change these individual peaks.

The DSC curves for irradiated UHMWPE in air showed traces of two peaks at low doses and three at higher doses for the initial heating, as shown in Figure 2. Second heating and cooling showed shoulders at recrystallization for samples irradiated by 100 kGy and higher doses.

Irradiation in nitrogen gives different DSC curves, as shown in Figure 3. Only one peak appears in the initial heating, but increasing

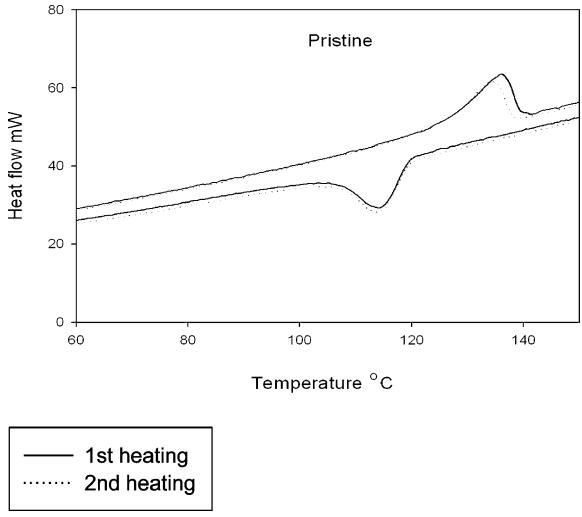


Figure 1. DSC curves for pristine UHMWPE in the first and second heating and cooling.

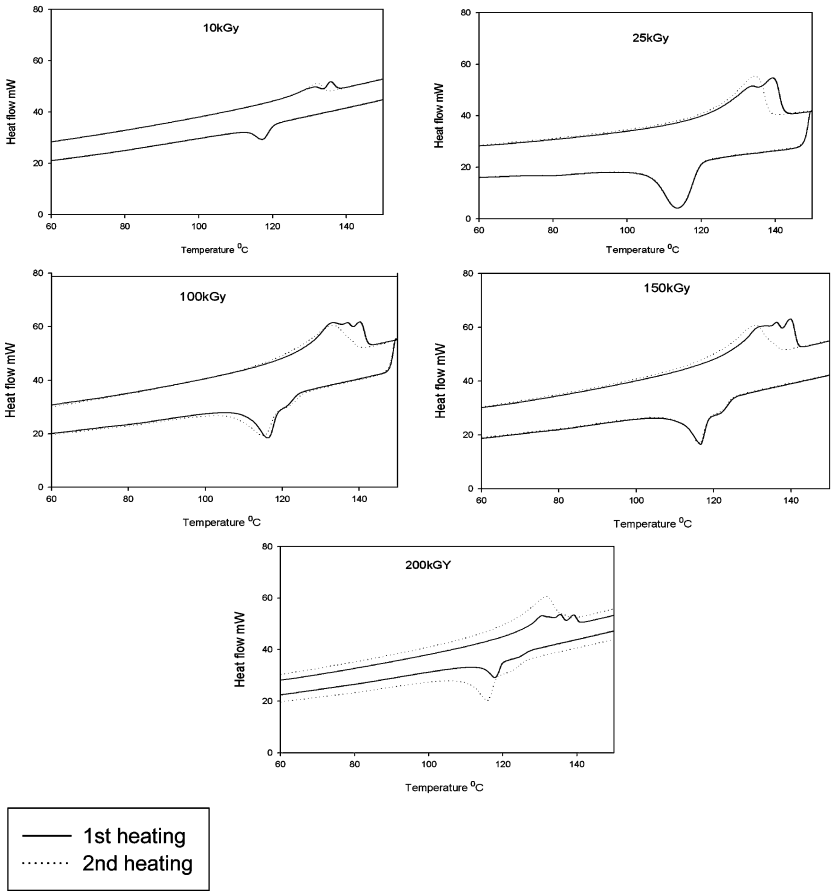


Figure 2. DSC for gamma-irradiated UHMWPE in air.

the irradiation dose up to more than 200 kGy provides a shoulder at recrystallization, and further increase up to 400 kGy introduces a new shoulder at the initial heating.

DSC curves for the first heating and cooling for both environments are shown in Figure 4.

The presence of a single peak (pristine and low radiation doses in nitrogen) suggests that the samples have a distribution of crystallite lamellae of one mean thickness.[21]

The small shoulders appearing at high irradiation doses in nitrogen and the new peaks in samples irradiated in air suggest a new population of crystallites formed after irradiation due to oxidative degradation, which causes recrystallization, which is very high for irradiation in air.

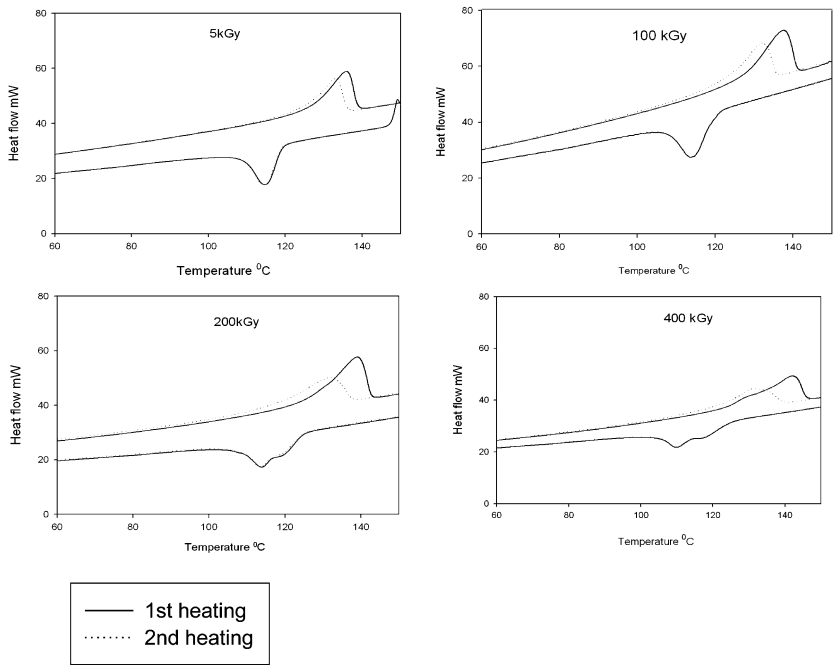


Figure 3. DSC for UHMWPE irradiated in nitrogen for the first and second heating.

Irradiation in air causes the formation of free radicals, which react with oxygen and cause more scission and growth of the crystalline regions. Oxidative degradation due to gamma irradiation in an inert gas was not observed unless a high value of more than 200 kGy was reached.

Second heating and cooling causes less obvious shoulders in both heating and cooling curves. This is due to the disappearance of small crystalline regions after exceeding the melting point.

Table I shows the estimated lamellar thicknesses from the melting point. For the first heating, increasing irradiation in a nitrogen environment causes an increase of lamellar thicknesses, while increasing the irradiation in air causes the formation of two or more new lamellae with higher thicknesses and consequently higher melting point, in agreement with another report.[22]

For the second heating and cooling in air and in nitrogen, UHMWPE exhibits approximately the same behavior and tendency to slight decrease of the lamellar thickness due to exceeding the melting point and breaking down and dissolution of the big crystals into smaller ones.

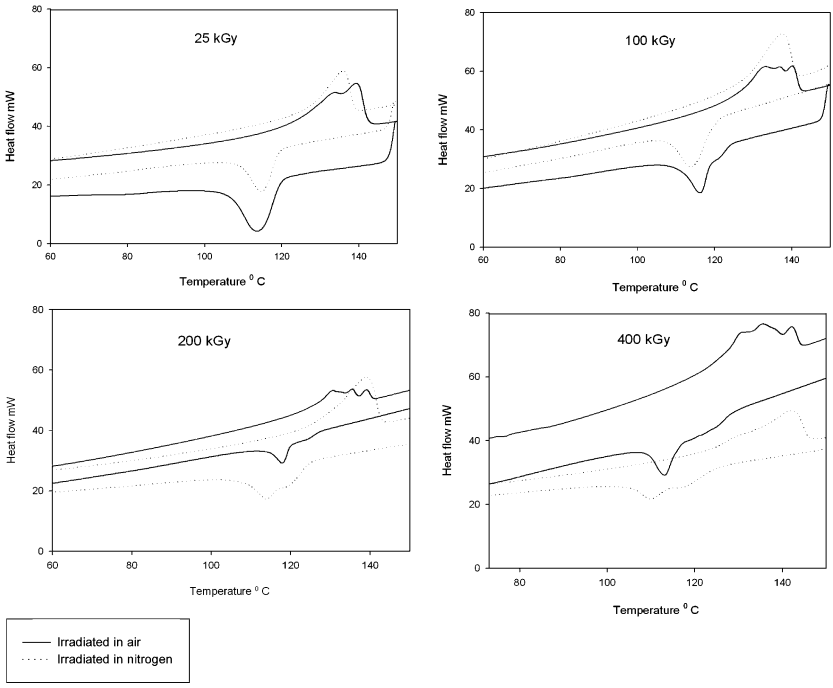


Figure 4. First heating for UHMWPE irradiated in air and in nitrogen.

Gel Fraction

The gel content percentage as a function of the dose is shown in Figure 5. Low doses (less than 100 kGy) have no significant effect on the cross-linking. The samples irradiated in nitrogen exhibited higher cross-linking, which indicates that the atmosphere free of oxygen promotes cross-linking and reduces scissions.[23]

Since the classical Charlesby-Pinner equation has been widely accepted and used to evaluate irradiation reactions,[24] it is used in this study to analyze the cross-linking due to irradiation:

$$S + S^{1/2} = \frac{p_0}{q_0} + \frac{1}{q_0} u_1 D$$

where S is the soluble fraction, p_0 is scission density per monomer unit; q_0 is cross-linking density per unit dose; D is irradiation dose; and u_1 is initial number of average degree of polymerization.

The experimental results were analyzed with a plot of $S + S^{1/2}$ versus $1/D$, as shown in Figure 6. At certain doses, agreement between the experimental data and those predicted by the theory is achieved; see

Table I. Lamellar thicknesses for the first and second heating for UHMWPE irradiated in air and irradiated in nitrogen

	UHMWPE irradiated in air				UHMWPE irradiated in N_2	
	First heating			Second heating	First heating	Second heating
Dose kGy	LC 1–1 (nm)	LC 1–2 (nm)	LC 1–3 (nm)	LC 2 (nm)	LC 1 (nm)	LC 2 (nm)
0	28.3979592	—	—	20.79348	28.3979592	23.92127
10	19.690109	27.92214	—	19.92554	27.9221431	21.74219
20	23.2556196	—	43.03386	—	30.4685789	22.62602
50	—	—	—	19.92126	33.5301205	23.92127
100	22.0278613	31.625	49.39652112	19.23688	—	—
150	22.0278613	29.38754	46.63985252	18.38906	32.8687847	19.92554
200	18.288756	27.01942	41.43218699	19.46154	40.9264706	19.46154
250	22.0278613	29.39685	73.23684211	18.18954	—	—
400	18.8040541	27.01942	76.58227848	16.89739	70.1537686	19.01736

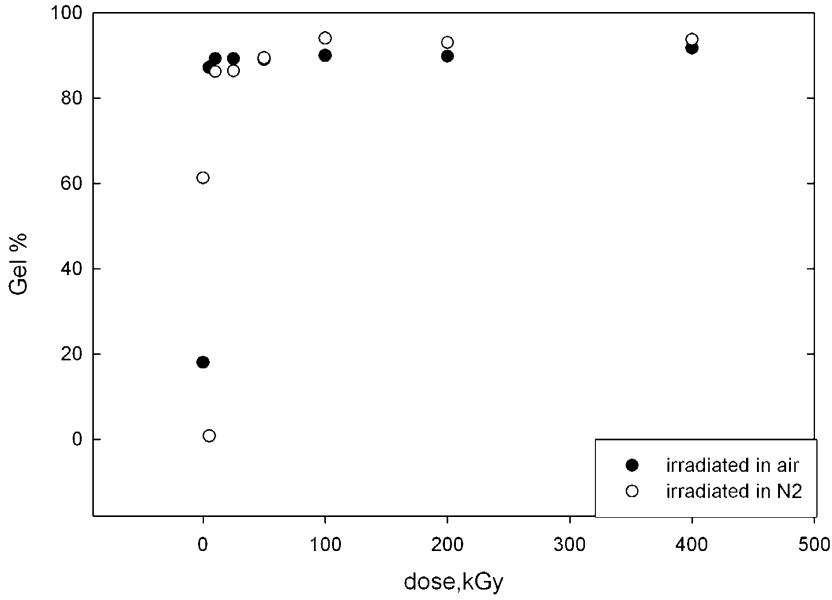


Figure 5. Gel percentage as a function of gamma dose for UHMWPE irradiated in air and in nitrogen.

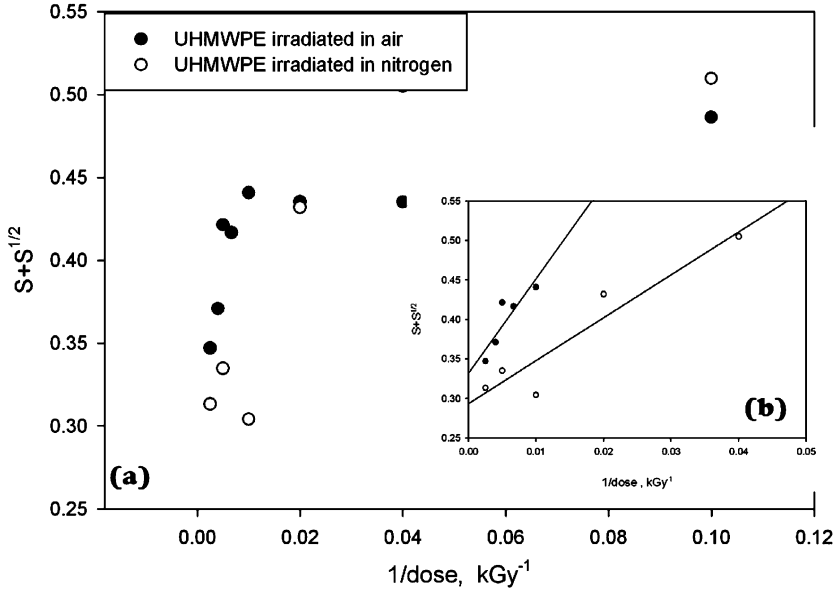


Figure 6. Charlesby-Pinner plots for UHMWPE irradiated in air and in nitrogen (a) in the full range and (b) linear plot range.

Figure 6(b). The cross-linking in this range is random and occurs between units in the amorphous phase.[25] Deviation from the linearity at lower doses is due to nonrandomness of the initial weight distribution where the cross-linking of the polymer is not random, whereas the Charlesby-Pinner

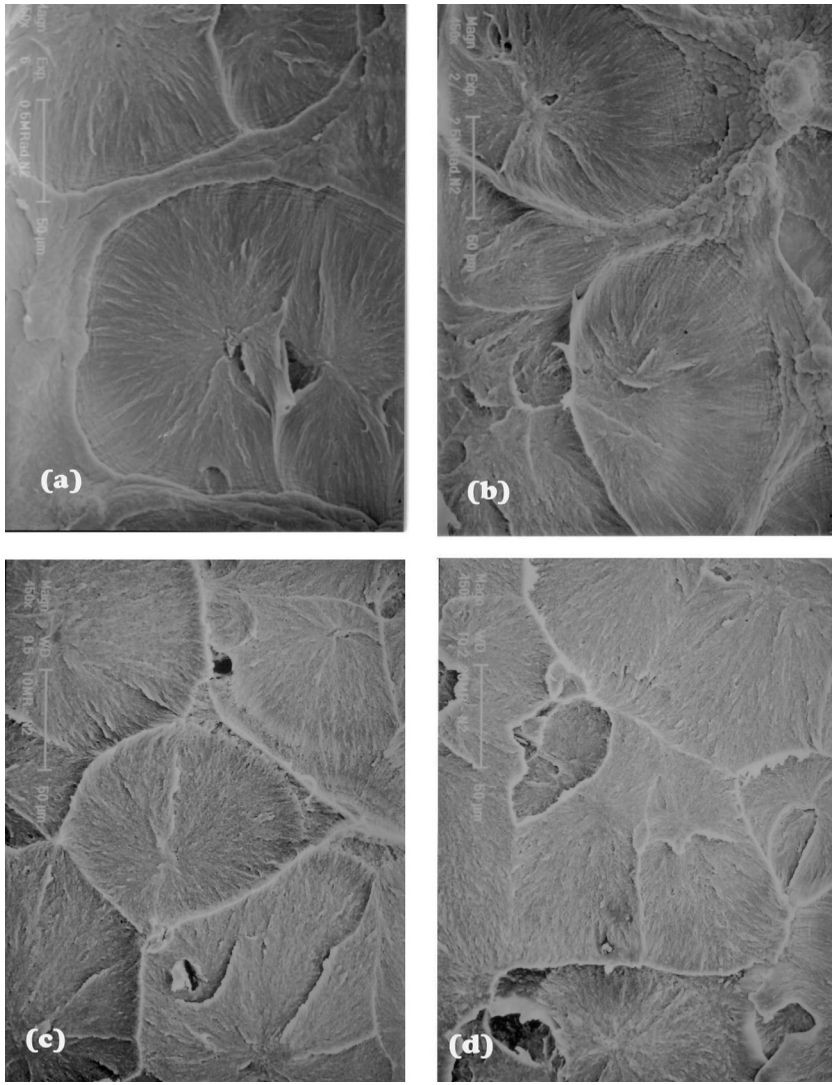
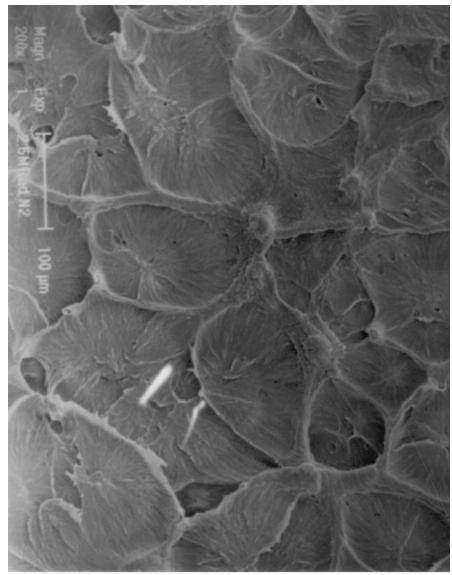
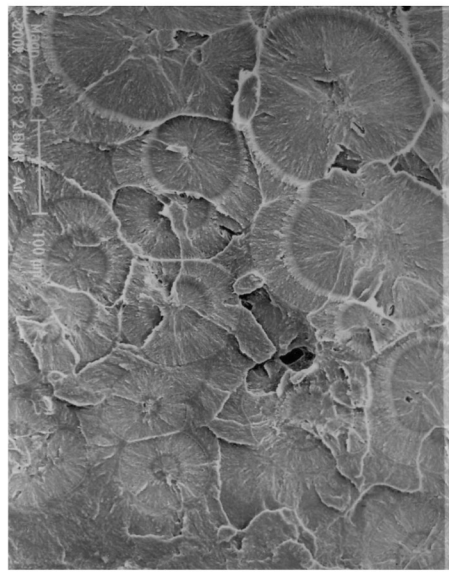


Figure 7. Fracture shape morphology by SEM for UHMWPE irradiated by gamma rays in nitrogen at a magnification of 450: (a) 5 kGy, (b) 25 kGy, (c) 100 kGy, (d) 200 kGy.



(a)



(b)

Figure 8. Fracture shape morphology by SEM at a magnification of 200 for UHMWPE irradiated by 25 kGy (a) in nitrogen and (b) in air.

equation can be applied under conditions of normal molecular weight distribution (MWD). The Charlesby-Pinner equation is more applicable within a certain dose range for samples irradiated in nitrogen than for those irradiated in air.

The lower value of the ratio of p_0/q_0 (0.29) for the samples irradiated in nitrogen than for those irradiated in air (0.33) supports increased cross-linking in the absence of oxygen.

SEM Analysis

Figure 7 represents scanning electron micrographs of fracture surfaces of the UHMWPE samples irradiated in nitrogen from 5 kGy up to 200 kGy. The dose changes the surface of the fracture and causes the smooth topography of the sample to change into a rougher one with an increased number of micro-voids. Higher irradiation causes a brittle fracture mechanism; the surfaces are no longer smooth, and an inter-lamellar type of fracture occurred.

SEM micrographs for UHMWPE irradiated by 25 kGy in nitrogen (Figure 8(a)) and in air (Figure 8(b)) show the fracture surface difference as more micro-voids, and less ductility is noticed for the sample irradiated in air due to oxidative degradation and to the evolution of new crystallites as discussed above.

CONCLUSIONS

Irradiation conditions strongly influence the lamellar morphology of UHMWPE as was evidenced by characterization using DSC and SEM. Irradiation in air causes the formation of smaller crystalline lamellae, which are not detected in samples irradiated in nitrogen, although exceeding the melting point, and cooling the samples cause the disappearance of these smaller crystallines. Higher irradiation in nitrogen (exceeding 200 kGy) causes recrystallization. Irradiation in both environments causes cross-linking that is higher than degradation where p_0 (scission density per monomer unit) is less than q_0 (cross-linking density per unit dose), i.e., p_0/q_0 of 0.29 for the samples irradiated in nitrogen and 0.33 for the samples irradiated in air. A decrease in cross-linking in the latter case is due to crystallinity changes, lamellae alignment changes, and formation of new and more lamellae with higher thicknesses, which causes the change from a ductile to a brittle material, as confirmed by the micro-voids seen by SEM. The higher applicability of the Charlesby-Pinner equation in nitrogen confirms the randomness of the concerned processes in nitrogen. The increase in crystallinity cause change of material from ductile to brittle.

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