Effect of electron beam irradiation on simultaneously biaxially drawn ultra-high molecular weight polyethylene dried gel films

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The effect of electron beam irradiation on the morphology and mechanical properties of biaxially drawn ultra-high molecular weight polyethylene dried gel films was investigated as a function of irradiation dose in terms of cross-linking and main-chain scission. Tensile strength and elongation decrease drastically, even with small irradiation doses, while the storage modulus increased with increasing dose up to 20 Mrad over a temperature range from 0 to 120°C. This indicates that electron beam irradiation causes cross-linking and main-chain scission; the former improves heat resistance and the latter causes deterioration of tensile strength.

(Keywords: ultra-high molecular weight polyethylene; gel film; simultaneous biaxial drawing; irradiation; electron beam)

INTRODUCTION

The preparation of polymeric materials with high modulus has been extensively investigated and results of interest have been obtained for polyethylene (PE). Although the theoretical Young's modulus of PE is one of the highest among crystalline polymers, the range of applications is limited by its low melting point. Attempts have been made to remove this defect by cross-linking. Cross-linking of ultra-high strength ultra-high molecular weight PE (UHMW-PE) fibres has been studied by Pennings's group[1-3]. According to their reports, the tensile strength at break decreased with γ-irradiation even at an irradiation level as low as 2 Mrad, while the Young's modulus remained unchanged. The decrease in tensile strength is thought to be due to main-chain scission induced by the irradiation. A similar treatment was carried out by Sawatari and Matsuo[4] using highly uniaxially drawn UHMW-PE films irradiated by electron beam, in order to study heat resistance and deterioration of mechanical properties by main-chain scission with increasing dosage. They pointed out that electron beam irradiation did not improve, but rather caused the favourable mechanical properties to deteriorate for uniaxially ultra-drawn PE films with almost perfect crystalline phase. Patel and Keller[5,6] suggested that cross-linking of PE by high-energy irradiation occurs exclusively in the amorphous region and not within the crystal lattice. Thus, for highly uniaxially drawn UHMW-PE films with high crystallinity it is expected that the number of cross-linkages might be fewer than within usual PE materials with lower crystallinity, and that high-energy irradiation might cause predominantly main-chain scission.

Based on the approaches of Pennings and Sawatari, this paper is focused on the effects of electron beam irradiation on morphology and mechanical properties of biaxially drawn UHMW-PE films. As described in previous papers[7,8], biaxially drawn UHMW-PE films have the following particular features: (1) they comprise microfibrils of infinite length and several tens of nanometres in width; (2) the fibrils are not always straight along their whole length, and are oriented randomly with respect to the film normal direction; (3) the fibrils form networks, termed 'fibrillar networks' whose junction points are of two types: 'ordinary junction points' at which two straight fibrils cross each other, and 'fibrillar entanglement' formed by two deeply folded fibrils. It is of interest to study the effect of electron beam irradiation on the morphology and mechanical properties of UHMW-PE biaxially drawn films with a fine structure quite different from that of uniaxially drawn materials. Thus, the effect of electron beam irradiation on highly biaxially drawn UHMW-PE gel films is analysed mainly in terms of the cross-linking effects of intra- and interfibrils which contribute to mechanical and thermal properties.

EXPERIMENTAL

Sample preparation

The sample material and preparation methods were the same as in our previous paper[7]: UHMW-PE Hizex Million (Mitsui Petrochemical Co. Ltd) with $M_v = 4.5 \times 10^6$ was homogenized in a decahydronaphthalene solution containing 4 wt% polymer, using a separate

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flask at 160°C. Antioxidant di-tert-butyl-*p*-cresol (0.5 wt%, based on the polymer) was added to the solution. The solution was cooled gradually to room temperature to form a gel. The gel was taken out of the flask and pressed between aluminium flat plates with mirror-finished surfaces under a pressure of 100 K g cm^{-2} at 150°C for 10 min, followed by quenching in water at 20°C. It may be pointed out that this sample preparation is different from that of the so-called dried gel films of Smith and Lemstra[9]. In this case the film was formed by heat compression of a gel instead of being formed as a gel sheet directly from the solution. In our method the chain re-entanglement must occur more or less during heat compression, resulting in less drawability. Nevertheless, our method was better for preparing uniform sheets which were absolutely necessary for biaxial drawing. It should be mentioned that 150°C was the best temperature for making sheets of uniform thickness. Thus, prepared gel sheets were dried at room temperature, resulting in samples with a thickness of 0.11–0.13 mm. The structural aspects of the dried sheet were described in our previous paper[7]. The dry gel film was cut to make a sheet with dimensions 100 mm × 100 mm for simultaneous biaxial drawing and was cut into strips of length 40 mm and width 10 mm for uniaxial drawing. These drawings were performed at 135°C using an Iwamoto biaxial film stretcher. Drawn samples were placed under an electron beam in a nitrogen atmosphere at 35°C and were irradiated on the face and reverse sides to ensure uniform irradiation. Irradiation was performed over the range of doses from 1 to 40 Mrad using a Nishin High Voltage Curetron EBC-200-20-15.

Characterization methods

The thermal behaviour was estimated from the melting endotherm in differential scanning calorimetry (d.s.c.) curves using a Seiko Denshi SSC 5000. Samples, approximately 2 mg in weight, were heated at a constant rate of 10°C min^{-1}. The melting point and the heat of fusion were calibrated with indium (melting point 156.5°C, heat of fusion 28.8 J g^{-1}), as a standard. The temperature dependence of the complex dynamic tensile modulus was measured for drawn samples of length 25 mm and width 8 mm, using a Toyo Seiki Reolograph Piezo instrument. The measurements were carried out over a temperature range from 0 to 120°C at a constant heating rate of 3°C min^{-1} at a fixed frequency of 10 Hz. The tensile strength was measured for the films of length 20 mm and width 5 mm using a Toyo Baldwin Tensilon UTM-II-20 at 25°C at constant speed (10 mm min^{-1}). Tensile creep was measured for the films of length 25 mm and width 8 mm using a Shinku Riko TM-7000 at 25°C at constant load, corresponding to a stress of 10 MPa calculated before loading.

RESULTS AND DISCUSSION

Figures 1a and *b* show d.s.c. melting thermograms denoting the effect of irradiation on the melting behaviour of biaxially drawn UHMW-PE films. As described in the previous paper[7], the melting profile of the unirradiated ($\lambda = 10 \times 10$) film consists of two broad peaks. The higher temperature peak at 150°C is due to superheating of the structure with highly extended chains caused by high

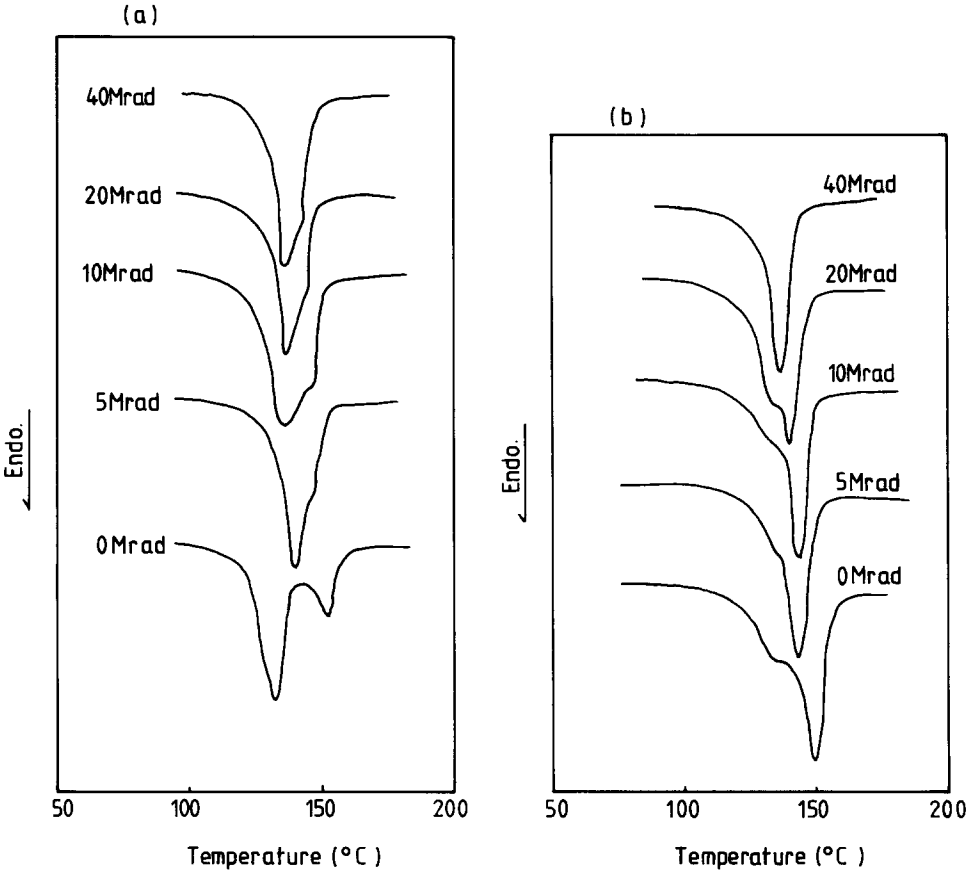

Figure 1 D.s.c. curves of simultaneously biaxially drawn UHMW-PE films irradiated by electron beam with the indicated doses: (a) $\lambda = 10 \times 10$; (b) $\lambda = 16 \times 16$

biaxial drawing. The higher temperature peak shifts to the lower temperature side with increasing irradiation dose, while the main lower temperature peak associated with a folded-type crystal shifts to the higher temperature side. It may be that the former phenomenon is attributed to main-chain scission within extended-chain crystals and the latter is ascribed to an increase in crystallinity due to scission of tie molecules, followed by recrystallization. In the case of the film with $\lambda = 16 \times 16$, before irradiation the high temperature peak at 150°C becomes much stronger at the sacrifice of the low temperature peak, because of a decrease in the amount of folded crystals with low melting point. The change in the melting profiles of the $\lambda = 16 \times 16$ films with increasing irradiation is similar to those of the $\lambda = 10 \times 10$ films. That is, the peak at 150°C for $\lambda = 16 \times 16$ films shifts to the lower temperature side, while the low temperature peak shifts slightly to the high temperature side and finally the film has only a single peak at 40 Mrad irradiation. *Figure 2* shows d.s.c. melting thermograms of uniaxially drawn ($\lambda = 20$) films obtained from the same dried gel. In this case, the single peak at 140°C before irradiation shifts to the lower temperature side with increasing irradiation. *Figure 3* shows the heat of fusion estimated from the areas of the d.s.c. melting peaks. The heat of fusion for biaxially drawn films increases with increasing irradiation doses up to 20 Mrad and then decreases at 40 Mrad, whereas the fusion for the uniaxially drawn ($\lambda = 20$) film decreases remarkably with irradiation dose. The initial increase in heat of fusion for biaxially drawn films is attributed mainly to an increase in crystallinity occurring

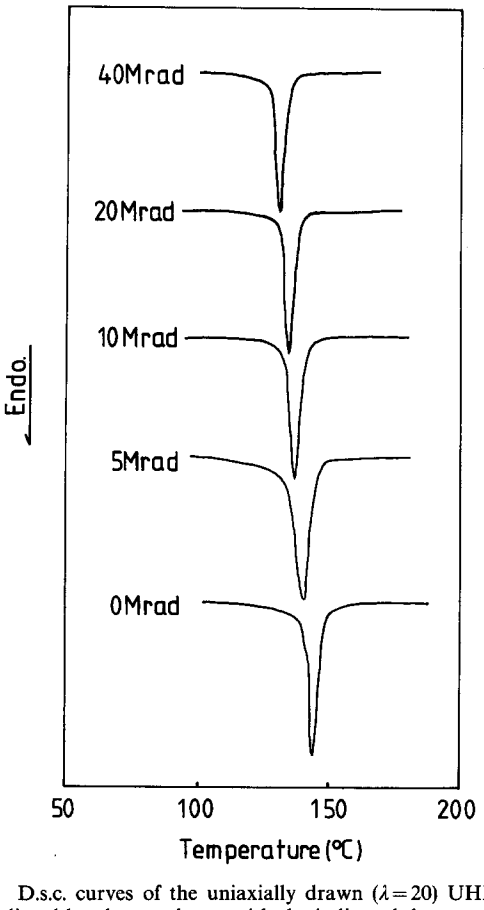

Figure 2 D.s.c. curves of the uniaxially drawn ($\lambda = 20$) UHMW-PE films irradiated by electron beam with the indicated doses

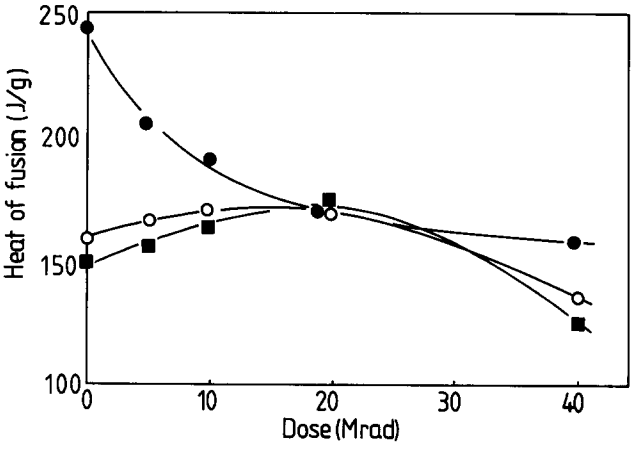

Figure 3 Heat of fusion of simultaneously biaxially and uniaxially drawn UHMW-PE films irradiated by electron beam: ■, $\lambda = 10 \times 10$; ○, $\lambda = 16 \times 16$; ●, $\lambda = 20$

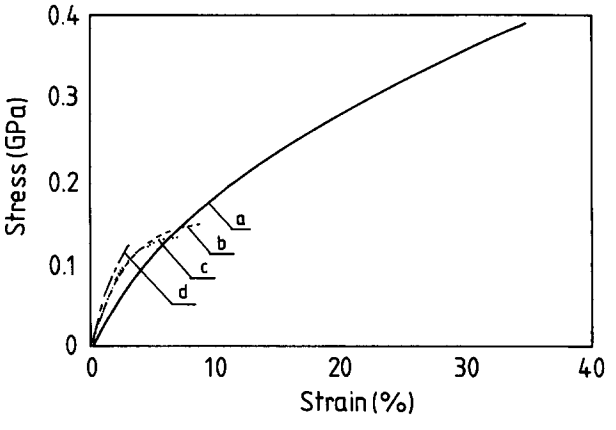

Figure 4 Stress *versus* strain curves for biaxially drawn ($\lambda = 16 \times 16$) UHMW-PE films irradiated by electron beam: (a) 0 Mrad; (b) 5 Mrad; (c) 20 Mrad; (d) 40 Mrad

by the scission of tie molecules, and the decrease at 40 Mrad is attributed to main-chain scission within extended-chain crystals. On the other hand, the drastic decrease for uniaxially drawn films is ascribed to considerable main-chain scission within extended-chain crystals. It may be supposed that the difference in heat of fusion between the irradiated biaxially and uniaxially drawn films is caused by a number of tie molecule chains, since the amorphous content of biaxially drawn films is higher than that of uniaxially drawn films. Even in the $\lambda = 16 \times 16$ film a comparatively large amount of a folded-type crystal remains without being involved in the transformation into the highly drawn structure[7].

Figure 4 shows the stress–strain curves of the $\lambda = 16 \times 16$ films at room temperature, indicating that a distinct change of tensile properties is induced with irradiation. The unirradiated $\lambda = 16 \times 16$ film has a breaking point beyond 30% strain[10]. Such high breaking elongation of biaxially drawn films is due to the particularly fine structure consisting of microfibrils with a random orientation with respect to the film normal direction. It may be noted that the microfibrils were oriented easily to the stretching direction by the rotation of their axes and interfibrillar slippage at the crossing of fibrillar networks, consequently a remarkable extension of the fibrils themselves becomes difficult. This is the most striking mechanical behaviour characteristic of highly biaxially drawn UHMW-PE

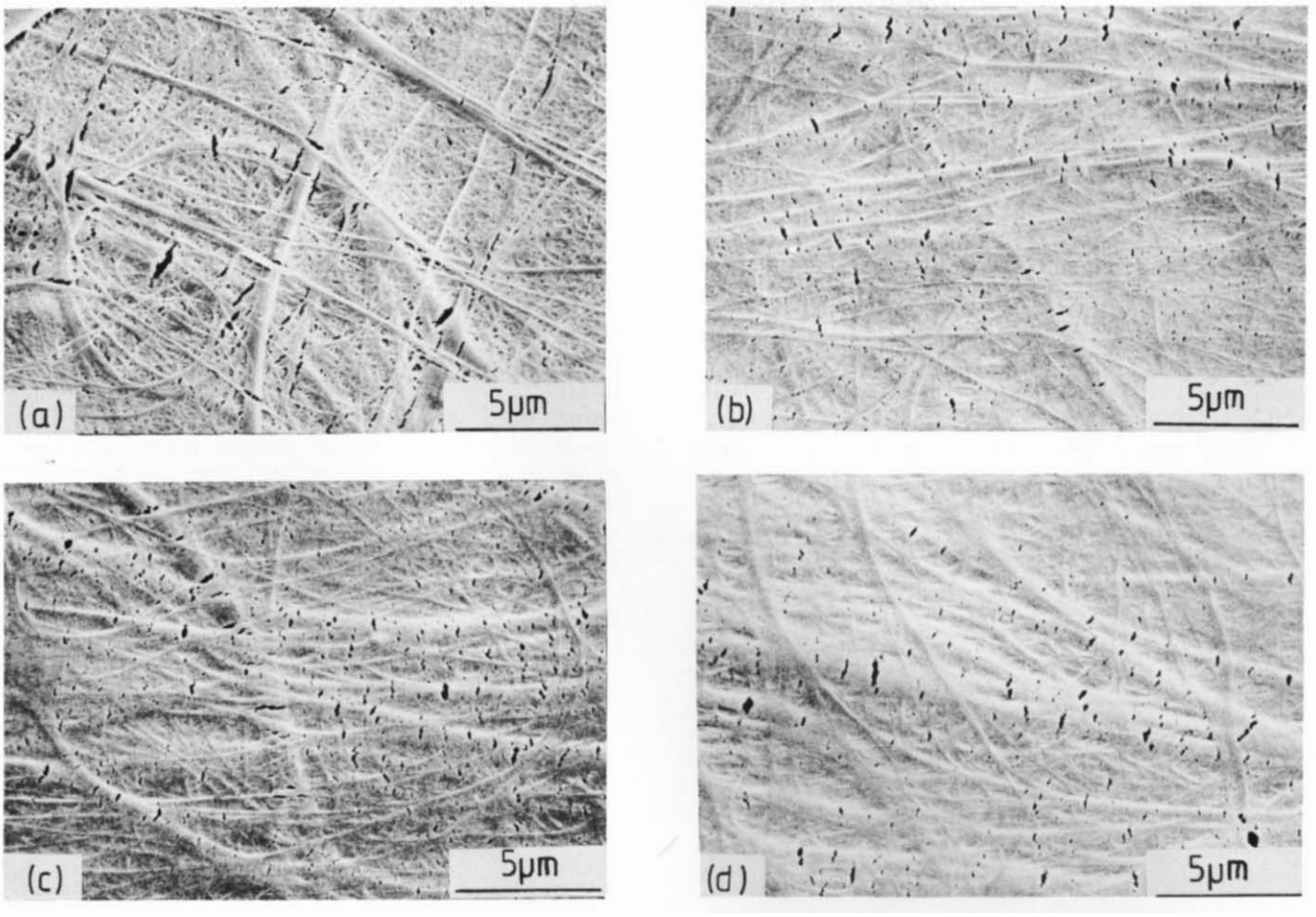

Figure 5 SEM photographs of biaxially drawn ($\lambda = 16 \times 16$) UHMW-PE films with various stretching: (a) 5 Mrad irradiated film with 5% stretching; (b) unirradiated film with 5% stretching; (c) unirradiated film with 20% stretching; (d) unirradiated film with 30% stretching; stretching direction is horizontal

films. Electron beam irradiation decreases both their tensile strength and elongation. It seems that the large decrease in tensile strain is attributed to cross-linking which inhibits interfibrillar slippage, and that the large decrease in tensile strength is due to the inhibition of interfibrillar slippage and the decrease in the strength of each microfibril caused by the main-chain scission, as suggested by d.s.c. melting data. *Figure 5* shows SEM photomicrographs of the biaxially drawn ($\lambda = 16 \times 16$) UHMW-PE films stretched in one direction. *Figures 5b–d* show the unirradiated films stretched at 5, 20 and 30%, while *Figure 5a* shows the film stretched at 5% and irradiated with 5 Mrad. The fibrils of unirradiated films tend to orient in the stretching direction and the number of microcracks increases with increasing strain. Comparing the film with 5 Mrad irradiation (*Figure 5a*) with the unirradiated film (*Figure 5b*) at a given strain, it is seen that the fibrils of the irradiated film do not orient in the stretching direction and microcracks are larger both in size and number. By the cross-linking of interfibrils, the fibrils in the irradiated films seem to be broken easily by the scission of intrafibrillar molecular chains and the inhibition of fibrillar slippage.

The dynamic mechanical storage modulus E' of biaxially drawn films irradiated by electron beam is shown in *Figure 6* as a function of irradiation dose. The measurements were done at 20°C. In the $\lambda = 4 \times 4$ film, E' increases with increasing irradiation up to 20 Mrad, then decreases with increasing irradiation. The $\lambda = 16 \times 16$ and 10×10 films irradiated with over

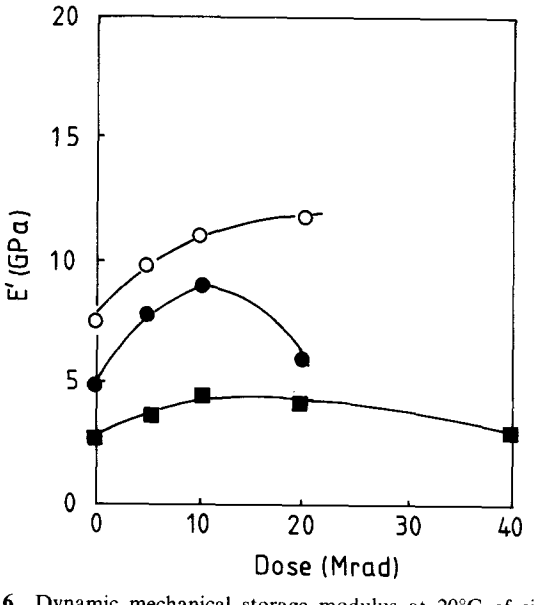

Figure 6 Dynamic mechanical storage modulus at 20°C of simultaneously biaxially drawn UHMW-PE films as a function of irradiation dose: ■, $\lambda = 4 \times 4$; ●, $\lambda = 10 \times 10$; ○, $\lambda = 16 \times 16$

20 Mrad were too brittle to be applied to the dynamic measurements. The maximum attainable modulus was about 12 GPa for the $\lambda = 16 \times 16$ film irradiated with 20 Mrad. *Figure 7* shows the dynamic mechanical storage modulus E' at 20°C of the uniaxially drawn ($\lambda = 20$) film irradiated by electron beam. The E' increases slightly

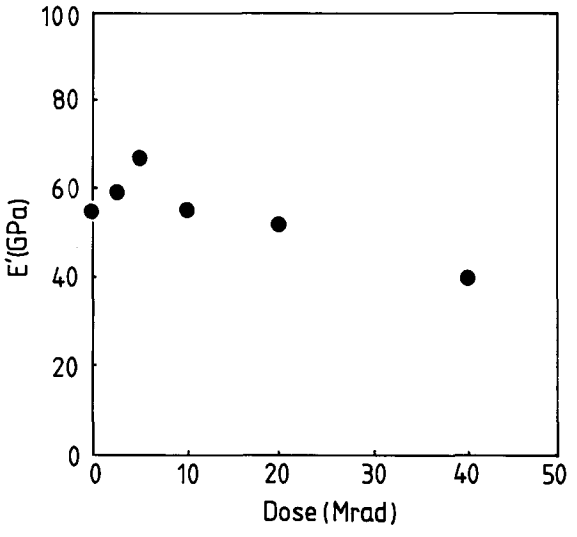

Figure 7 Dynamic mechanical storage modulus at 20°C of uniaxially drawn ($\lambda = 20$) UHMW-PE films as a function of irradiation dose

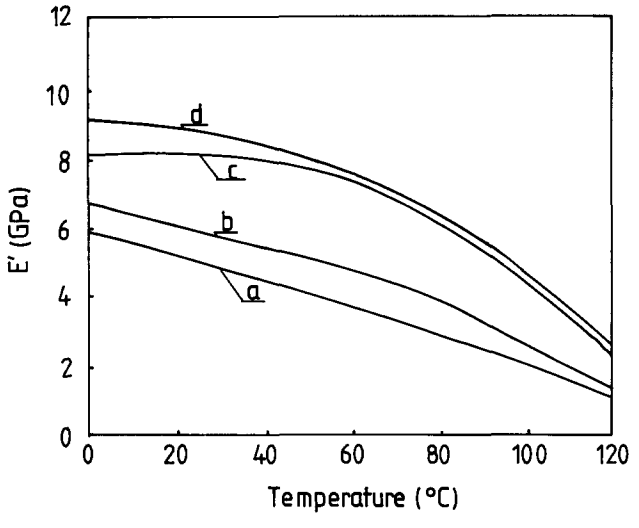

Figure 8 Temperature dependence of the storage modulus at a frequency of 10 Hz for simultaneously biaxially drawn ($\lambda = 10 \times 10$) UHMW-PE films with the indicated irradiation doses: (a) 0 Mrad; (b) 5 Mrad; (c) 10 Mrad; (d) 20 Mrad

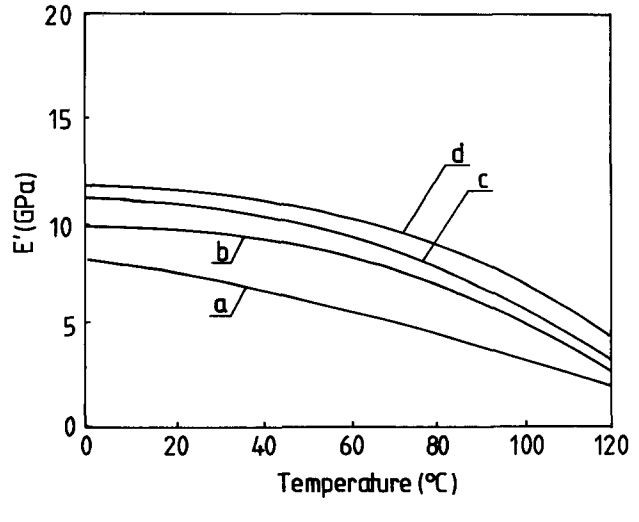

Figure 9 Temperature dependence of the storage modulus at a frequency of 10 Hz for simultaneously biaxially drawn ($\lambda = 16 \times 16$) UHMW-PE films with the indicated irradiation doses: (a) 0 Mrad; (b) 5 Mrad; (c) 10 Mrad; (d) 20 Mrad

with increasing irradiation up to 5 Mrad, and then decreases with increasing irradiation dose. This indicates that the irradiation dose dependence of E' for the uniaxially drawn film is smaller than that for biaxially drawn films, and that the considerable increase in the modulus of irradiated biaxially drawn films is caused by cross-linking which inhibits interfibrillar slippage. *Figures 8* and *9* show the temperature dependence of E' of biaxially drawn films as a function of irradiation dose. The values of E' of these films decrease with increasing temperature. The values of E' of irradiated films are higher than those of the unirradiated film over the whole temperature range, and furthermore these films have improved thermal properties. *Figure 10* shows the temperature dependence of E' of the uniaxially drawn ($\lambda = 20$) film as a function of irradiation dose. The values of E' of both the unirradiated and irradiated films decrease with increasing temperature. The values for irradiated films over 10 Mrad are smaller than those of the unirradiated film.

Figure 11 shows creep curves of electron beam irradiated biaxially drawn UHMW-PE dried gel films at 25°C. The irradiation decreases creep in the timespan

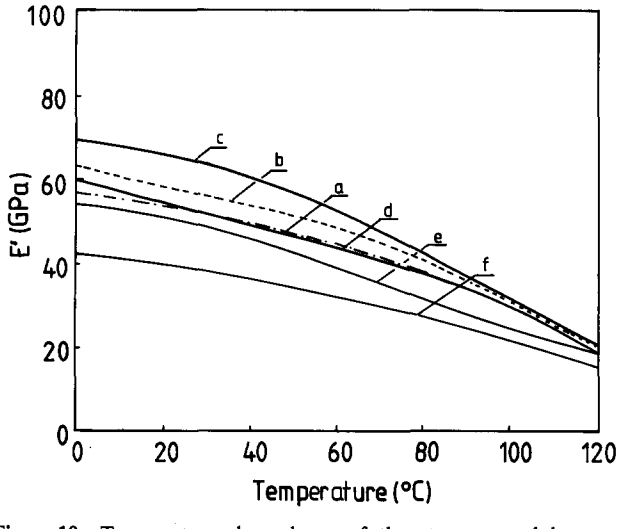

Figure 10 Temperature dependence of the storage modulus at a frequency of 10 Hz for uniaxially drawn ($\lambda = 20$) UHMW-PE films with the indicated irradiation doses: (a) 0 Mrad; (b) 1.3 Mrad; (c) 5 Mrad; (d) 10 Mrad; (e) 20 Mrad; (f) 40 Mrad

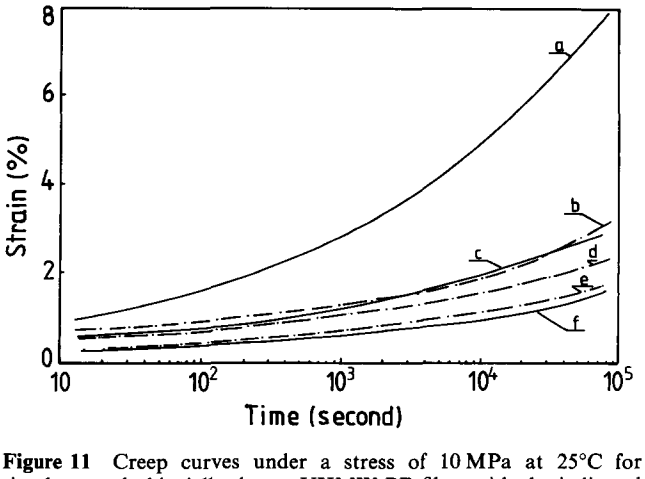

Figure 11 Creep curves under a stress of 10 MPa at 25°C for simultaneously biaxially drawn UHMW-PE films with the indicated irradiation doses: (a) $\lambda = 4 \times 4$ (0 Mrad); (b) $\lambda = 4 \times 4$ (10 Mrad); (c) $\lambda = 10 \times 10$ (0 Mrad); (d) $\lambda = 10 \times 10$ (10 Mrad); (e) $\lambda = 16 \times 16$ (0 Mrad); (f) $\lambda = 16 \times 16$ (5 Mrad)

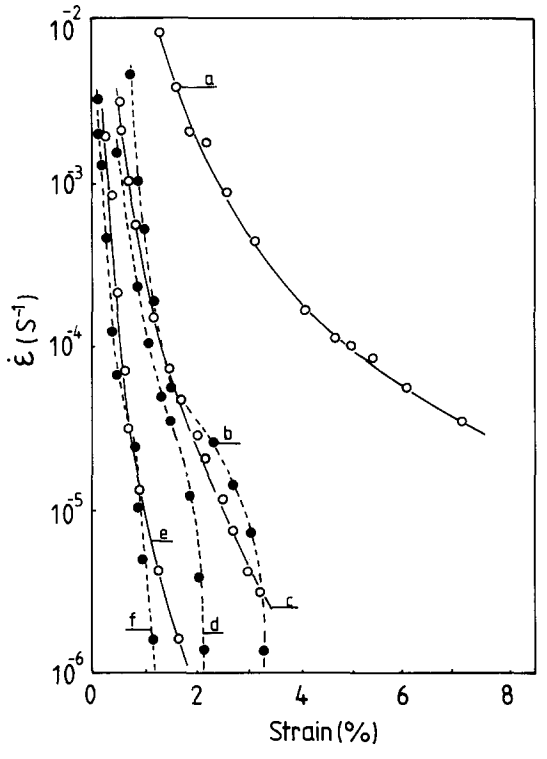

Figure 12 Creep strain rate as a function of strain under a stress of 10 MPa at 25°C for simultaneously biaxially drawn UHMW-PE films with the indicated irradiation doses: (a) $\lambda = 4 \times 4$ (0 Mrad); (b) $\lambda = 4 \times 4$ (10 Mrad); (c) $\lambda = 10 \times 10$ (0 Mrad); (d) $\lambda = 10 \times 10$ (10 Mrad); (e) $\lambda = 16 \times 16$ (0 Mrad); (f) $\lambda = 16 \times 16$ (5 Mrad)

measured. For the $\lambda = 4 \times 4$ film, irradiation treatment considerably improves the creep behaviour. The curves for irradiated films are almost linear in the earlier stages but gradually turn upwards later. This improvement is due primarily to the stiffness of these films. For the purpose of analysis, a more instructive way of presenting the data is to plot the creep strain rate *versus* the creep strain. In *Figure 12*, creep strain rate ($\dot{\varepsilon}$) is shown as a function of strain for irradiated and unirradiated biaxially drawn films, following Sherby and Doron[11]. This figure indicates that the creep rate is reduced with increasing radiation for all films. The strain rate for the irradiated, $\lambda = 4 \times 4$ film is approximately two orders of magnitude smaller than that for the unirradiated film, and the rate for the irradiated, biaxially drawn $\lambda = 10 \times 10$ films is about one order of magnitude smaller than that for the unirradiated films in the high strain regions.

SUMMARY

The effect of electron beam irradiation on the morphology and mechanical properties of biaxially drawn UHMW-PE dried gel films was studied as a function of the irradiation dose. The following results were derived.

1. D.s.c. melting thermograms showed two peaks, in which the higher temperature peak shifted to lower temperatures with increasing irradiation, while the lower peak shifted to higher temperatures.
2. Tensile strength and strain decreased even at small irradiation doses. This behaviour was considered to be caused by main-chain scission and the inhibition of interfibrillar slippage.
3. The storage modulus at room temperature increased with increasing radiation up to 20 Mrad. The maximum attainable value of the storage modulus was about 12 GPa for the $\lambda = 16 \times 16$ films irradiated with 20 Mrad.
4. Creep strain rate of the irradiated films with $\lambda = 10 \times 10$ was one order of magnitude smaller than that of the unirradiated films.

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