Mechanical properties of biaxially drawn films of ultra-high molecular weight polyethylene dried gels

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Mechanical properties of biaxially drawn films of ultra-high molecular weight polyethylene dried gels were studied and were compared with the results of uniaxially drawn films prepared from the same gels. Although the tensile storage modulus (E') of biaxially drawn films is much smaller than that of uniaxially drawn films, their temperature dependence is similar. The largest attainable shear storage modulus of biaxially drawn film is 1.1 GPa at 20°C for the specimen with a draw ratio of 16×16, while E' is 7 GPa for the same specimen. The tensile creep rate of biaxially drawn films at 25°C is much bigger than that of uniaxially drawn films, although it decreases with increasing draw ratio. The large creep rate of biaxially drawn films is supposed to be mainly due to the easy orientation of fibrils in the strained direction.

(Keywords: ultra-high molecular weight polyethylene; gel film; simultaneous biaxial drawing; mechanical properties)

INTRODUCTION

In our previous papers[1,2], the structure and properties of drawn films as a function of draw ratio were investigated for biaxially drawn ultra-high molecular weight polyethylene (UHMW PE) gel films. Our study showed that the biaxially drawn films were comprised of microfibrils, with diameters of several tens of nanometres, orienting at random in the film plane forming networks. This was also confirmed by Gerrits[3]. SEM observation showed that microfibrillation was almost complete at a draw ratio of 10×10, and further drawing was accomplished by slippage of microfibrils across each other, while slight thinning of each fibril was caused. As a special case, some microfibrils entangled with each other. Field emission SEM of the fracture surface perpendicular to the film surface showed that thin layers ($< 1\,\mu m$) were formed for low draw ratio films, suggesting that biaxial drawing (formation of fibrils) was performed in each layer. As to the fine structure of the fibrils, the small-angle X-ray scattering (SAXS) peak due to the long spacing disappeared at a draw ratio of 10×10. As to the mechanical properties of biaxially drawn UHMW PE gel films, Minami and Itoyama[4] first studied the relationship between the tensile modulus (E') and draw ratio, and showed that the highest attainable E' was ~ 7 GPa at room temperature for the 16×16 specimen. Recently, Bastiaansen *et al.*[5] calculated the Young's modulus (E) of biaxially drawn balanced UHMW PE films which are hypothetically composed of single crystals and have different structures. According to them, the modulus varies over a wide range from 8 to 111 GPa depending on the assumed structure. However, their calculations combined with the structural data on UHMW PE films indicate that the theoretical maximum modulus of such films is ~ 8–12 GPa. Gerrits *et al.*[6] showed that the E of biaxially drawn UHMW PE gel films is ~ 0.375 of that of uniaxially drawn films; there is a large difference in elongation at break while both types of materials have similar tensile strength. In the present paper, the mechanical properties of drawn films are studied with particular interest in shear dynamic, tensile creep measurements as well as ordinary tensile dynamic measurements, and their temperature dependences.

EXPERIMENTAL

Sample preparation

The sample material and preparation methods were the same as those in our previous paper[1]. 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 flask at 160°C. The 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 obtain a gel. The gel was removed from the flask and pressed between aluminium flat plates with mirror finished surfaces under a pressure of 100 kg cm^{-2} at 150°C for 10 min, followed by quenching in water at 20°C. The specimens were prepared by heat compression of gel material instead of being prepared as gel sheets directly from the solution. Although our method decreased the drawability due to chain re-entanglement during heat compression, it was better for making uniform sheets which were essential for biaxial drawing.

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The prepared gel sheets were dried at room temperature, resulting in samples 0.11–0.13 mm thick. Samples $10 \times 10\,cm^2$ cut from the dried sheets were supplied for simultaneous biaxial drawing, and samples 40 mm long and 10 mm wide were supplied for uniaxial drawing. The drawing process was performed at 135°C using an Iwamoto film stretcher.

Mechanical properties

Dynamic mechanical properties were measured under tensile and shear stress modes. The former was measured on samples 25 mm long and 8 mm wide using a Toyo Seiki Reolograph Piezo at 10 Hz over a temperature range of 0–120°C and the heating rate was 3°C min^{-1}. The latter was measured on samples 18 mm long and 12 mm wide using a Seiko Denshi dynamic viscoelastic spectrometer (SDM 5500) at 0.5, 1, 2 and 5 Hz over a temperature range of 0–120°C and the heating rate was 2°C min^{-1}.

Tensile creep and recovery were measured on samples 15 mm long and 8 mm wide using a Sinku-Riko TM-7000 at 25°C under a constant load (6.7 MPa).

RESULTS AND DISCUSSION

Figure 1 shows the dynamic tensile storage modulus (E') at 20°C of biaxially drawn UHMW PE films as a function of draw ratio. The modulus increases with increasing draw ratio. Although the largest modulus was 7 GPa at a draw ratio of 16×16 in the previous paper[1], a value of ~8.5 GPa was attained at a draw ratio of 20×20 in this study. Biaxially drawn films were comprised of microfibrils which are extremely long but not straight throughout their whole length and orient at random in the film plane. It is difficult to describe theoretically the modulus of these films with discontinuous structure consisting of microfibrils. However, it is still interesting to compare the values of E' of our biaxially drawn films with the modulus of a PE crystal averaged on the b–c plane. The reason why we use this mode of averaged PE crystal modulus is due to the fact that, in these films, the a axes of all crystals orient in the thickness direction of the films, while the c axes orient at random in the film plane. The compliance of a single crystal in the direction making an angle θ against the c axis on the b–c plane S'_{3333} is given by:

$$S'_{3333} = C_{3i}C_{3j}C_{3k}C_{3l}S_{ijkl} \quad (1)$$

$$E = 1/S'_{3333} \quad (2)$$

where E is the Young's modulus in the particular direction, S_{ijkl} is the $ijkl$ component of the compliance

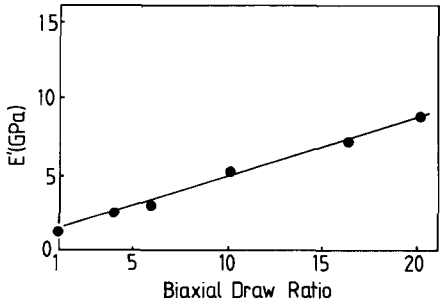

Figure 1 Dynamic tensile storage modulus (E') at 20°C of simultaneously biaxially drawn UHMW PE films as a function of biaxial draw ratio

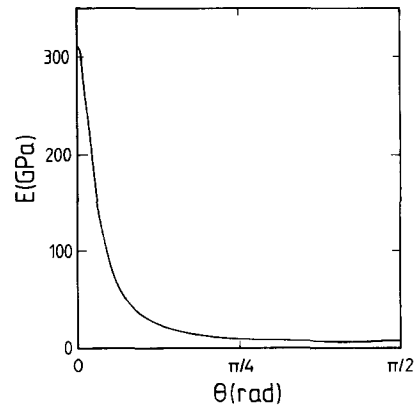

Figure 2 Theoretical crystal modulus (E) of polyethylene on the b–c plane as a function of the angle θ measured from the c (chain) axis

defined in the coordinate in which 1, 2 and 3 correspond to the a, b and c axes of the PE crystal, and C_{3i} is given in this case by:

$$C_{31} = 0, \quad C_{32} = \sin\theta, \quad C_{33} = \cos\theta \quad (3)$$

When S_{ijkl} values for the PE crystal calculated by Tashiro *et al.*[7] are used, S'_{3333} (in GPa) is given by:

$$S'_{3333} = (11.67\sin^4\theta + 31.19\sin^2\theta\cos^2\theta + 0.32\cos^4\theta) \times 10^{-2} \quad (4)$$

Figure 2 shows the calculated E value as a function of the angle θ, indicating that the modulus decreases steeply with θ. Recently, Bastiaansen *et al.*[5] calculated E of biaxially drawn PE films composed of single crystal elements, using two models of laminate and aggregate modes. In their model, the c axes randomly orient in the film plane with several modes of the orientation of the a and b axes, and the value of the theoretical modulus varies widely depending on the models. The fine structure characterized by microfibrils and experimental data on E of biaxially drawn UHMW PE films implies that the aggregate mode might be the most accurate case. According to Bastiaansen *et al.*[5], the theoretical maximum modulus of such films was ~8–12 GPa. The value of 35 GPa for the modulus of the PE crystal averaged over θ seems to correspond to the laminate type model. If the theoretical maximum E is between 8 GPa and 12 GPa, it might be considered that our experimental values from dynamic viscoelastic measurements have achieved almost the highest limit. However, this is unreasonable when we consider the structure of biaxially drawn UHMW PE films consisting of fibrils whose modulus must be much lower than that of the crystal. This means that the theoretical modulus of a biaxially drawn PE film should be 12 GPa, although it must be much lower than 35 GPa based on the single crystal assumption. However, our experimental value of 8.5 GPa is doubtless close to the limiting value of the real biaxially drawn PE films, when the fine structure of the films consisting of microfibrils is taken into consideration.

Figures 3 and *4* show the temperature dependence of E' and the loss modulus (E'') for biaxially drawn films. E' increases with increasing draw ratio and decreases with increasing temperature, while E'' has the α_c transition peak over a range of 50–80°C. The intensity of E'' increases with increasing draw ratio. The α_c transition of PE has been identified as molecular motions in the crystal[8] and in the crystal grain boundary[9]. *Figures 5*

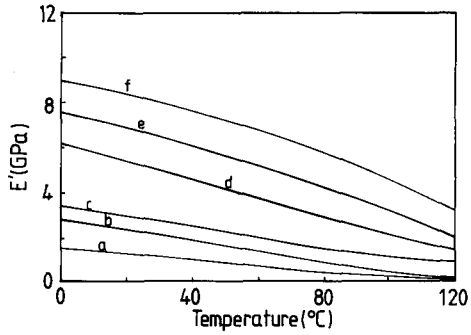

Figure 3 Temperature dependence of the tensile storage modulus (E') at a frequency of 10 Hz for simultaneously biaxially drawn UHMW PE films: (a) $\lambda = 1 \times 1$; (b) $\lambda = 4 \times 4$; (c) $\lambda = 6 \times 6$; (d) $\lambda = 10 \times 10$; (e) $\lambda = 16 \times 16$; (f) $\lambda = 20 \times 20$

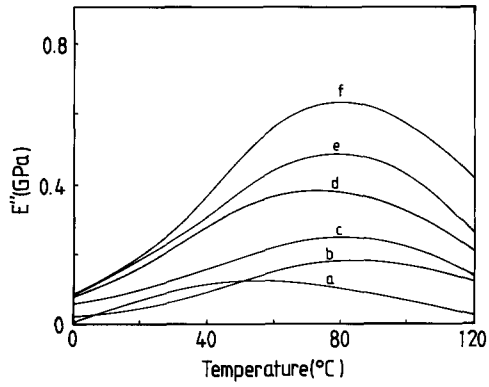

Figure 4 Temperature dependence of the tensile loss modulus (E'') at a frequency of 10 Hz for simultaneously biaxially drawn UHMW PE films: (a) $\lambda = 1 \times 1$; (b) $\lambda = 4 \times 4$; (c) $\lambda = 6 \times 6$; (d) $\lambda = 10 \times 10$; (e) $\lambda = 16 \times 16$; (f) $\lambda = 20 \times 20$

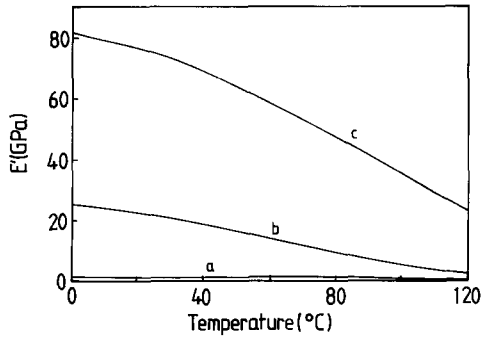

Figure 5 Temperature dependence of the tensile storage modulus (E') at a frequency of 10 Hz for uniaxially drawn UHMW PE films: (a) $\lambda = \times 1$; (b) $\lambda = \times 10$; (c) $\lambda = \times 30$

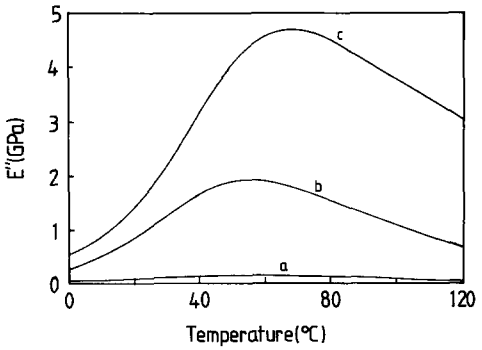

Figure 6 Temperature dependence of the tensile loss modulus (E'') at a frequency of 10 Hz for uniaxially drawn UHMW PE films: (a) $\lambda = \times 1$; (b) $\lambda = \times 10$; (c) $\lambda = \times 30$

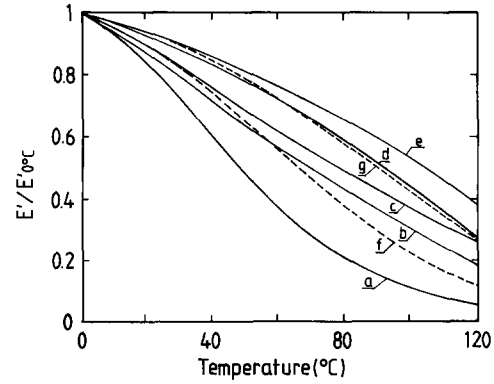

Figure 7 Temperature dependence of the tensile storage modulus (E') of biaxially (——) and uniaxially (– –) drawn UHMW PE films normalized by the value at 0°C in *Figures 3* and *5*: (a) $\lambda = 1 \times 1$; (b) $\lambda = 4 \times 4$; (c) $\lambda = 10 \times 10$; (d) $\lambda = 16 \times 16$; (e) $\lambda = 20 \times 20$; (f) $\lambda = \times 10$; (g) $\lambda = \times 30$

and *6* show the temperature dependence of E' and E'' of uniaxially drawn films from the same dried gel film as that of biaxially drawn films. Although the values of E' and E'' of uniaxially drawn films are far larger than those of biaxially drawn films, the temperature dependence of uniaxially drawn films is similar to that of biaxially drawn films. *Figure 7* shows the relative change of E' with temperature. The slopes of the curves decrease with increasing draw ratio over the whole temperature range in both uniaxially and biaxially drawn films. Especially in the high temperature range over 50°C, the thermal stability of biaxially drawn materials is higher than uniaxially drawn ones. Prior to the experiment, we supposed that the temperature dependence of E' of biaxially drawn films might be much larger than that of uniaxially drawn ones. This was because the interfibrillar contact area is much smaller in biaxially drawn films in which fibrils orient at random, crossing each other, than in uniaxially drawn ones in which fibrils orient in parallel. One of the most important reasons for the remarkable decrease in E' of highly drawn gel-spun (uniaxially drawn) UHMW PE films with increasing temperature may be the deteriorated interfibrillar frictional properties with heating. The data indicated that the temperature dependence of E' of 20×20 biaxially drawn films is smaller than that of $\times 30$ uniaxially drawn ones, although the value of E' of biaxially drawn films is far smaller than that of uniaxially drawn ones. The reason for the smaller temperature dependence of E' of biaxially drawn films may be related to the smaller value of E'. In our previous paper[1] the SAXS peak due to the long spacing disappeared at a draw ratio of $\sim 10 \times 10$ in biaxial drawing, while it occurred at a draw ratio between $\times 20$ and $\times 50$ in uniaxial drawing[10]. SEM observations also showed that fibrils in biaxially drawn films are finer than those of uniaxially drawn ones, and make a network structure at high draw ratios. This suggests that E' of each fibril in biaxial drawn films with a draw ratio of 10×10 might be larger than that in uniaxial drawn films with a draw ratio of $\times 10$, and that the interfibrillar contact may be tight due to the development of a fibrillar network structure even in biaxially drawn films. *Figure 8* shows the temperature dependence of $\tan\delta$ of biaxially and uniaxially drawn films. Tan δ in dynamic tensile deformation of all samples decreases with increasing draw ratio and the value of 20×20 biaxially drawn films is

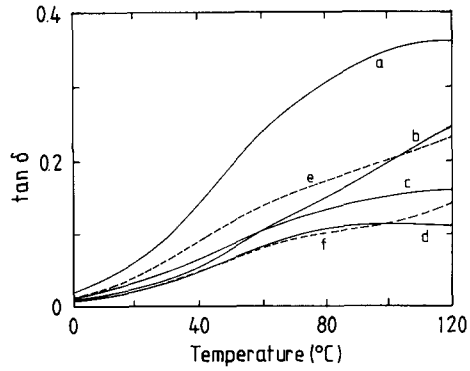

Figure 8 Temperature dependence of tan δ at a frequency of 10 Hz for biaxially (——) and uniaxially (– –) drawn UHMW PE films: (a) $\lambda = 1 \times 1$; (b) $\lambda = 4 \times 4$; (c) $\lambda = 10 \times 10$; (d) $\lambda = 20 \times 20$; (e) $\lambda = \times 10$; (f) $\lambda = \times 30$

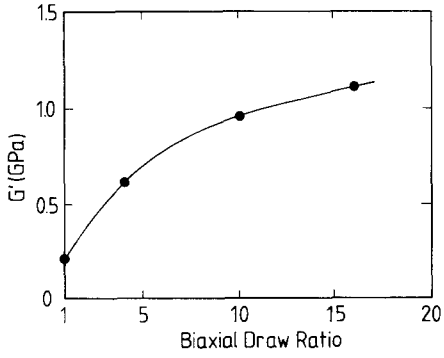

Figure 9 Dynamic shear storage modulus (G') at a frequency of 1 Hz at 20°C of simultaneously biaxially drawn UHMW PE films as a function of biaxial draw ratio

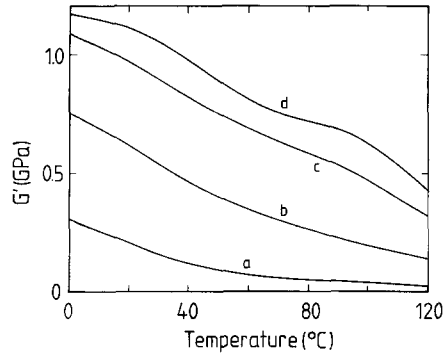

Figure 10 Temperature dependence of the storage shear modulus (G') at a frequency of 1 Hz for simultaneously biaxially drawn films: (a) $\lambda = 1 \times 1$; (b) $\lambda = 4 \times 4$; (c) $\lambda = 10 \times 10$ (d) $\lambda = 16 \times 16$

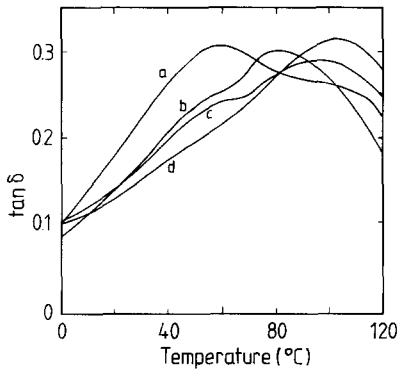

Figure 11 Temperature dependence of dynamic shear (tan δ) at a frequency of 1 Hz for simultaneously biaxially drawn films: (a) $\lambda = 1 \times 1$; (b) $\lambda = 4 \times 4$; (c) $\lambda = 10 \times 10$; (d) $\lambda = 16 \times 16$

similar to that of $\times 30$ uniaxially drawn materials. This also shows that the fibrillar network is made up of tightly bound junction points in highly biaxially drawn films.

Figure 9 shows the dynamic mechanical storage shear modulus (G') at 20°C of biaxially drawn UHMW PE films as a function of draw ratio. It should be noted that G' increases remarkably between 4×4 and 10×10, followed by a milder increase at draw ratios above 10×10, whereas E' increased monotonously with increasing draw ratio, as mentioned above. The largest value of G' attained is ~ 1 GPa. *Figure 10* shows the temperature dependence of G': the value of G' increases with increasing draw ratio and decreases with increasing temperature, with a plateau at high draw ratios. *Figure 11* shows the temperature dependence of tan δ in dynamic shear deformation. For the 1×1 (undrawn) film a peak and shoulder appear at 50 and 120°C, respectively. For the 4×4 and 10×10 films, the main peak shifts toward higher temperature with increasing draw ratio, while a weak shoulder remains at ~ 50°C. For the 16×16 film, the main peak appears at 100°C and the 50°C peak almost disappears. It is noted that this change corresponds well to the morphological change with increasing draw ratio observed by SEM. As reported in previous papers[1,2], in the 4×4 film, fibrillar structure appears with a large number of remaining particles, although the particle size had become much smaller than before drawing. In the 10×10 film, the particles had almost completely disappeared and the film was composed of thick and thin microfibrils. In the 16×16 film, microfibrils further increased in number and in uniformity, and fibrillar networks developed.

The activation energy for the mechanical dispersion, shown in *Figure 11*, was estimated for each film by changing the frequency of shear deformation. *Table 1* shows the estimated activation energies, calculated from Arrhenius plots of tan δ maximum temperature against frequency. The values are in the range from ~ 190 to ~ 209 kJ mol^{-1}. These values show that this mechanical dispersion is due to the same relaxation mechanism relating to the crystal phase α_c as that in high-density polyethylene[11,12]. On the other hand, the shoulder of tan δ around 120°C for the 1×1 films is related to the melting, and seems to shift to higher temperatures with increasing draw ratio. In the previous paper[1], it was shown that the biaxially drawn films had two melting peaks at 135 and 150°C, and that the fraction of the latter increased, while the former decreased, with increasing draw ratio.

It should be noted that the value of tan δ in the tensile mode vibration at 10 Hz measured at 20°C is about four times smaller than that in the shear mode at 1 Hz deformation at the same temperature. This may be due to the fact that the stress applied to the sample is larger in the tensile test than in the shear test.

Figure 12 shows creep and the recovery curves of biaxially drawn films at 25°C as a function of time. Increased draw ratio decreases creep extension. The

Table 1 Activation energies (kJ mol^{-1}) of α_c dispersion in shear deformation, obtained from the frequency dependence, as a function of biaxial draw ratio

1×1	4×4	10×10	16×16
196.6	190.3	196.1	208.8

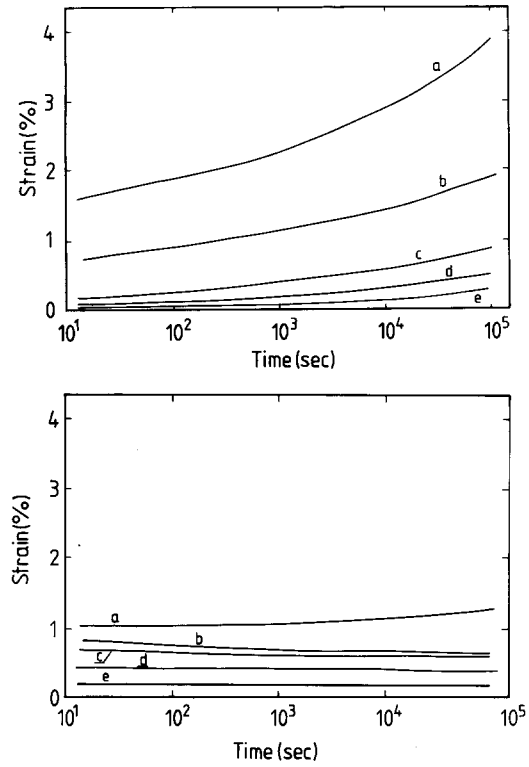

Figure 12 (Top) creep and (bottom) recovery curves under a stress of 6.7 MPa at 25°C for biaxially and uniaxially drawn UHMW PE films as a function of time: (a) $\lambda = 4 \times 4$; (b) $\lambda = 10 \times 10$; (c) $\lambda = 16 \times 16$; (d) $\lambda = \times 10$; (e) $\lambda = \times 20$

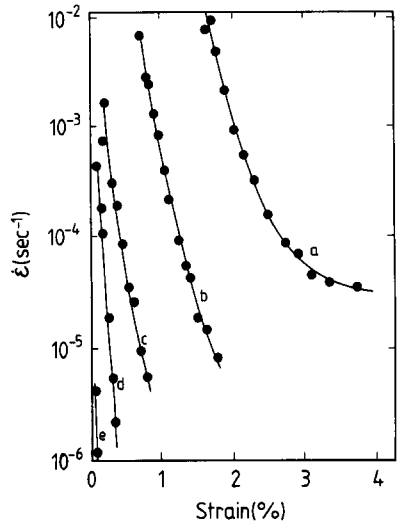

Figure 13 Creep strain rate ($\dot{\varepsilon}$) as a function of strain under a stress of 6.7 MPa at 25°C for simultaneously biaxially and uniaxially drawn UHMW PE films: (a) $\lambda = 4 \times 4$; (b) $\lambda = 10 \times 10$; (c) $\lambda = 16 \times 16$; (d) $\lambda = \times 10$; (e) $\lambda = \times 20$

curves are almost linear initially but gradually turn upwards later. The creep and its recovery of biaxially drawn UHMW PE films are similar to those of highly uniaxially drawn normal molecular weight PE shown by Wilding and Ward[13,14]. The creep strain of the 16×16 films is larger than those of the $\times 10$ and $\times 20$ drawn films whose data are also shown in *Figure 12*. As to the creep recovery, in the case of 4×4 film, the sample still extends during the creep recovery experiment. This is due to a creep extension under a small weight which was applied to keep the film straight during the recovery experiment. In *Figure 13*, following the example of Sherby and Dorn[15], the creep strain rate is shown as a function of creep strain for biaxially drawn films. The creep strain rate decreases with increasing draw ratio. In the 4×4 sample, the strain rate has a plateau with a constant creep rate, which means the steady state of creep extension, while in 10×10 and 16×16 specimens, no plateau appears and the strain rate gradually decreases with time. The strain rate for the 16×16 sample is approximately two orders of magnitude or more greater than that of the uniaxially $\times 10$ and $\times 20$ drawn samples. This very large creep reflects the morphology of simultaneously biaxially drawn films characterized by microfibrils randomly orienting in the film plane: the creep strain of biaxially drawn films is attributed mainly to the orientation of fibrils in the straining direction, accompanying the straightening of bent fibrils and the rotation as well as the slippage of fibrils.

CONCLUSIONS

The mechanical properties of simultaneously biaxially drawn UHMW PE dried gel films were studied with the following results.

1. The dynamic tensile storage modulus E' was 8.5 GPa at a draw ratio of 20×20 which was the highest ever achieved, while the dynamic shear storage modulus G' was 1.1 GPa.
2. The temperature dependence of the dynamic tensile modulus of biaxially drawn films was unexpectedly similar to that of uniaxial drawn films.
3. The creep strain rate in the 16×16 film was over two orders of magnitude greater than those of $\times 10$ and $\times 20$ uniaxially drawn films, reflecting the particular structure consisting of microfibrils which orient at random in the film plane.

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