Preparation of ultra-high modulus polyethylene films by the zone-annealing method

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The zone-annealing method has been used to prepare uniaxially oriented ultra-high modulus polyethylene films from single crystal mats of ultra-high molecular weight polyethylene. The maximum dynamic modulus and tensile strength at room temperature of superdrawn films were 232 and 6 GPa, respectively. The present paper discusses the advantages of the zone-annealing method, the determination of the optimum conditions for zone drawing and zone annealing, and the changes in superstructure and mechanical properties with processing.

(Keywords: zone annealing; ultra-high molecular weight polyethylene; single crystal mat; double orientation; ultra-high modulus; high strength)

INTRODUCTION

Since Pennings *et al.*[1,2] succeeded in preparing high-strength polyethylene fibres by the Couette flow technique, several techniques for superdrawing of ultra-high molecular weight polyethylene (UHMW PE) have been developed, including gel spinning[3,4], drawing of gel films[5-9] and drawing of single crystal mats[10-13]. In particular, it is worth noting that the moduli near or above 200 GPa have recently been attained by Miyasaka *et al.*[10,11], Kanamoto *et al.*[12,13] and Matsuo *et al.*[9].

In 1979[14], we proposed an annealing method, the 'Zone-annealing Method', to achieve effective drawing and annealing. Since then, the method has been successfully applied to a variety of semicrystalline polymers, such as poly(ethylene terephthalate)[14-20], nylon 6[14,19,21-24], polyethylene[19-25], polypropylene[26], and poly(ether-ether-ketone)[27].

In this work, the method was applied to drawing of UHMW PE single crystal mats. The ultradrawn films showed remarkably high dynamic moduli and tensile strength up to 232 and 6 GPa, respectively. The purpose of this paper is to report the drawing behaviour and the physical and mechanical properties of the ultradrawn films obtained.

EXPERIMENTAL

Material

The original material was UHMW PE powder, Hizex Million 340 M ($M_v = 4.5 \times 10^6$), supplied by Mitsui Petrochemical Industries Ltd.

Preparation of single crystal mats

The mats were carefully prepared for the studies. The powder was dissolved in *p*-xylene at a concentration of 0.1% at the boiling temperature. The dilute solution was cooled at a low cooling rate of 0.5°C min^{-1} from 140 to 120°C and then allowed to cool to room temperature without stirring. Upon cooling, the crystals were deposited as a gel-like precipitate. The solvent was removed by filtration followed by squeezing out between filter papers under a slight pressure. The mats were then pressed under gradually increasing pressure up to 150 kg mm^{-2} at room temperature. The mats were subsequently dried in a vacuum at 45°C for 24 h between stainless steel plates.

Zone drawing and zone annealing

From the mats thus prepared, the strips used for zone drawing were cut into a size of 2 mm width and about 100 mm length. The strips were initially zone drawn and then zone annealed. The conditions for zone drawing and zone annealing are described in detail below. The apparatus used in this study is the same as that described previously[14-27].

Measurements

Birefringence was measured with a polarizing microscope equipped with a Berek compensator. Infra-red spectra, d.s.c. curves and X-ray equatorial diffraction patterns in two directions with incident beams both perpendicular and parallel to the film surface were obtained.

Dynamic viscoelasticity E' and E'' were measured at 110 Hz and at a heating rate of 2.7°C min^{-1} from 0°C to about 140°C with a Vibron DDV-II dynamic viscoelastometer (Toyo-Bardwin Co. Ltd). The tensile tests were carried out at 23–25°C and relative humidity 65% on films of about 30 mm in gauge length and at a crosshead speed of 10 mm min^{-1} using a Tensilon II tensile tester (Toyo-Bardwin Co. Ltd). Tensile modulus, strength and elongation at break were evaluated from strain–stress curves. Due to a low frictional coefficient and the very small cross-section of the ultradrawn PE films, a gripping method described by Professor Kanamoto, Science University of Tokyo, was used. The film was fixed with adhesive between two aluminium plates and then the sandwiches of sample ends were fitted by jaws in the cross-head.

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RESULTS AND DISCUSSION

Preparation of single crystal mats

There are a number of papers on the preparation of single crystal mats[10-13] or dried gel films[5-9] from dilute solutions of UHMW PE. It is well known that the dried gel films and the single crystal mats have essentially identical structures in which plate-like lamellae are laminated nearly parallel to the surface of the films or mats. When these studies are compared with each other in detail, however, one can find significant differences in various parameters, such as molecular weight (1×10^6–4×10^6), solvent, concentration of solution (0.1–2%), the method of gel or crystal generation, preparation of films or mats (casting or filtration), and the techniques of solvent removal, drying and pressing of the films or mats. To obtain the most suitable mats for zone drawing, we carried out preliminary experiments. The following points were checked: (1) molecular weight (1.4, 3.0 and 4.5×10^6); (2) solvent (decalin and *p*-xylene); (3) solution concentration (0.05, 0.1 and 0.2%); (4) deposition (isothermal crystallization at 90°C, rapid and slow cooling); (5) pressing and drying methods for wet mats; (6) thickness of mats (ca. 200, 300, 500, and 1000 μm). The experiments were performed with the intention of preparing mats which consisted of lamellae as regularly folded and stacked as possible. We thought that such a structure would be very suitable for lamella unfolding by zone drawing. On the basis of drawability of the mats, the mat preparation method was finally decided upon as described in the experimental section. It was confirmed by X-ray analysis that, in the mats thus obtained, the *c* axis is well oriented in the thickness direction of the mats, while the *a* and *b* axes are distributed at random in the plane parallel to the mat's surface.

Comparison of drawing techniques for single crystal mats

A variety of techniques have been applied to the drawing of UHMW PE single crystal mats and dried gel films, including drawing in an oven[8,9,13], drawing in water or silicone oil baths[6,10], swelling drawing in hot xylene[5] and coextrusion[12]. For the single crystal mats prepared by our method, we examined three kinds of drawing techniques, drawings in an oven, in hot water and silicone oil, and compared them with zone drawing.

As a result of the comparison, we were able to establish some characteristics of each technique. Two distinct characteristics of zone drawing will be described below.

(1) In the case of zone drawing, a sharp necking was observed. A similar sharp necking boundary has already been observed on drawing at room temperature of dried gel films cast from 0.6 and 0.5% solutions by Smith *et al.*[28] and Matsuo *et al.*[29], respectively. Zone drawing can involve a very sharp necking boundary even at fairly high drawing temperatures. It is expected that the sharp-necking zone drawing promotes regular chain unfolding of the lamellae if drawing is carried out at a temperature high enough for the lamellae to become fully soft. *Figure 1* indicates a schematic representation of ideal chain unfolding of the mat upon zone drawing. *Figure 2* shows polarizing microscope photographs which show the drawn–undrawn boundaries of the zone drawn film under optimum conditions and of the film drawn in a hot water bath. The former exhibits a sharp boundary, whereas the latter has no clear boundary. According to scanning electron microscope observations, the drawn part of the latter contains undrawn blocks of various sizes.

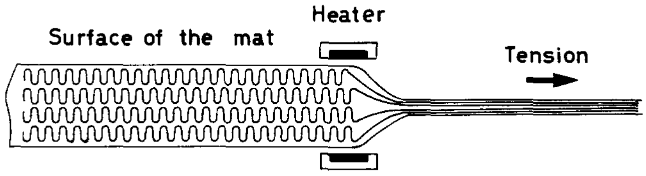

Figure 1 Ideal unfolding of the single crystal mat by zone drawing. It is not necessary that the unfolded chains are aligned and extended as shown in *Figure 1*

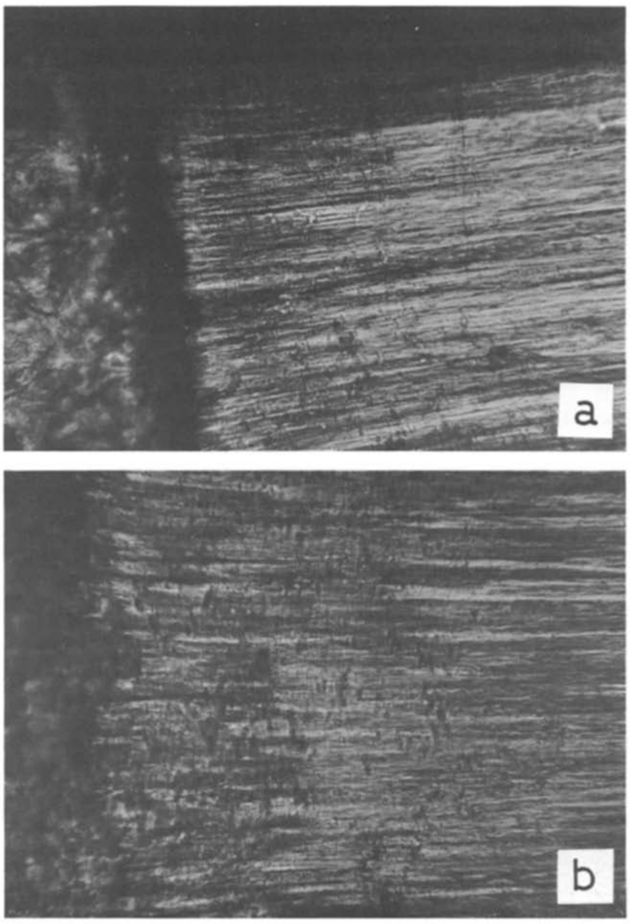

Figure 2 Polarizing microscope photographs of the undrawn–drawn boundary for the films zone-drawn (a) and drawn by another method (b)

(2) In the case of zone drawing, the mats are not subjected to any heat treatment until the narrow heater approaches. The undrawn part in zone-drawing did not change at all in its long period. It is known that heat treatment of single crystal mats causes some distortion of lamellar stacking, thickening of lamellae and increase in chain entanglements. Upon zone-drawing, the mats always enter into the heating zone as-virgin, and are drawn under the given conditions without preheating.

Determination of the optimum conditions for zone drawing and zone annealing

As it is difficult to change from lamellar to extended chain structures in one step, we adopted a multi-step zone annealing method. First, the procedure was divided into two stages, i.e. zone drawing and zone annealing. Further, each stage was repeated four times. These steps are abbreviated as ZD-1, -2, -3, -4 and ZA-1, -2, -3, -4, respectively. We expected that each step plays the following roles. ZD-1 is involved mainly in chain unfolding of lamellae. Therefore, we did not expect a highly oriented alignment of unfolded molecular chains such as in *Figure 1*, and considered that the molecular chains after ZD-1 were much more released and disordered in orientation. ZD-2 ~ ZD-4 promote step-by-step alignment and extension of the unfolded molecular chains, and ZA-1 ~ ZA-4 complete the extended-chain crystallization.

The effect of temperature on zone drawing was examined at intervals of 5°C from 90 to 135°C; 90°C is just below the d.s.c. melting point peak for the mat, and 135°C is just above the d.s.c. melting point peak for the mat. The tension applied to the sample was also examined at each step. The first drawing, i.e. ZD-1, is very important in achieving effective unfolding. After many preliminary experiments it was found that ZD-1 must be carried out at a temperature sufficiently high for the lamellae to become fully soft and at a low heater speed. In order to add sufficient tension to the molecular chains, ZD-2 ~ ZD-4 were carried out at a temperature lower than that in ZD-1 and by increasing the tension to the limit at which the films did not sever at each step, Similarly, the effects of temperature and tension on zone annealing were examined over the ranges from 110 to 145°C and 5 to 40 kg mm^{-2}, respectively. The conditions of 145°C and 40 kg mm^{-2} on zone-annealing are surprisingly harsh for PE films.

For each of the ZD and ZA films, the draw ratio, birefringence and mechanical properties were measured. The maximum draw ratio achieved was 435, but the modulus of this film was not so high at 150 GPa. The modulus was not necessarily high when the draw ratio was high. So we judged whether the conditions were optimal or not mainly on the mechanical properties of the films. After exploratory examinations, the preferred conditions were determined. The three examples are shown in *Table 1*. The conditions in example 1 were selected as the best conditions, and were used in the following study.

Change in the superstructure

By repeating zone drawing and zone annealing under the example 1 conditions, the draw ratio was increased as shown in *Figure 3*. The draw ratio reached 170, but it was smaller than those (200–300) obtained by other researchers[9,11,12]. The increase of birefringence with the processing is shown in *Figure 4*. The maximum value, 0.072, is extremely high in spite of the relatively low draw ratio. It exceeds the intrinsic crystal birefringence values, Δ_c°, of 0.0572 or 0.0585 reported in the literature[30,31]. However, very high values are proposed as the intrinsic birefringence of perfectly oriented amorphous region, Δ_a°. Wedgewood *et al.*[31] have reported Δ_c° and Δ_a° of 0.0585 and 0.12, whereas Fukui *et al.*[32] have proposed 0.057 and 0.210, respectively. According to Stein,

$$\Delta_t = \Delta_c^\circ X_c f_c + \Delta_a^\circ (1 - X_c) f_a + \Delta_f \quad (1)$$

where Δ_t and Δ_f are the total birefringence as measured and the form birefringence; the latter is negligible. f_c and f_a are the orientation functions of crystalline and amorphous regions, respectively. X_c is the crystallinity of the sample. On the other hand, it is known that ultra-

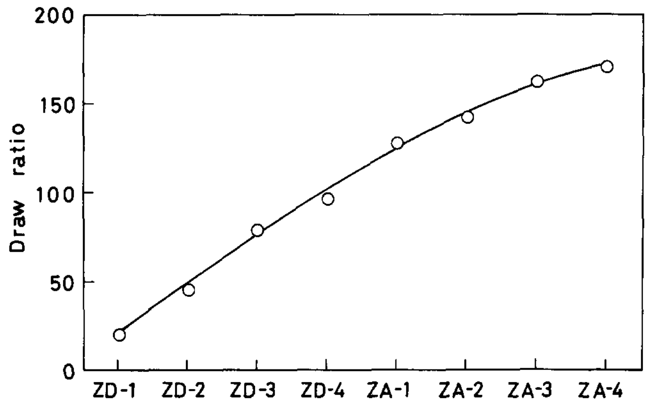

Figure 3 Change in draw ratio with processing

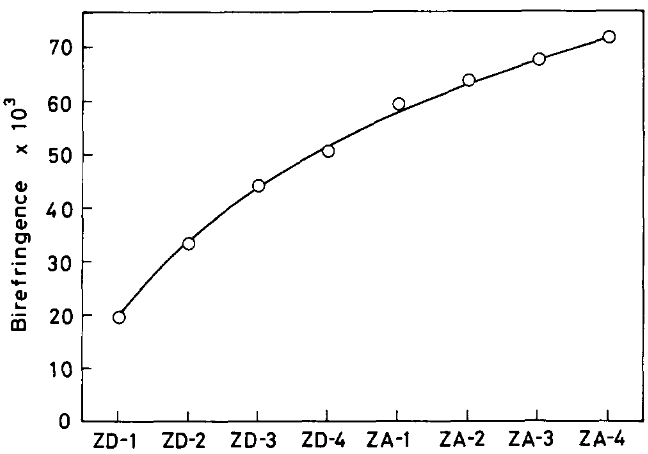

Figure 4 Change in birefringence with processing

Table 1 Examples of suitable conditions for zone drawing and zone annealing

Conditions	ZD-1	ZD-2	ZD-3	ZD-4	ZA-1	ZA-2	ZA-3	ZA-4
Example 1								
Temperature (°C)	125	115	115	115	135	135	135	135
Tension (kg mm^{-2})	0.3	6	12	20	10	20	30	40
Moving speed (mm min^{-1})	5	10	10	10	75	75	75	75
Example 2								
Temperature (°C)	135	115	115	115	140	140	140	140
Tension (kg mm^{-2})	0.3	6	12	20	10	20	30	40
Moving speed (mm min^{-1})	5	10	10	10	75	75	75	75
Example 3								
Temperature (°C)	135	120	120	120	145	145	145	145
Tension (kg mm^{-2})	0.3	6	12	20	10	20	30	40
Moving speed (mm min^{-1})	5	10	10	10	75	75	75	75

drawn UHMW PE films have very high values of crystallinity and c axis orientation in crystals. For example, X_c values were found to be 0.875 by Miyasaka *et al.*[11] and 0.92 by Matsuo *et al.*[9]. Now, assuming $f_c = 1$, $f_a = 1$ and $X_c = 0.90$, the right-hand side of equation (1) $\{\Delta_c^\circ X_c f_c + \Delta_a^\circ(1 - X_c)f_a\}$ is calculated to be 0.0647 from Wedgewood's values, and 0.072 from Fukui's values respectively. As f_a is actually less than unity, these values do not reach the measured value, 0.072. We often obtained values between 0.070 and 0.076 in preliminary experiments. Further, f_a is represented as follows, provided that $\Delta_f = 0$ in equation (1):

$$f_a = (\Delta_t - \Delta_c^\circ X_c f_c)/\Delta_a^\circ(1 - X_c) \quad (2)$$

where f_c is almost unity and Δ_t is 0.072.

If Wedgewood's values of 0.0585 and 0.12 are substituted in equation (2), f_a is calculated to be 1.67 at $X_c = 0.90$. In the case of Fukui's values of 0.057 and 0.210, f_a becomes unity. In other words, equation (2) should not fold at $X_c > 0.78$ for the former and at $X_c > 0.90$ for the latter. We believe that the Δ_c° value should at least be re-evaluated.

The relationship between draw ratio and birefringence is shown in *Figure 5*. It is clear that the relation is linear in the draw ratio range from 50 to 170. In the cases of coextrusion[33] and drawing in hot water studied by us or by Furuhata *et al.*[11] for UHMW PE single crystal mats, the birefringence increases rapidly up to a draw ratio of about 50 and then levels off in the range up to 0.062, as shown in *Figure 5*. This observation suggests that the zone annealing method has a particular drawing behaviour which differs from other drawing techniques.

Figure 6 shows changes in part of the i.r. spectrum with zone drawing and zone annealing. Although three *gauche* bands in the i.r. spectrum of the original mat can be seen at 1303, 1350 and 1359 cm^{-1}, these bands almost disappear on zone drawing only once. They are not detected at all in the spectrum of ZA-4 film. As the bands belong to the amorphous region and have been assigned to *gtg* (1303 cm^{-1}), *gg* (1353 cm^{-1}) and *gtg* or *gttg*

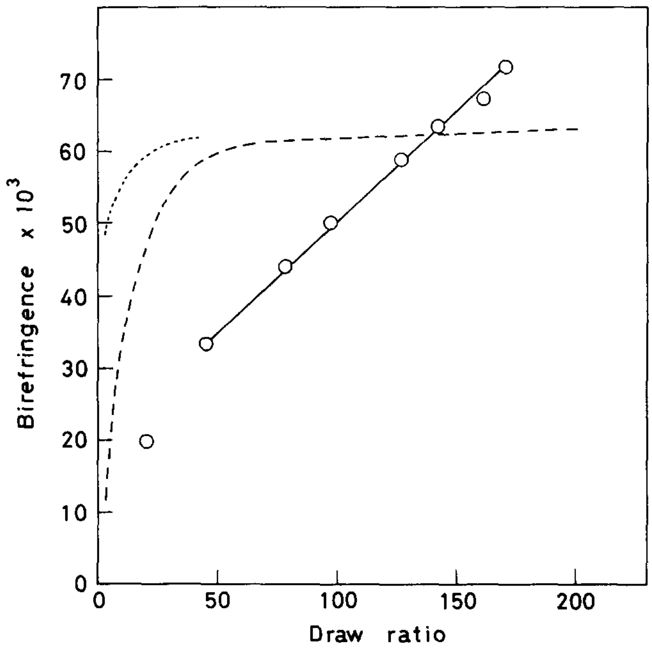

Figure 5 Relationship between draw ratio and birefringence for zone-drawing (○), drawing in hot water (---) and coextrusion (···)

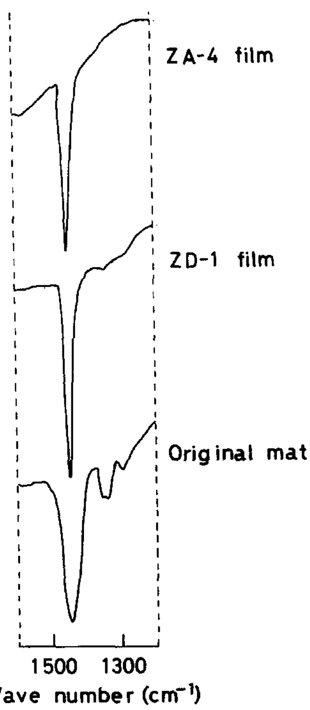

Figure 6 Change in portion of i.r. spectrum with zone drawing and zone annealing

(1359 cm^{-1}) respectively[34], the disappearance of the bands suggests an increase in crystallinity or *trans* conformation of the molecular chains.

The rapid increases in crystallinity and crystal orientation with ZD-1 are also evidenced by the wide-angle X-ray photographs. *Figure 7* shows the through and edge views of a ZD-1 film. It is clear that they differ from each other in the number and intensity of the X-ray diffraction arcs. In order to clarify this difference, two equatorial X-ray diffraction patterns were taken with an X-ray diffractometer. As seen in *Figure 8*, the (2 0 0) and (2 2 0) diffraction peaks are remarkably high in the edge pattern compared with the through pattern, whereas the (0 2 0) peak is weak. This means that the b axis is almost perfectly oriented parallel to the film's surface. Although such phenomena have been already reported by others[11,28,35], uniaxial planar crystal orientation or double orientation appears more strongly and at lower draw ratios on zone drawing. *Table 2* shows the changes in thickness and width on zone drawing and zone annealing. After ZD-1, both dimensions, particularly the thickness, are rapidly decreased. This seems to be due to an effective unfolding of the lamellae. After ZD-1, the thickness is further decreased by subsequent processing. Since the width remains constant, double orientation is more enhanced. If a wider film is drawn or a narrower heater is used, double orientation becomes more prominent. This tendency has so far been observed on drawing of poly(ethylene terephthalate) films[20] and nylon 6 films[36].

Mechanical properties

Figure 9 shows the temperature dependences of dynamic modulus for the zone-drawn films and zone-annealed films. The dynamic modulus E' increased step by step with the processing. The ZA-4 film had a modulus of 222 GPa at room temperature. The broken line shown in *Figure 9* is the example which showed the highest modulus with a dynamic modulus at room temperature of 232 GPa. In general, when the modulus at room temperature is high, the modulus at elevated temperature is also high. For example, the modulus of the ZA-4 film stated at 127 GPa, even at 100°C. The relation of dynamic modulus at room temperature to draw ratio and birefringence is shown in *Figure 10*. This linear relation indicates that the draw ratio steadily increased the molecular orientation, and consequently increased the modulus step by step. It may be said that each step in the processing played more or less the expected role. Such a linear relation between modulus and birefringence for ultra-high strength UHMW PE films has not so far been reported in the literature.

The tensile properties were also measured. For the ZA-4 film, tensile modulus, strength and elongation at break were 180–221 GPa, 3.5–6 GPa and 2.9–4 %, respectively. These data were very scattered. The break of the ultra-drawn films often began with fibril generation on a side or surface of the film, and then propagated momentarily. The stress concentrations occur at weak points and a variety of defects, and deformations or breaks take place at the points. Therefore, the reproducibility and reliability of these data are fairly low compared with the data for dynamic viscoelasticity.

Figure 11 shows the temperature dependence of the loss modulus E'' for the zone-drawn films and zone-annealed films. In the case of ZD-1 and ZD-2 films, a broad dispersion peak occurred in the vicinity of 75°C. The peak increased in height with processing. After ZD-3, a new dispersion peak appeared at about 110°C and grew with repeating ZA. These two peaks overlap each other and form a complicated feature. However, it is clear that the secondary peak is more strongly affected by the treatments than the primary peak. According to Takayanagi *et al.*[37,38], the primary peak is attributed to crystalline dispersion (α_c) which is related to frictional viscosity between the (2 0 0) planes in crystallites. But the

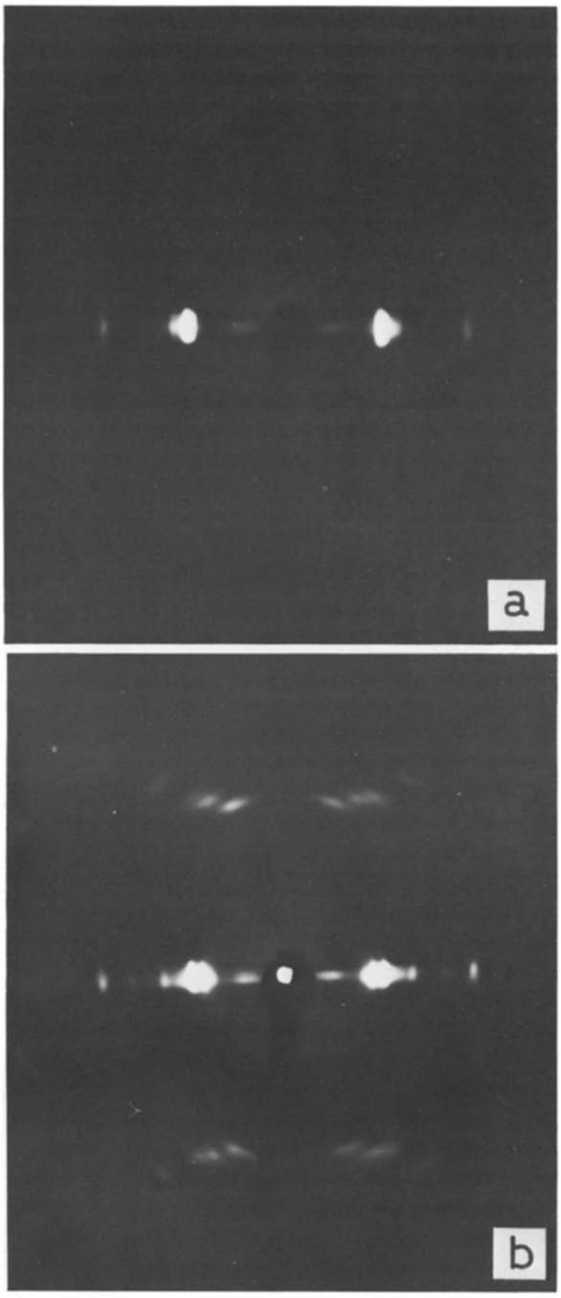

Figure 7 Wide-angle X-ray photographs of ZD-1 film; (a) through view; (b) edge view

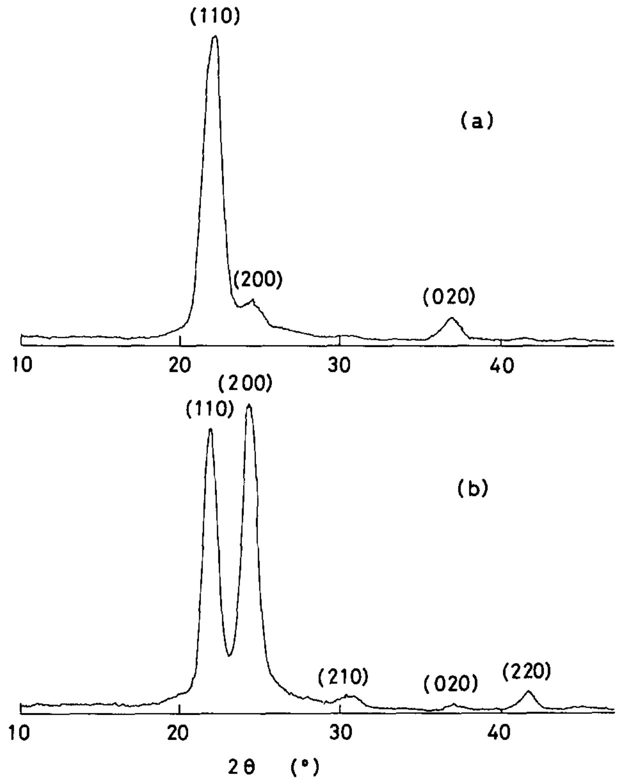

Figure 8 Equatorial X-ray diffraction patterns of ZD-1 film; (a) through pattern; (b) edge pattern

Table 2 Change in dimension of the film with zone drawing and zone annealing

	Original mat	ZD-1	ZD-2	ZD-3	ZD-4	ZA-1	ZA-2	ZA-3	ZA-4
Thickness (μm)	170	12	11	8	5	5	5	4	3
Width (mm)	2	1.1	1.0	1.0	1.0	1.0	1.0	1.0	0.9

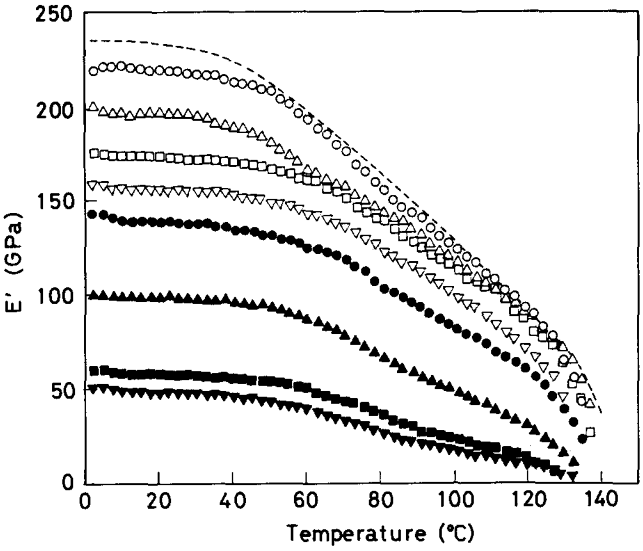

Figure 9 Temperature dependence of the dynamic modulus *E'* for the zone drawn and zone annealed films; ▼, ZD-1; ■, ZD-2; ▲, ZD-3; ●, ZD-4; ▽, ZA-1; □, ZA-2; △, ZA-3; ○, ZA-4; ----, data obtained for maximum *E'*

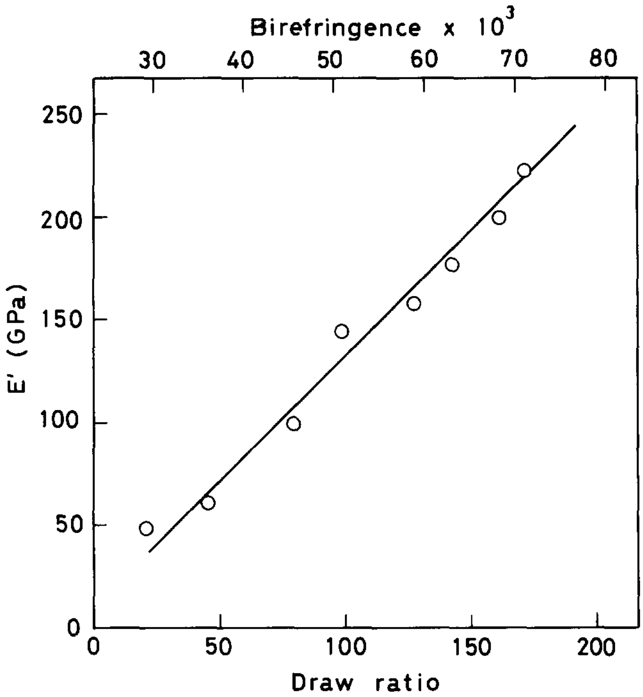

Figure 10 Relationship between dynamic modulus and draw ratio or birefringence

secondary peak has not previously been reported. Compared with the α_c peak of the normal molecular weight PE fibre reported by us[25], the primary peak in this study appeared at a higher temperature by 20°C and is markedly higher in intensity by 10 to 25 times. This indicates that the interplane slip in the crystals is significantly suppressed in the ultradrawn UHMW PE films.

On the other hand, the origin of the secondary peak is not yet clear. At present, on the basis of d.s.c. data and X-ray diffraction patterns we suggest that the peak could be related to another crystal form generated by zone annealing. This will be discussed further in a future report.

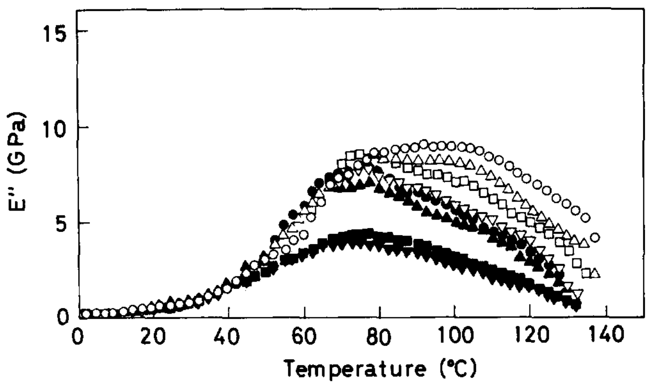

Figure 11 Temperature dependence of the loss modulus *E''* for zone drawn and zone annealed films: ▼, ZD-1; ■, ZD-2; ▲, ZD-3; ●, ZD-4; ▽, ZA-1; □, ZA-2; △, ZA-3; ○, ZA-4

CONCLUSIONS

(1) UHMW PE single crystal mats were effectively converted into PE fibres with very high chain orientation and crystallinity by the multi-step zone annealing method.

(2) The relationship between draw ratio and birefringence gave an essentially straight line.

(3) The mat was zone drawn mainly through a decrease in thickness. The zone-drawn and zone-annealed films showed very sharp double orientation.

(4) The maximum dynamic modulus and tensile strength at room temperature reached 232 GPa and 6 GPa, respectively.

(5) Dynamic modulus at room temperature was increased linearly with increasing draw ratio and birefringence over the range of examination.

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REFERENCES

1 Pennings, A. J., Zwijnenburg, A. and Lageveen, R. *Kolloid Z. Polym.* 1973, **251**, 500
2 Zwijnenburg, A. and Pennings, A. J. *Colloid Polym. Sci.* 1976, **254**, 864
3 Smith, P., Lemstra, P. J., Kalb, B. and Pennings, A. J. *Polym. Bull.* 1979, **1**, 733
4 Kalb, B. and Pennings, A. J. *J. Mater. Sci.* 1980, **15**, 2584
5 Barham, P. J. *Polymer* 1982, **23**, 1112
6 Cannon, C. G. *Polymer* 1982, **23**, 1123
7 Smith, P. and Lemstra, P. J. *J. Mater. Sci.* 1980, **15**, 505
8 Smith, P. and Lemstra, P. J. *Colloid Polym. Sci.* 1980, **258**, 891
9 Matsuo, M., Inoue, K. and Abumiya, N. *Sen-i Gakkaishi* 1984, **40**, T-275
10 Furuhata, K., Yokokawa, T. and Miyasaka, K. *J. Polym. Sci., Polym. Phys. Edn* 1984, **22**, 133
11 Furuhata, K., Yokokawa, T., Seoul, C., Takeda, M. and Miyasaka, K. *J. Polym. Sci., Polym. Phys. Edn* 1986, **24**, 59
12 Kanamoto, T., Tsuruta, A., Tanaka, M. and Porter, R. S. *Polym. J.* 1983, **15**, 327
13 Kanamoto, T., Tsuruta, A., Tanaka, T. and Takeda, M. *Polym. J.* 1984, **16**, 75

14 Kunugi, T., Suzuki, A., Akiyama, I. and Hashimoto, M. *Polym. Prepr., Am. Chem. Soc.* 1979, **20**, 778
15 Kunugi, T., Suzuki, A. and Hashimoto, M. *J. Appl. Polym. Sci.* 1981, **26**, 213
16 Kunugi, T., Suzuki, A. and Hashimoto, M. *J. Appl. Polym. Sci.* 1981, **26**, 1951
17 Kunugi, T. 'New Materials and New Processes', The US Office of ECS of Japan, 1981, Vol. 1, p. 58
18 Kunugi, T. *Sen-i Gakkaishi* 1980, **36**, P-411
19 Kunugi, T. *Chem. Ind. (Japan)* 1981, **32**, 289
20 Kunugi, T., Ichinose, C. and Suzuki, A. *J. Appl. Polym. Sci.* 1986, **31**, 429
21 Kunugi, T., Akiyama, I. and Hashimoto, M. *Polymer* 1982, **23**, 1193
22 Kunugi, T., Akiyama, I. and Hashimoto, M. *Polymer* 1982, **23**, 1199
23 Kunugi, T., Ikuta, T., Hashimoto, M. and Matsuzaki, K. *Polymer* 1982, **23**, 1983
24 Kunugi, T. *Polym. Commun.* 1982, **23**, 176
25 Kunugi, T., Aoki, I. and Hashimoto, M. *Kobunshi Ronbunsyu* 1981, **38**, 301
26 Kunugi, T., Ito, T., Hashimoto, M. and Ooishi, M. *J. Appl. Polym. Sci.* 1983, **28**, 179
27 Kunugi, T., Mizushima, A. and Hayakawa, T. *Polym. Commun.* 1986, **27**, 175
28 Smith, P., Lemstra, P. J., Pijpers, J. P. L. and Kiel, A. M. *Colloid Polym. Sci.* 1981, **259**, 1070
29 Matsuo, M. and Manley, St John *Macromolecules* 1982, **15**, 985
30 Stein, R. S. and Norris, F. H. *J. Polym. Sci.* 1956, **21**, 381
31 Desper, C. R., Southern, J. H., Ulrich, R. D. and Porter, R. S. *J. Appl. Phys.* 1970, **41**, 4284; Wedgewood, A. R. and Seferis, J. C. *Polym. Eng. Sci.* 1984, **24**, 328
32 Fukui, Y., Asada, T. and Onogi, S. *Polym. J.* 1972, **3**, 100
33 Kanamoto, T., Sherman, E. S. and Porter, R. S. *Polym. J.* 1979, **11**, 497
34 Wedgewood, A. R. and Seferis, J. C. *Pure Appl. Chem.* 1983, **55**, 873
35 Ishikawa, K., Miyasaka, K. and Maeda, M. *J. Polym. Sci. (A-2)* 1969, **7**, 2029
36 Kunugi, T., unpublished results
37 Takayanagi, M., Aramaki, T., Yoshino, M. and Hoashi, K. *J. Polym. Sci.* 1960, **46**, 531
38 Takayanagi, M. *Kogyo Kagaku Zasshi* 1960, **63**, 1492