Preparation of high modulus and high strength PEEK film by the zone drawing/annealing method

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In order to prepare poly(ether ether ketone) films with high modulus and high strength, the zone drawing/annealing method was used. The maximum dynamic modulus at room temperature was 13.3 GPa, which is 4.4 times that of a commercially available PEEK film. The modulus also remained at a high level even at elevated temperatures. For example, these were 12 GPa at 100°C, 7 GPa at 200°C, and 5 GPa at 300°C. The zone drawn/zone annealed films indicated a double orientation. The present paper discusses the characteristic of the zone drawing/annealing method, the determination of suitable conditions for zone drawing and zone annealing, and the changes in superstructure and mechanical properties with processing.

(Keywords: zone drawing/zone annealing method; high modulus and high strength PEEK film; double orientation; dynamic viscoelasticity; tensile properties)

INTRODUCTION

Poly(ether ether ketone), PEEK, is an outstanding thermoplastic with useful properties including particularly excellent resistance to heat, chemicals and radiation. Recently the applications of PEEK have been developed as a high temperature fibre or film as well as a super-engineering plastic. PEEK has a high melting point of 336°C, but its melt is fairly stable. Thus T die extrusion or melt spinning can be applied for producing films or fibres. The as-extruded films or as-spun fibres are subsequently drawn and annealed in order to provide desirable properties in a variety of applications.

To date many drawing techniques have been attempted for PEEK. These include, drawing in an oven[1,2] or hood[3], drawing in a poly(ethylene glycol) bath[3], drawing in contact with a hot-plate[3,4] or roll[5], die drawing[6], solid-state extrusion[7] and others[8].

We proposed[9] the zone annealing method in 1979, and since then have applied the method to various crystalline polymers, such as nylon 6[10-12], poly(ethylene terephthalate)[13-15], it-polypropylene[16] and polyethylene[17,18]. The method was very useful for producing high modulus and high strength films or fibres, provided the conditions for drawing and annealing were suitable. In a previous paper[19], we briefly reported that the method was also useful for PEEK film. The purpose of the present paper is to present the results in detail and some additional results.

EXPERIMENTAL

Material

The original material used in the present study was an amorphous unstretched PEEK film of about 110 μm in thickness, supplied by Mitsui Toatsu Chemical Co. Ltd. The film has a density of 1.26 g cm^{-3} and a birefringence of 17.5×10^{-3}. The glass transition temperature and melting point are 143°C and 336°C, respectively.

Zone drawing and zone annealing

Figure 1 shows a photograph of the apparatus used in this study. The original film was cut into strips 2 mm in width and about 280 mm in length. The strip was set in an upper holder and a tension was applied to the lower end of the strip by weighting. The strip was then passed through a narrow heater controlled at a suitable temperature. The narrow heater is attached on the crosshead of a tensile tester. Therefore, the heater may be moved up or down at a selected speed.

The zone annealing method is divided into two steps; zone drawing and zone annealing. The former is intended for stretching and aligning molecular chains, and the latter for forming extended chain crystals. In this study, a multi-step technique was adopted, namely, zone drawing (ZD) and zone annealing (ZA) which were repeated three and four times, respectively.

Measurements

The birefringence was measured with a typical polarizing microscope equipped with Berek compensator. The density was measured at 25°C by a flotation method using toluene–carbon tetrachloride mixtures. The crystallinity (X_c) was calculated from the density (d) by the following equation using a crystal density (d_c) (ref. 2) of 1.378 and an amorphous region density (d_a) (ref. 2) of 1.264 g cm^{-3}.

$$X_c = \{d_c(d-d_a)/d(d_c-d_a)\} \times 100$$

The dynamic viscoelasticity, i.e., dynamic modulus E', loss modulus E'' and $\tan\delta$, were measured at 110 Hz at a heating rate of 5.7°C min^{-1} from room temperature to 300°C with a viscoelastmeter, Vibron DDV-II (Orientec

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Co. Ltd). The tensile tests were carried out at 23–25°C and relative humidity 65% on the films of about 30 mm in gauge length at a crosshead speed of 10 mm min^{-1} using a Tensilon II tensile tester (Orientec Co. Ltd). Tensile modulus, strength and elongation at break were evaluated from stress–strain curves.

Further, wide angle X-ray photographs were taken in both directions perpendicular and parallel to the film surface. X-ray diffraction patterns also were taken in the above two directions using a fibre sample holder. D.s.c. curves were obtained at a heating rate of 10°C min^{-1} in air. The changes in dimension on heating were measured in a silicon oil bath and during the measurements of dynamic viscoelasticity.

RESULTS AND DISCUSSION

Characteristics and advantages of the zone annealing method

Zone drawing and zone annealing possess the following characteristics and advantages. Because films or fibres are heated only in a narrow zone for a short time on zone drawing or zone annealing, thermal degradation can be prevented. It is an important advantage of this method in the application to polymers having a high glass transition temperature or a high crystallization temperature, such as PEEK and Polyimide. The films or fibres always enter the heating zone first. Therefore, undesirable heat effects before drawing, such as thickening of lamellae, hardening and crystallization, can be prevented. This can be easily understood by comparing with drawing in an oven or in a hot-oil bath. Because the heating zone is very narrow, heat energy required to draw or anneal can be saved, especially in the case of high temperature polymers.

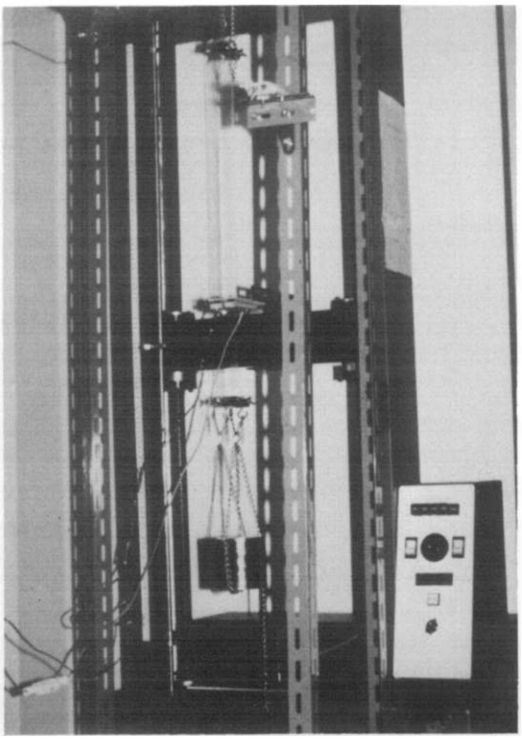

Figure 1 Photograph of the apparatus used for zone drawing and zone annealing

Determination of conditions for zone drawing and zone annealing

In this study, the four routes shown in *Table 1* were attempted. Then the most suitable route was decided on the basis of results of measurements on molecular orientation, crystallinity and mechanical properties. In routes 1 and 2, zone drawing was carried out at 140°C, whereas in routes 3 and 4 it was carried out at 170°C. These temperatures, 140 and 170°C, are near the glass transition temperature (143°C) and the crystallization temperature on heating (173°C), respectively. In route 1, zone annealing was repeated at 200°C, 240°C, 260°C, 280°C and 300°C under a constant tension of 12 kg mm^{-2}, successively. In route 2, however, the tension was increased step by step with increasing zone annealing temperature. In routes 3 and 4, the tension was also increased, though the tension values differ from those in route 2.

Fairly large differences in draw ratio, birefringence, crystallinity and mechanical properties were detected among routes. It was found that the tensions on zone annealing were too small in route 1 and were too large in route 4. Because, particularly, the final conditions of route 4, 300°C and 45 kg mm^{-2}, were too severe, the resulting film was whitened. Also the temperature on zone drawing strongly influenced drawability of the original films. In the case of zone drawing at 170°C, the crystallization takes place and impedes the extension and orientation of molecular chains. The generated crystallites may also interfere with the formation of extended chain crystals on the subsequent zone annealing.

As all of the data in the four routes cannot be described here, those of routes 2 and 3 will be compared in the next section, which deals with the changes in superstructure with processing. In conclusion, route 2 was determined as the most suitable route.

Changes in superstructure with zone drawing and zone annealing

Figures 2 and *3* show the changes in draw ratio and birefringence with processing for routes 2 and 3. In the

Table 1 Conditions of zone drawing and zone annealing. Moving speed of the heater: 57 mm min^{-1}

Route	Conditions	ZD-1	ZD-2	ZD-3	ZA-1	ZA-2	ZA-3	ZA-4	ZA-5
1	Temperature (°C)	140	140	140	200	240	260	280	300
	Tension (kg mm^{-2})	1.6	6	9	12	12	12	12	12
2	Temperature (°C)	140	140	140	200	240	260	280	
	Tension (kg mm^{-2})	1.6	6	9	12	14	15	17	
3	Temperature (°C)	170	170	170	200	220	240	260	280
	Tension (kg mm^{-2})	1.6	6	9	12	14	16	18	20
4	Temperature (°C)	170	170	170	200	240	260	280	300
	Tension (kg mm^{-2})	1	7	10	15	25	35	40	45

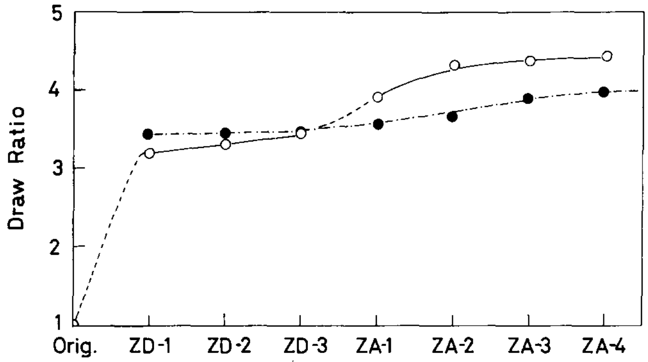

Figure 2 Change in draw ratio with processing: ○, route 2; ●, route 3

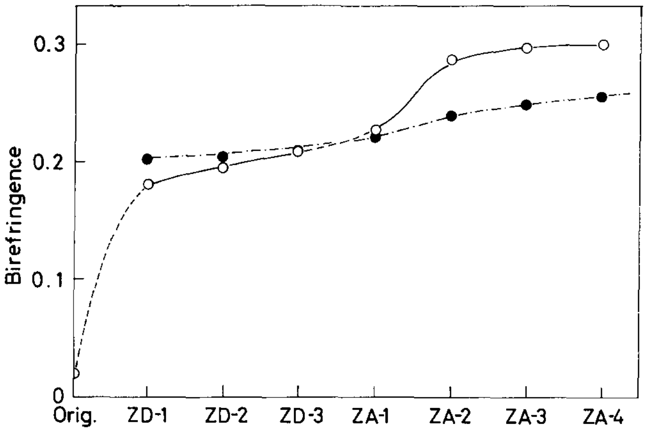

Figure 3 Change in birefringence with processing: ○, route 2; ●, route 3

case of route 2, the draw ratio and birefringence were apparently increased by zone annealing, whereas in route 3 both the draw ratio and the birefringence were increased and became smaller than those of route 2 in the stage of zone annealing. The maximum values were 4.4 for draw ratio and 0.298 for birefringence. These values were achieved at ZA-4 of route 2. The birefringence of 0.298 is close to the intrinsic crystal birefringence of 0.321 reported by Shimizu *et al.*[8]. This fact indicates that the molecular orientation of the ZA-4 film reached a high level.

Figure 4 shows the crystallinity at each stage for routes 2 and 3. The crystallinity of the ZD-1 film of route 3 is 16.7% which is twice that of route 2 (8.2%). This is due to the crystallization which occurred during zone drawing at 170°C. The crystallites generated at ZD-1 rather depress the increases in crystallinity at the following zone drawing (ZD-2 ~ ZD-3) and zone annealing (ZA-1 ~ ZA-5), and gave an increasing curve of crystallinity in routes 3 and 4.

On the other hand, the crystallinity in route 2 increased stepwise between zone drawing and zone annealing. This means that the molecular orientation not accompanied by crystallization promotes effectively the crystallization at zone annealing. However, the maximum value is only 35.1% even in route 2, which is smaller than 40% of a undrawn sample crystallized isothermally at 320°C for 16 h (ref. 20). It can be understood from these experimental facts that PEEK is very difficult to crystallize to a high degree.

Figure 5 shows wide angle X-ray photographs taken in the directions perpendicular and parallel to the film surface for the zone drawn film and zone annealed film. *Figure 6* also shows the equatorial X-ray diffraction patterns of through and edge views for the ZA-4 film. In *Figures 5* and *6*, the difference between the edge view and the through view was found. The peak intensities of (110), (200) and (020) planes differ from each other. In the edge view, the (110) and (020) peaks seen clearly in the through view are weakened, and the (200) peak, in contrast, is strengthened. This indicates the double orientation which is a structural characteristic of zone drawn or zone annealed films. The double orientation has been reported for PET film[16] and PE film[18]. The ZA-4 PEEK film has a high molecular orientation and a phenylene ring orientation nearly parallel to the film surface.

Dynamic viscoelasticity

Figure 7 shows the temperature dependence of dynamic modulus E' for the original film, the zone drawn films and the zone annealed films. The E' increased in order of the processing. The E' values of the finally obtained film, ZA-4, are 13.3 GPa at room temperature, 12 GPa at 100°C, 7 GPa at 200°C, and 5 GPa at 300°C. Although the 13.3 GPa is higher than the E' values in the literature, 2.6–7 GPa, the value is only 21% of the crystal modulus along molecular chains[21], 63 GPa. It seems to be due to the limited crystallization, namely the crystallinity of the ZA-4 film was 35.1% as described above. However, the increment in modulus by this method is significant, for example, the modulus reached 8 GPa by one time zone drawing, ZD-1. Also the zone drawn and zone annealed films have very high moduli at elevated temperatures. The modulus of 5 GPa at 300°C can be expected to be used for high temperature applications.

Figure 8 shows the temperature dependence of tan δ for the original film, ZD-1, ZD-3, ZA-1, and ZA-4 films. A dispersion peak is seen in the figure. From the peak temperature, the peak is considered to be the α dispersion. With the processing, the peak decreased in intensity and shifted to higher temperature. Although the peak for the original film was not measurable, the α dispersion peak shifted from 160°C for the ZD-1 film to 175°C for the ZA-4 film. From the results, it is found that the movement of amorphous chains is gradually inhibited by zone drawing and zone annealing. The judgement of mobility

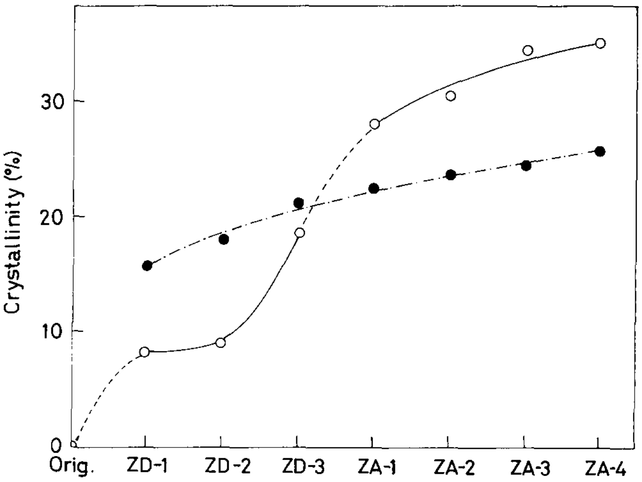

Figure 4 Change in crystallinity with processing: ○, route 2; ●, route 3

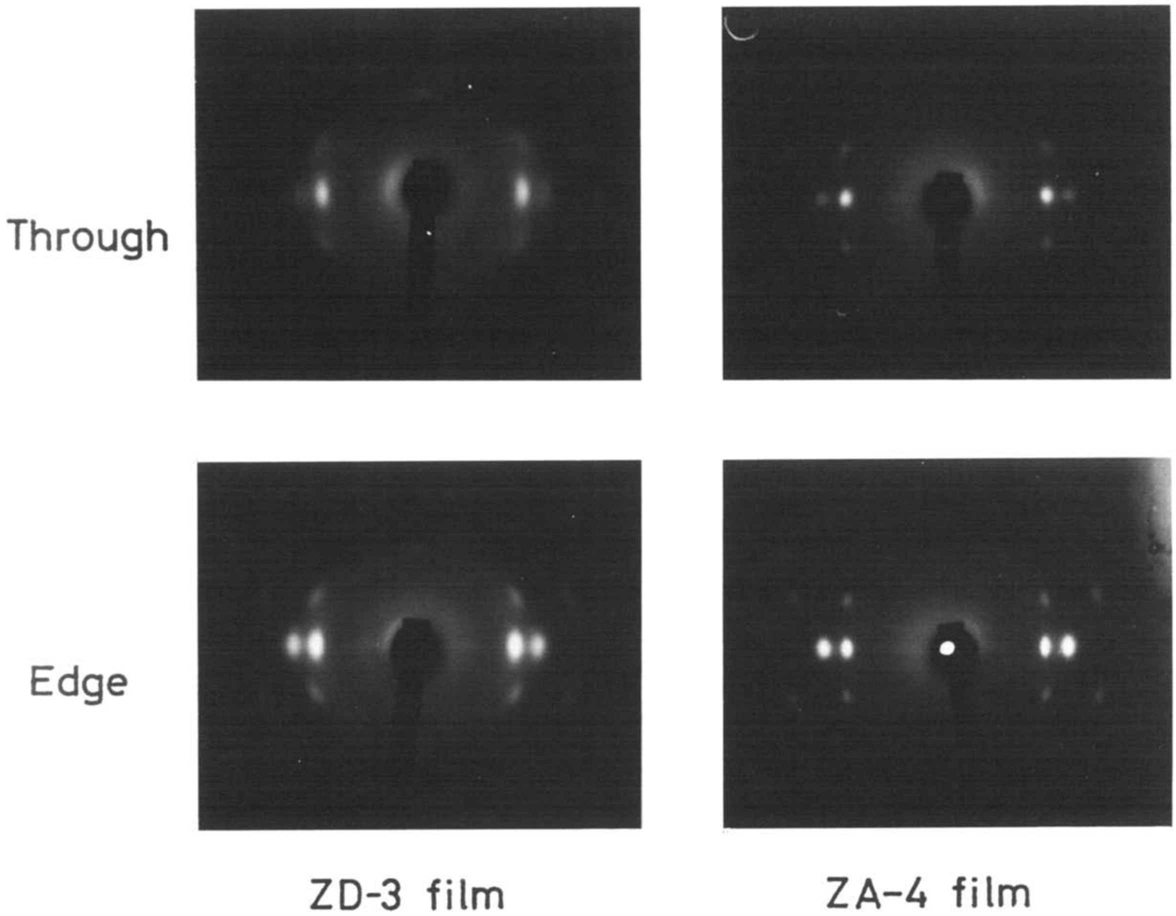

Figure 5 Wide-angle X-ray photographs in through and edge views for the zone drawn (ZD-3) film and the zone annealed (ZA-4) film

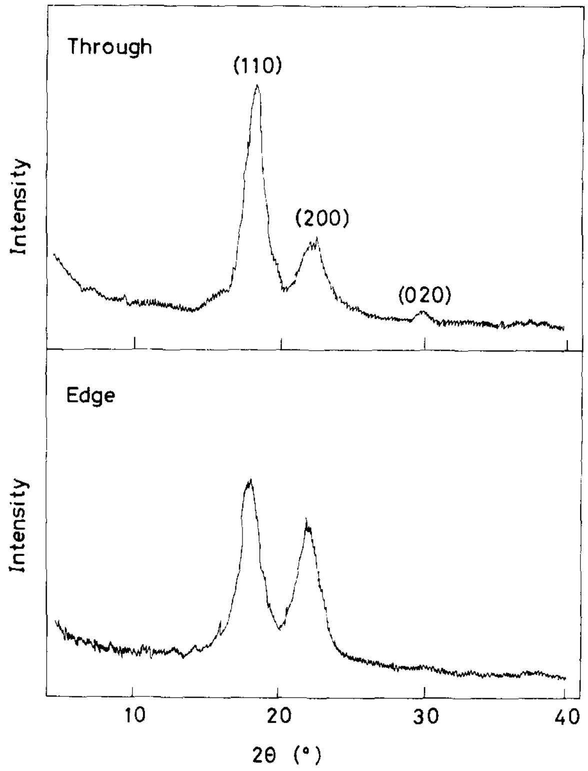

Figure 6 Anisotropy of X-ray equatorial diffraction pattern in each step film

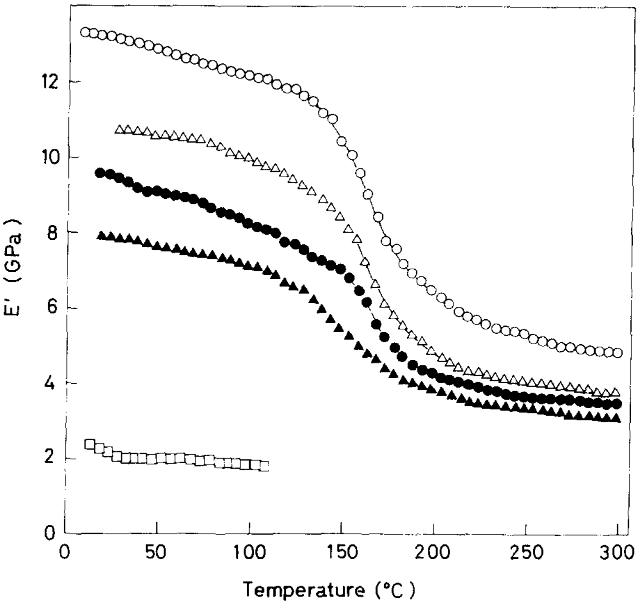

Figure 7 Temperature dependence of the dynamic modulus E' for the original film, the zone drawn films and the zone annealed films: □, original film; ▲, ZD-1; ●, ZD-3; △, ZA-1; ○, ZA-4

of molecular chains with a variety of segmental sizes by the dynamic viscoelastic measurements is superior to that by d.s.c. measurements. The intensity and temperature position of a mechanical dispersion peak reflect sensitively the changes in superstructure.

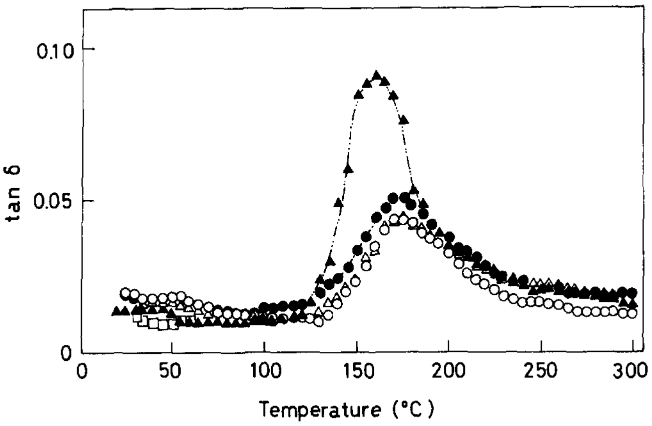

Figure 8 Temperature dependence of the tangent δ ($\tan\delta$) for the original film, the zone drawn films and the zone annealed films: □, original film; ▲, ZD-1; ●, ZD-3; △, ZA-1; ○, ZA-4

Table 2 Mechanical properties of the various samples

Sample	Young's modulus (GPa)	Strength at break (GPa)	Elongation at break (%)
Original	2.39	–	–
ZD-1	5.42	0.32	17.5
ZD-2	8.52	0.52	15.0
ZD-3	10.16	0.82	14.3
ZA-1	10.72	0.85	13.3
ZA-2	11.50	0.88	11.0
ZA-3	11.69	0.89	10.8
ZA-4	11.78	1.17	13.0

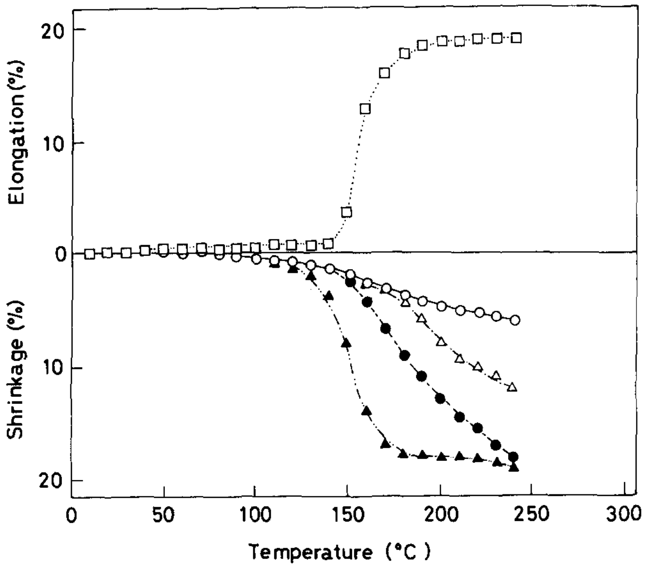

Figure 9 Dimensional change with increasing temperature in a silicon oil bath for the original film, the zone drawn films and the zone annealed films: □, original film; ▲, ZD:1; ●, ZD-3; △, ZA-1; ○, ZA-4

Tensile properties

Table 2 shows the changes in Young's modulus, tensile strength and elongation at break with the processing. Although the absolute values of Young's modulus did not agree with the E' values at room temperature in each stage, Young's modulus was increased step by step with zone drawing and zone annealing. The tensile strength also gradually increased and finally reached 1.17 GPa. Such a high value has not appeared in the literature so far. The elongation at break of 13%, however, is relatively high.

Dimensional stability

Figure 9 indicates the dimension changes with increasing temperature in a silicon oil bath. The elongation or shrinkage of the films had begun in the vicinity of the glass transition temperature, 120–150°C, on heating in the silicon oil bath. The original film elongated rapidly in the temperature range from 140 to 190°C up to 19% with whitening. On the contrary, the ZD-1 film shrank up to 18.5% in the same temperature range. The extent of shrinkage decreased remarkably with processing. In the case of the ZA-4 film, the shrinkage became somewhat smaller, for example, 6% even at 250°C.

In *Figure 10*, the changes in the sample length on measuring the dynamic viscoelasticity are indicated. As the dynamic viscoelasticity is measured under stretching, the samples are generally elongated. The original film was elongated as soon as the measurement began, because the structure was loose. However, the zone drawn films were elongated above 140°C, and the magnitude of elongation was decreased as the processing proceeded. For the zone annealed films, the changes in length became significantly small and could not be observed in the ZA-4 film. It is supposed that such a high dimensional stability of the ZA film results from high molecular orientation and high crystallinity.

CONCLUSIONS

It was found that the zone annealing method was useful to improve the mechanical properties of PEEK films. The maximum dynamic modulus at room temperature was 13.3 GPa. Young's modulus of 11.8 GPa and a tensile strength of 1.17 GPa had been reached.

The zone drawn and zone annealed film shows a very high modulus at elevated temperatures, i.e., 12 GPa at 100°C, 7 GPa at 200°C or 5 GPa at 300°C.

The zone drawn and zone annealed film has a high birefringence of 0.298 which is close to the intrinsic birefringence of 0.321. However, the crystallinity was only 35.1%.

The double orientation clearly appeared in the zone

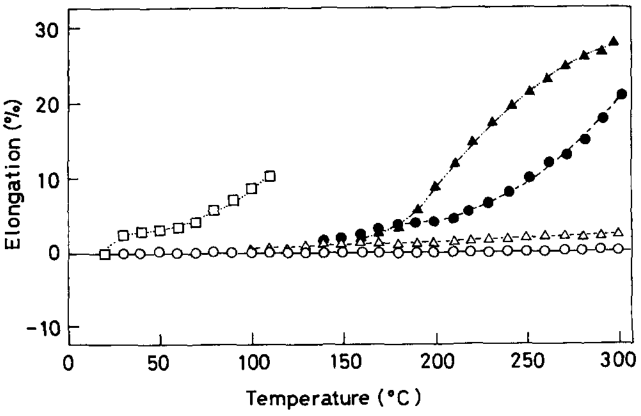

Figure 10 Elongation of the original film, the zone drawn and the zone annealed films during measuring the dynamic viscoelasticity with Vibron II: □, original film; ▲, ZD-1; ●, ZD-3; △, ZA-1; ○, ZA-4

drawn and zone annealed films in the same manner as PET and nylon 6 films.

The dimensional stability has increased with the processing. This is thought to be caused by the increase in crystallinity and the difficulty of movement in the amorphous chains.

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