

Preparation of High-Modulus and High-Strength Poly(ethylene Terephthalate) Film by Zone-Annealing Method

TOSHIO KUNUGI, CHIE ICHINOSE, and AKIHIRO SUZUKI,
*Department of Applied Chemistry, Faculty of Engineering, Yamanashi
University, Takeda-4, Kofu 400, Japan*

Synopsis

The zone-annealing method was attempted to prepare high-modulus and high-strength poly(ethylene terephthalate) (PET) film. The film having Young's modulus of 14.5×10^{10} dyn/cm² and a tensile strength of 86.9 kg/mm² in the drawing direction was obtained. These values correspond to four times those of a biaxial-stretched PET film available commercially. The dynamic viscoelastic properties also were measured. The dynamic storage modulus was 15.4×10^{10} dyn/cm² at room temperature, and a high value of 3.6×10^{10} dyn/cm² even at 200°C. The latter value is slightly higher than the room temperature modulus of the commercially available film. From the intensity and temperature position of α -dispersion E'' peak, it was suggested that the amorphous chains in the zone-annealed film was densely packed in a highly oriented state. Furthermore, the crystallinity, orientation, especially double orientation, and molecular chain conformation of the films in the zone-annealing process are discussed in the present paper.

INTRODUCTION

A novel annealing method termed the "zone-annealing method" was proposed by us¹ in 1979. The method has so far been applied to the preparation of high-modulus and high-strength fibers of semicrystalline polymers, such as poly(ethylene terephthalate)¹⁻⁶, nylon 6,^{1,5,7-10} polyethylene,^{5,11} and polypropylene.¹² The resulting fibers exhibited excellent mechanical properties and dimensional stability at elevated temperatures.

Fortunately, this method can also be applied to the preparation of high-modulus and high-strength films solely by the use of a slit-shaped heater instead of a ring-shaped one in the case of fibers.

The object of the present paper is to report the results obtained in the case of poly(ethylene terephthalate) film. The film obtained has a remarkably high modulus of 14.5×10^{10} dyn/cm² and a high strength of 87 kg/mm², which correspond to about four times those of commercially available biaxially stretched films. Further, the superstructural characteristic of the film was described in this paper.

EXPERIMENTAL

Materials

The original material used in the present study is an unstretched poly(ethylene terephthalate) film produced by T-die extrusion method, sup-

plied by DIA HOIL Co. Ltd. The film has a crystallinity of 1.8%, \overline{M}_w of 5.8×10^4 , and \overline{M}_n of 1.62×10^4 . The thickness of the original film is 60 μm .

Zone Drawing and Zone Annealing

The zone-annealing procedure consists of two steps of zone drawing and zone annealing since it is difficult to directly convert the original unoriented film into a highly oriented and highly crystalline film. Zone drawing is done on the original film in order to fully extend and align the molecular chains, whereas zone annealing is subsequently carried out on the zone-drawn film with the intention of forming extended-chain crystals under high tension. The apparatus employed in this study is the usual tensile tester partially reconstructed. A slit-shaped heater 2 mm wide, 3 mm thick, and 80 mm long was attached to the crosshead, and its temperature was controlled throughout the experimental period.

The upper end of the film 40 mm wide and 300 mm long was fixed, and then the lower was weighted to add suitable tension. The film was zone drawn by moving the slit-shaped heater from the lower part of the film to the upper part. The film was drawn easily, quickly producing necking four times the initial length. Subsequently, the zone-drawn film was zone-annealed at the most suitable temperature for crystallization under high tension. The temperature and tension for zone annealing were much higher than those for zone drawing. The zone annealing was repeated six times by moving up and down three heaters superimposed vertically, as seen in Figure 1. The detailed conditions for zone drawing and zone annealing will be discussed later on.

Measurements

The birefringence was measured with a polarizing microscope equipped with a Berek compensator. In the measurements on the films with high retardation, X-Y quartz planes of various thickness (15 kinds, 0.05–3 mm) which were cut from a single crystal were used as an additional compensator.

The density of the films was measured at 25°C by a flotation method using toluene–carbon tetrachloride mixtures. The crystallinity was calculated from the density by the usual method using a crystal density¹³ of 1.455 and an amorphous region density¹³ of 1.335 g/cm³.

The tensile properties of the films were determined at 23–25°C, RH 65%, with a tensile tester, Tensilon UTM-II, SS-105 (Toyo-Baldwin Co., Ltd.). Young's modulus, the tensile strength, and the elongation at break were estimated from the stress–strain curves. The dynamic viscoelastic properties, dynamic storage modulus E' , loss modulus E'' , and loss tangent $\tan \delta$ were measured at 110 Hz with a dynamic viscoelastometer, Vibron DDV-II (Toyo-Baldwin Co., Ltd.). The measurements were carried out in two temperature ranges; one from room temperature to 220°C, and the other from room temperature to –130°C. The higher temperature measurements were performed at a heating rate of 3.6°C/min in a stream of nitrogen gas, while the lower temperature measurements were done at a cooling rate of

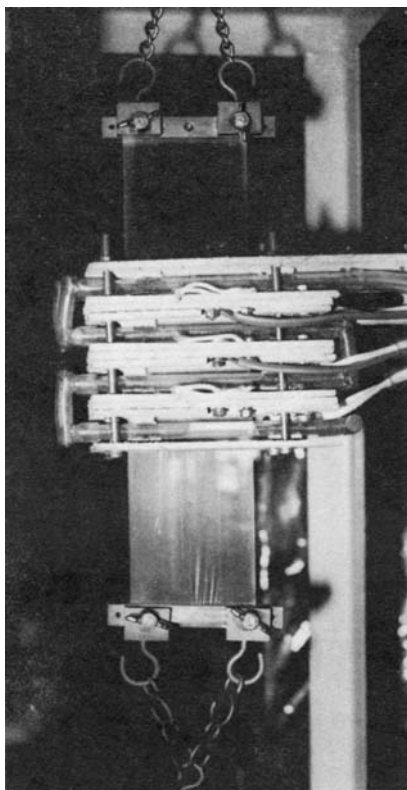


Fig. 1. Photograph of the apparatus for zone-annealing method.

2°C/min in a stream of dry air cooled with liquid nitrogen. Further, IR spectra, DSC curves, and X-ray Laue photographs were also taken.

RESULTS AND DISCUSSION

Application and Advantages of the Zone-Annealing Method

The characteristic of the zone-annealing method is that the drawing and annealing processes are achieved by shifting a narrow heating zone at a constant speed producing a suitable tension in the sample.

Figure 2 shows a comparison of the mode of deformation on zone drawing with one on hot drawing in an oven on a laboratory scale. Zone drawing can produce a drawn film with a much more homogeneous structure and a constant width, compared with conventional hot drawing in an oven. Although necking takes place during zone drawing, the decrease in width of the film is small because the heating zone is narrow. The decrease in width further becomes small with broadening of the film and/or decreasing of the vertical width of the heating zone. Deformation of the film is attained mainly in support of decrease in thickness. In this study, the original film sizes of 40 mm in width and 40 μm in thickness were changed to 38 mm and 28 μm with zone-drawing, respectively. It is

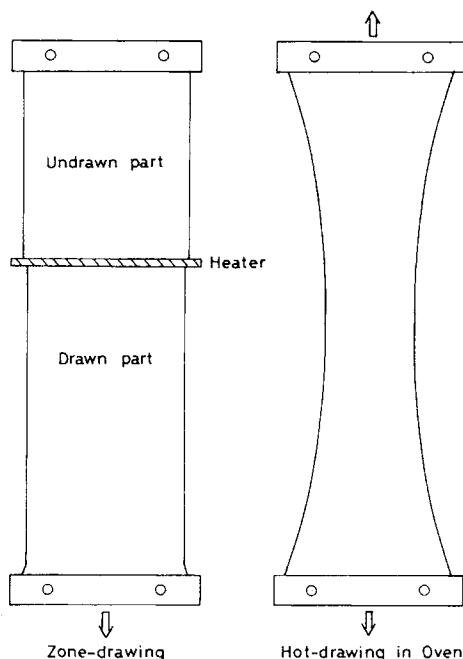


Fig. 2. Comparison of the mode of deformation on zone-drawing with one on hot-drawing in an oven.

clear that the decrease in thickness (30%) is significantly large in contrast to the decrease in width (5%).

On the other hand, this method has the following advantages on a laboratory scale or on an industrial scale. The zone-annealing process does not need a long and large-scale oven as used in the conventional biaxial stretching process, and the film is locally heated only in a narrow linear heating zone. Therefore, the quantity of heat required for drawing and annealing can be decreased remarkably. Also the temperature control and the operation of the apparatus are very easy. This method, furthermore, shows superior effects in drawing and annealing, because the applied high tension acts concentrically and effectively on the narrow area softened by heating. Thermal degradation of the film can be prevented because of the short heating time. The generation of numerous crystal nuclei can also be prevented, because the film is not heated over a wide range at the same time.

If necessary, zone drawing and zone annealing can be repeated under the same conditions or varying conditions of temperature and tension. Thereby, the unfolding of lamellae, the extension of molecular chains, and the extended-chain crystallization are further promoted. In this case, the required heaters are fixed with separation by cooling zones and roller systems for generating the desired tension, and then the film is passed continuously through these heaters. Infrared rays, laser beams, and microwaves, as well as electrical resistance, may be used as a heat source.

Determination of Suitable Conditions for Zone Drawing and Zone Annealing

The purpose of zone drawing is to obtain a film with as high an orientation as possible, preventing crystallization. Therefore, the zone-drawing tem-

perature must be selected from temperature above T_g (69°C) and below the cold-crystallization temperature (120°C) of this polymer. After many preliminary experiments, 90°C was determined to be a suitable temperature for zone drawing. The tension applied on the film during zone drawing was selected so that the necking portion was situated in the center of the heater.

As zone annealing was carried out with the intention of pulling out molecular chains from the softened crystallites and forming the extended-chain crystals, the zone-annealing temperature was examined in the range above the cold-crystallization temperature (120°C) and below the melting point (248°C). Consequently, 190–200°C was selected as a suitable zone-annealing temperature. On the other hand, the tension applied on the film during zone annealing is also an important condition for improving the mechanical properties of the film. It is desired to use as high a tension as possible within a range such that the film is not whitened, fibrilized, or severed. 15–16 kg/mm² was the most suitable tension in the range of the examination. The conditions thus obtained are summarized in Table I.

Tensile Properties

Table II shows the tensile properties of the original film, the zone-drawn film, and the zone-annealed film. Although Young's modulus and the tensile strength are still small in the zone-drawing step, these values are increased up to two and three times by zone annealing, respectively. Young's modulus and the tensile strength of the zone-annealed film reach 14.5×10^{10} dyn/cm² and 86.9 kg/mm², respectively, which are about four times larger than those of commercially available biaxial-stretched film, 3.6×10^{10} dyn/cm² and 20–22 kg/mm². Also these values are almost comparable to those of commercial high-tenacity PET fiber, 11.8 – 19.6×10^{10} dyn/cm² and 78–111 kg/mm². Conversely, the elongation at break of the zone-annealed film, 7.4%, is very small compared with 90–120% for the biaxial-stretched film and 7–17% for the high-tenacity fiber. This is closely related to the dimensional stability of the film under stress.

Superstructure

Table III shows the changes in birefringence and crystallinity with zone drawing and zone annealing. The birefringence reached a fairly high level by zone drawing but further increased by zone annealing up to 0.217. Although the value is smaller than that of the zone annealed fiber, 0.247, reported in the previous paper,^{2,3} it can be said that it is very high because the datum was obtained from the film samples.

TABLE I
Conditions for Zone Drawing and Zone Annealing

Conditions	Zone drawing	Zone annealing
Temperature of the heating zone (°C)	90	190–200
Moving speed of the heater (mm/min)	40	20
Tension applied to the film (kg/mm ²)	0.78	15–16
Repetition (times)	1	6

TABLE II
Tensile Properties of Original Film, Zone-Drawn Film, and Zone-Annealed Film

Sample	Young's modulus, $\times 10^{-10}$ dyn/cm ²	Strength at break (kg/mm ²)	Elongation at break (%)
Original film	1.4	—	—
Zone-drawn film	7.0	26.0	23.8
Zone-annealed film	14.5	86.9	7.4

The crystallinity was also increased by zone drawing and zone annealing and finally reached 45.5%. Zone annealing is particularly effective for increasing the crystallinity. Although a detailed description about the effects of temperature, time, and concentration is omitted in this paper, the weight loss of the zone-annealed film by a treatment with mixed solution of amine-water was much smaller than that of the zone-drawn film. Because the amorphous region is selectively dissolved in amine, this indicates the higher crystallinity of the zone-annealed film.

Figure 3 shows X-ray Laue photographs of the zone-drawn film and the zone-annealed film, which were taken in the three directions, through, edge, and end. Although the increases in orientation and crystallinity by zone-annealing are also clear from these photographs, it is more important to note the difference in pattern between the through and edge photographs. The through photographs have strong bright spots of (010) diffraction, whereas the edge photographs have those of the (100) one. This tendency can also be clearly seen in the X-ray diffraction patterns shown in Figure 4. Such anisotropy of the X-ray pattern had already been observed for the fiber which was rolled after uniaxial drawing. This is explained by a double orientation. Namely, in addition to the orientation of molecular chains in the stretching direction, phenylene rings are arranged in parallel with the film surface. This double orientation is enhanced as the width of the film is increased or the thickness is decreased. A film with such an orientation rarely peels off in a thin sheet in a way similar to mica, as seen in Figure 5.

On the other hand, it was found from infrared spectrum data that the *trans* conformation content increased and the *gauche* conformation content decreased rapidly in the order of the original film, the zone-drawn film, and the zone-annealed film. Also the fold-conformation band of 988 cm⁻¹ disappeared with zone drawing but appeared again as a very weak shoulderlike absorption with zone annealing. It can be presumed that the mo-

TABLE III
Birefringence and Crystallinity of Original Film, Zone-Drawn Film,
and Zone-Annealed Film

Sample	Birefringence	Crystallinity (%)
Original film	—	1.8
Zone-drawn film	0.142	21.4
Zone-annealed film	0.217	45.5

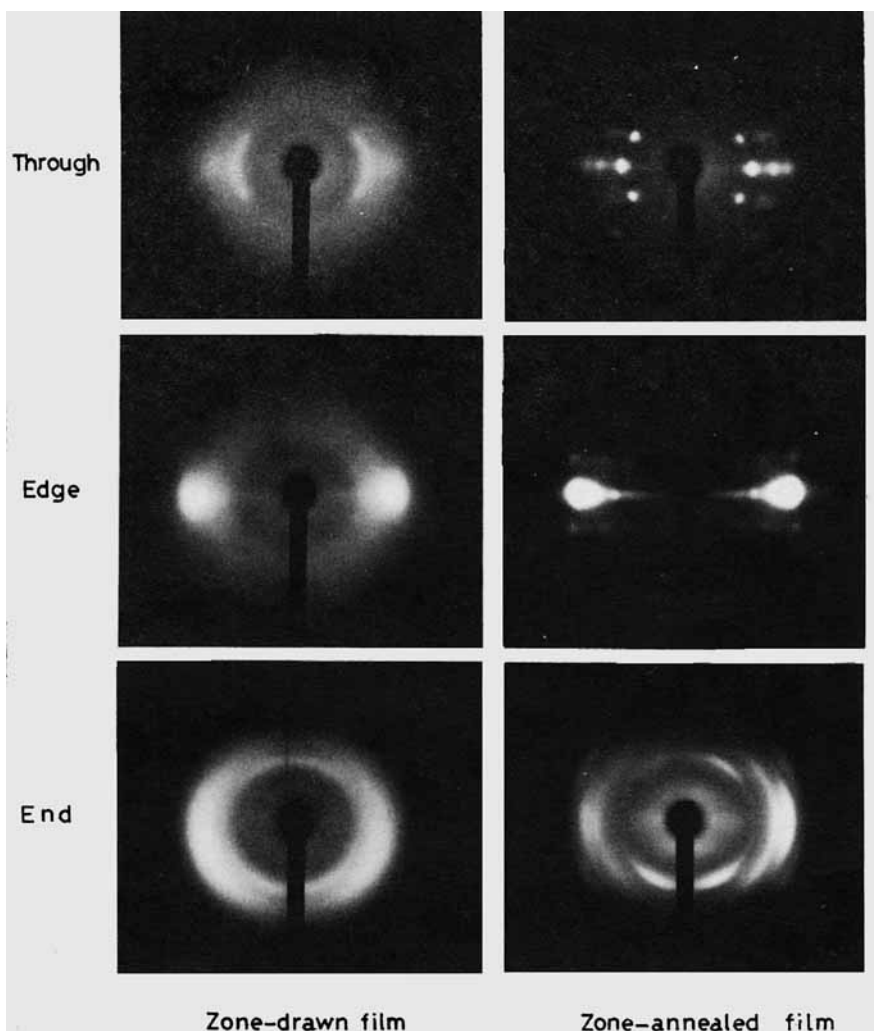


Fig. 3. X-ray Laue photographs of the zone-drawn film and the zone-annealed film.

lecular end chains free from stress fold back and then overgrow upon the extended-chain texture during zone annealing. However, the amount of the folded-chain crystals is considered to be much smaller in comparison with that of the extended-chain crystals.

Dynamic Viscoelasticity and Its Anisotropy

Figure 6 shows the temperature dependence of dynamic storage modulus E' and loss modulus E'' for the zone-drawn films and the zone-annealed films which were cut out in two directions parallel and perpendicular to the stretching direction. In order to avoid complexity, the following abbreviations are used: E'_{\parallel} , E''_{\parallel} , E'_{\perp} , and E''_{\perp} .

Compared with the E'_{\parallel} for the zone-drawn film, the E'_{\parallel} for the zone-annealed film is significantly high over the whole temperature range measured. The E'_{\parallel} value at room temperature is 15.4×10^{10} dyn/cm², which is

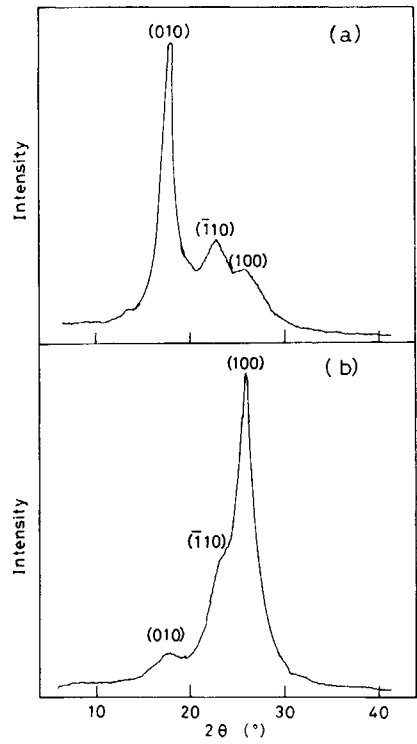


Fig. 4. X-ray diffraction patterns which were obtained in two directions parallel and perpendicular to the film surface.

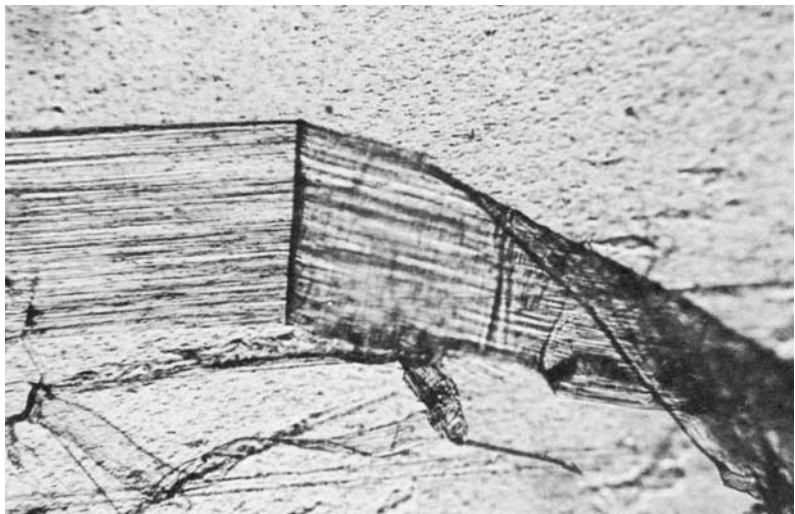


Fig. 5. Peeling in the zone-annealed film.

twice that for the zone-drawn film. In E'' -temperature curves, a distinct dispersion peak occurred at around 100°C. According to Illers and Breuer,¹⁴ this dispersion peak is assigned to α -dispersion of this polymer, which is attributed to micro-Brownian motion of large molecular segments in the amorphous regions. The peak increased in height with zone annealing and further shifted to a higher temperature, from 100 to 120°C.

In the case of the β -dispersion peak which occurred at -56°C , the peak height was increased again by zone annealing, but the peak temperature remained unaltered. The β -dispersion is ascribed to a rotational diffusional movement of the $-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-$ part of the amorphous chains.

Since the height of the E'' dispersion peak is proportional to the quantity of energy dissipated as frictional heat per cycle in a sinusoidal deformation, the increases in height of these peaks indicate increases in intermolecular friction caused by increasing orientation with zone annealing. On the other hand, the temperature position of a dispersion peak may be regarded as a measure of mobility of molecular chains. Therefore, the shift of the α -dispersion peak to a higher temperature indicates that the movements of molecular segments become more difficult in this temperature range, owing to the increases in crystallinity and orientation caused by zone an-

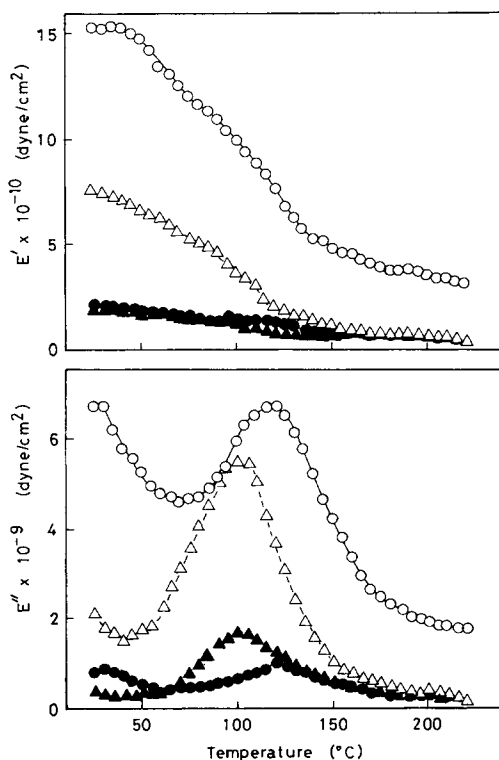


Fig. 6. Temperature dependence of dynamic storage modulus E' and loss modulus E'' in two vertical directions: (O, ●) the zone-annealed films which were cut out parallel and perpendicular to the stretching direction; (△, ▲) the zone-drawn films which were cut out parallel and perpendicular to the stretching direction.

nealing. However, as already reported on nylon 6,¹⁵ the temperature position of the β -dispersion peak was not sensitive to variation in the superstructure, because the movement units were too small. On the basis of the above results, it is suggested that the amorphous chains in the zone-annealed film are densely packed in a highly oriented state and their movements are strongly inhibited by the increased interaction between adjacent molecular chains and by crystallites.

Figure 7 shows a comparison of the E' and E'' anisotropy of the zone-annealed film with those of the biaxial-stretched film. The anisotropy of the latter is very slight, except for the E'' anisotropy appearing in the vicinity of the α -dispersion peak. The E' value at room temperature, $3.4\text{--}3.5 \times 10^{10}$ dyn/cm², decreased gradually with an increase in temperature. The E'' dispersion peak of the biaxial-stretched film appeared at 80°C, which was by far lower than that of the zone-annealed film, 120°C. This indicates that the amorphous chains aggregate relatively loosely in the film and can be diffused easily. On comparing the E' values of both films, the E'_1 at room temperature for the zone-annealed film is about 4.7 times that for the biaxial-stretched film, while the E'_1 is lower and ca. 67%. Above 80°C, how-

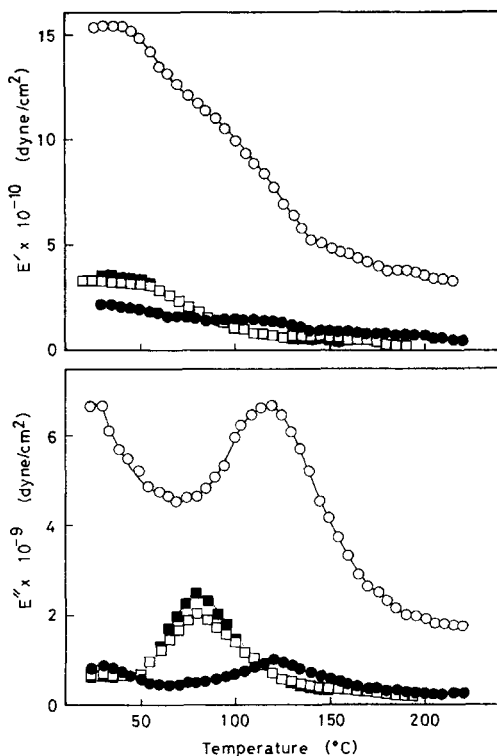


Fig. 7. Temperature dependence of dynamic storage modulus E' and loss modulus E'' in two vertical directions: (○, ●) the zone-annealed films which were cut out parallel and perpendicular to the stretching direction; (□, ■) a biaxial-stretched commercial PET films which were cut out parallel and perpendicular to the machine direction.

ever, the E'_1 for the zone-annealed film became higher than that for the biaxial-stretched film. Furthermore, it should be emphasized that the E'_1 value for the zone-annealed film maintained a high level at elevated temperatures. Even at 200°C, the E'_1 value was almost equal to the E' at room temperature for the biaxial-stretched film. This heat-resistant property is expected for the application to heat-resistant film.

CONCLUSIONS

1. A high-modulus/high-strength poly(ethylene terephthalate) film with Young's modulus of 14.5×10^{10} dyn/cm² and a tensile strength of 86.9 kg/mm² was produced by means of the zone-annealing method.

2. The zone-annealed film has a very high modulus even at elevated temperatures; for example, a dynamic modulus of 3.6×10^{10} dyn/cm² at 200°C. The value is slightly higher than the room temperature modulus of a biaxial-stretched PET film available commercially ($3.4\text{--}3.5 \times 10^{10}$ dyn/cm²).

3. The α -dispersion E'' peak of the zone-annealed film appears at 120°C, which is much higher than that (80°C) for a commercially available film.

4. From the results of orientation, crystallinity, infrared spectra, and dynamic viscoelasticity measurements, it is suggested that the amorphous chains are densely packed in a highly oriented state and their movements are inhibited by numerous crystals, which generated under a high tension during zone annealing.

5. The double orientation was developed with zone drawing and zone annealing: the molecular chains are oriented in the stretching direction, and further the phenylene rings are arranged in parallel with the film surface.

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