Drawing behaviour of polymer blends consisting of poly(ethylene terephthalate) and liquid crystalline copolyester

Michiyuki Amano and Koichi Nakagawa
NTT Electrical Communications Laboratories, Tokai, Ibaraki 319-11, Japan
(Received 7 April 1986; revised 3 July 1986)

The drawing behaviour of rods (2 mm in diameter) of a polymer blend based on poly(ethylene terephthalate) (PET) and a thermotropic liquid crystalline copolyester, poly(ethylene terephthalate-*co*-*p*-oxybenzoate) (PET–POB), was investigated under conventional heating and also under microwave heating. With increasing PET–POB fraction, the modulus increased, while the drawing tension and draw ratio decreased. The microwave heating effect was found to be minimal. Sonic modulus, X-ray and birefringence measurements showed that orientation of PET–POB was induced as well as that of PET during drawing. The samples were also assessed by dynamic mechanical analysis, differential scanning calorimetry and scanning electron microscopy.

(Keywords: poly(ethylene terephthalate); liquid crystalline copolyester; polymer blend; drawing; microwave heating)

INTRODUCTION

Recently, polymers with high mechanical performance have been extensively studied. The approaches employed in these studies included both mechanical processing of flexible polymers[1–4] and the preparation of rigid polymers exhibiting liquid crystalline order[5–7]. As for poly(ethylene terephthalate) (PET), several types of mechanical processing, e.g. zone annealing[8], solid-state extrusion[9], crystalline mat drawing[10] and microwave heat drawing[11], have been applied in order to obtain high modulus and high strength. However, the reported PET modulus values are less than 25% of its crystalline modulus (108 GPa)[12].

Jackson *et al.* prepared a copolyester in which rigid polyoxybenzoate (POB) segments were incorporated into a PET chain, and showed that it exhibited a thermotropic liquid crystalline phase[7]. They reported that a copolyester with a POB fraction of 60% was the most desirable because of its mechanical properties. Molecular orientation induced by a shear stress was also studied[13]. Polymer blends based on PET and PET–POB (40 mol% of PET and 60 mol% of POB) were investigated by Joseph *et al.*[14] They showed that the modulus and the crystallinity of the PET phase increased with an increase in the PET–POB fraction. However, an incompatibility between PET and PET–POB was suggested based on observations of the fracture surfaces.

In this study, polymer blends consisting of PET and PET–POB were prepared, and their drawing behaviour under conventional and microwave heating was investigated. A PET–POB containing 50 mol% of POB was used to improve the compatibility between the components. The optimum drawing conditions for the maximum modulus were examined, and the contribution of each component to the properties was assessed by X-ray, birefringence, dynamic mechanical, thermal, and scanning electron microscope measurements.

EXPERIMENTAL

Materials

The materials used were PET (AA-200) purchased from Akzo Co. and PET–POB (50 mol% of POB) supplied by Unitika Co. Rod-shaped samples (2 mm in diameter) were prepared from mixed pellets of PET and PET–POB by extrusion, in which the extrusion temperature and the screw rotation rate were set at 256°C and 7 rpm, respectively. The cylinder size from the extruder was a diameter of 40 mm and length of 1 m. Extrudates were cooled in a water bath immediately after extrusion. The PET–POB fractions were 10 wt%, 30 wt% and 50 wt%, referred to as LC-10, LC-30 and LC-50, respectively. The extrusion rate of LC-10, LC-30 and LC-50 were 11.6 m min^{-1}, 12.9 m min^{-1} and 13.5 m min^{-1}, respectively.

Drawing

The drawing apparatus is shown in *Figure 1*. The rod was fed into a heating oven, connected to the microwave power source (2.45 GHz, 1.5 kW), by the feeder at a speed of 0.05 m min^{-1}. The oven was equipped with electric heaters to control the temperature inside. The rod was continuously drawn by the take-up machine. The drawn samples were cooled at room temperature while applying the drawing tension, which was monitored with a tension meter. Details of the microwave heat-drawing technique are described in previous papers[11,15].

All the samples were drawn in two steps. In the first step, samples were drawn to a draw ratio of 3.8–4.3 at a drawing temperature of 70–100°C. The subsequent

0032-3861/87/020263-06$03.00

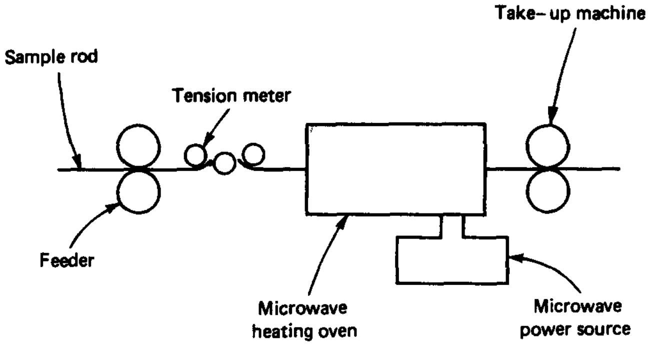

Figure 1 Apparatus used for drawing samples

drawing (ultradrawing) was able to be carried out under higher tensions and temperatures than the first step.

Measurements

The sonic modulus (E_s) was measured at room temperature on a direct-reading pulse propagation viscoelastometer, model DDV-5-B (Toyo-Baldwin Co. Ltd, Japan). The pulse frequency was 10 kHz and the pulse propagation distance was 400 mm. The temperature dependence of the storage modulus (E') and loss modulus (E'') of samples was measured at 3.5 Hz with a Rheovibron DDV-3-EA (Toyo-Baldwin) over the temperature range of – 150°C to 200°C. The heating rate was 3°C min^{-1}. The sample length and the amplitude were 70 mm and $\pm 20\,\mu$m, respectively. The cross-sectional areas of the samples were determined from the weight per unit length, and the densities of the samples were measured by a flotation method using n-hexane–carbon tetrachloride mixtures. Draw ratios were determined from the ratios of the cross-sectional areas before and after drawing. Birefringence (Δn) was determined for sliced specimens from the relative retardation (R) measured with a polarized microscope XTP-11 (Nicon Co. Ltd) using the following equation:

$$\Delta n = R\lambda_0/d \qquad (1)$$

where d and λ_0 are the sample thickness and the wavelength of light in vacuum, respectively. Wide-angle X-ray diffraction (WAXD) patterns were taken using Ni-filtered Cu Kα radiation (35 kV, 25 mA). The melting behaviour was examined using a Perkin–Elmer differential scanning calorimeter, DSC-2, at a heating rate of 10°C min^{-1}. The sample weight was about 30–50 mg. The temperature and the heat of fusion were calibrated with indium and tin. The cross sections of the samples, which were cleaved mechanically, were examined with a scanning electron microscope, EMAX-8700 (Horiba).

RESULTS AND DISCUSSION

Drawing behaviour

Drawing tensions and temperatures were examined for the optimum conditions for the highest modulus. Sonic moduli (E_s) at various drawing temperatures are shown in *Figure 2*. These E_s values were obtained under the optimum tensions at each temperature. There was an optimum drawing temperature for the maximum E_s for each sample. Optimum conditions (drawing tensions, drawing temperatures and draw ratios) and E_s obtained are listed in *Table 1*. The optimum drawing tension and drawing temperature decreased and E_s increased with increase in the PET–POB fraction. However, the optimum draw ratio decreased with increase in the PET–POB fraction. The attainable E_s obtained under the optimum conditions (see *Table 1* and *Figure 3* caption) as a function of draw ratio is shown in *Figure 3*. This figure shows that the PET–POB fraction contributes to the increase of E_s at every draw ratio, and the differences between E_s values of blended samples and those of pure PET increase with draw ratio. This means that the orientation of PET–POB fraction of blended samples as well as PET fraction increases with draw ratio.

For the optimum conditions for microwave heat drawing of PET–POB polymer blends, drawing temperatures, tensions and microwave powers were examined. The conditions for the maximum modulus are shown in *Table 2*. The optimum drawing temperatures were lower and the draw ratios and E_s values were a little higher than the corresponding values shown in *Table 1*. The difference between E_s values by the conventional method and by the microwave heating method were outside the limits of experimental error for E_s measurement (shown in *Table 1*), and very small effects of microwave heating (less than 5% enhancement of E_s)

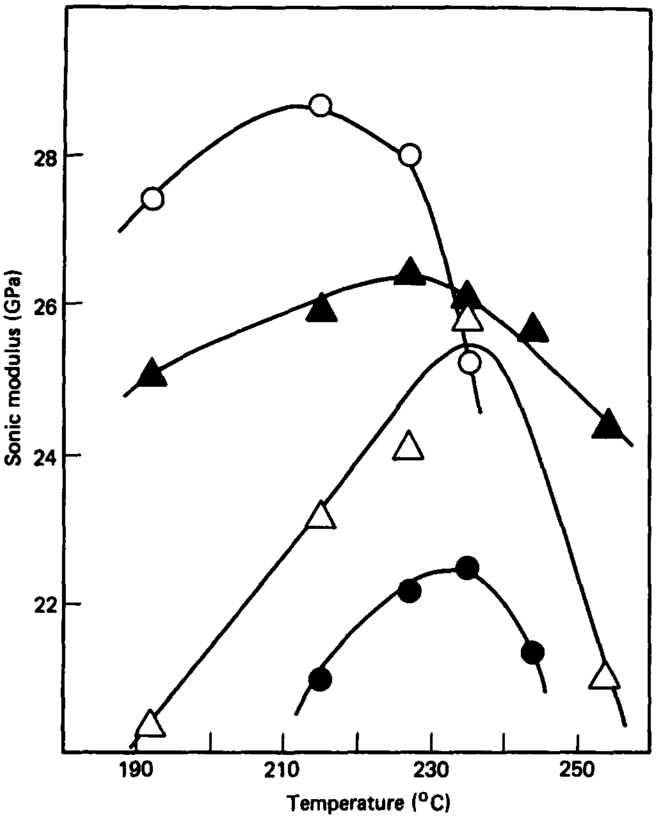

Figure 2 Sonic modulus as a function of temperature: (●) PET; (△) LC-10;, (▲) LC-30; (○) LC-50

Table 1 Optimum drawing conditions for heat drawing

Sample	Temperature (°C)	Draw ratio	Tension (kg)	E_s (GPa)
PET	234	8.3	12.0	22.5 (±0.2)
LC-10	234	8.4	9.0	25.8 (±0.2)
LC-30	226	7.9	8.0	26.4 (±0.3)
LC-50	216	7.5	5.1	28.7 (±0.3)

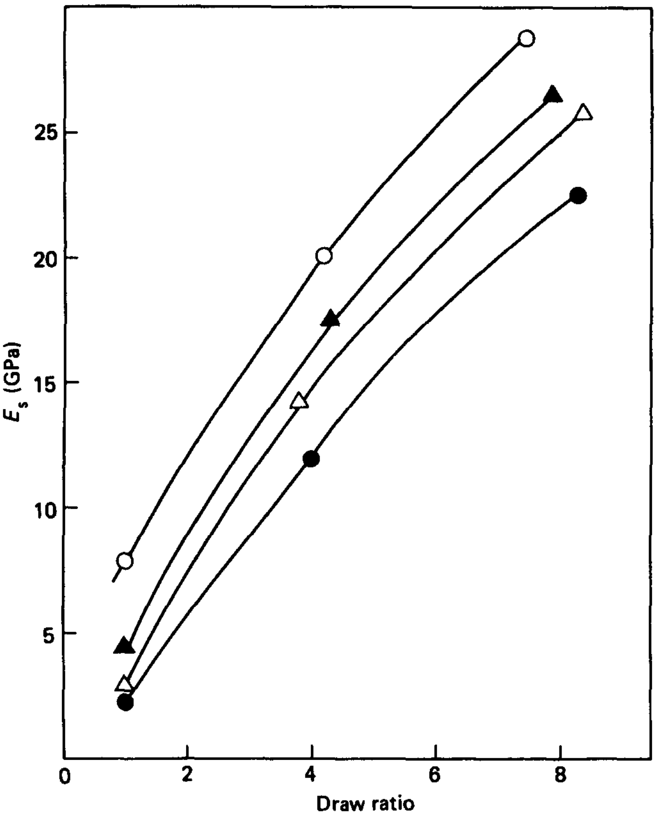

Figure 3 Sonic modulus as a function of draw ratio: (●) PET; (△) LC-10; (▲) LC-30; (○) LC-50. Drawing conditions for the higher draw ratios are shown in *Table 1*. Those for the lower draw ratios ($DR \sim 4$) were as follows: drawing temperatures of PET, LC-10, LC-30 and LC-50 were 100°C, 80°C, 70°C and 70°C with drawing tensions (for original samples with 2 mm diameter) of 6.0 kg, 3.5 kg, 3.5 kg and 3.5 kg, respectively

Table 2 Optimum conditions for microwave heat drawing

Sample	Temperature (°C)	Draw ratio	Tension (kg)	E_s (GPa)
PET	227	8.8	10.0	23.5 (±0.2)
LC-10	227	8.5	9.0	26.3 (±0.3)
LC-30	206	8.3	8.0	27.1 (±0.3)
LC-50	192	7.6	5.5	29.3 (±0.3)

were confirmed. Selective heating of the amorphous phase by microwaves, which was suggested for polyoxymethylene[15], was not obvious for the blend of PET and PET–POB. These small effects were also observed for the drawing of pure PET under microwave heating[11]. In these cases, uniform heating occurred, and the actual sample temperature (which cannot be known[15]) may be close to the conventional one.

Wide-angle X-ray diffraction

Figure 4 shows WAXD patterns of undrawn and drawn samples with maximum E_s of LC-50, for which the drawing condition is shown in *Table 1*. Diffraction spots derived from oriented crystalline PET were observed for two-stage drawn samples. The PET crystallites in the polymer blend were confirmed to be well oriented, just as they are in drawn PET rods. Diffraction from oriented PET–POB was also observed in the equatorial line (marked by arrows in *Figure 4*). This diffraction is thought to be from oriented POB[16]. PET–POB is oriented even in undrawn samples, in which the increase of E_s with increase of the PET–POB fraction was observed in *Figure 3*. This is because orientation is induced during the extrusion process, and a good orientation structure is shown. However, the increase of orientation with increase of draw ratio is not clear from *Figure 4*.

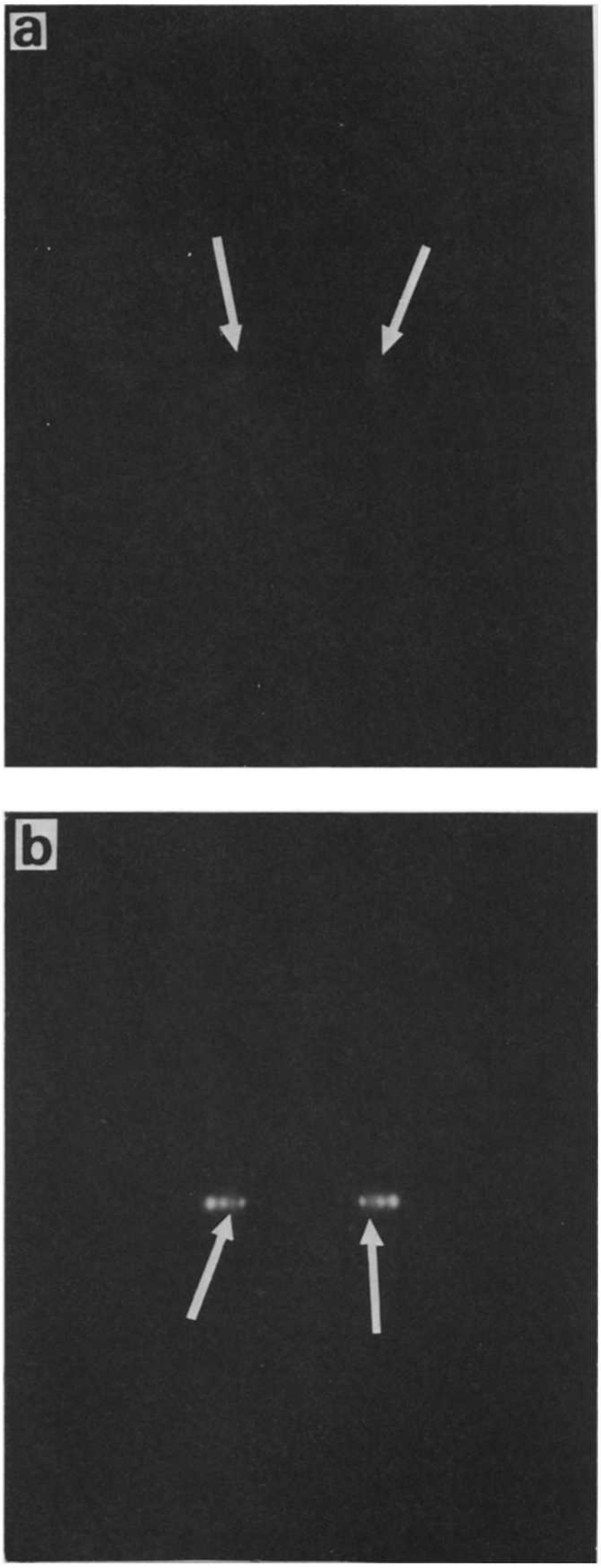

Figure 4 WAXD pattern of (a) undrawn and (b) drawn sample ($DR = 7.5$) of LC-50 which was processed according to the conditions shown in *Table 1*

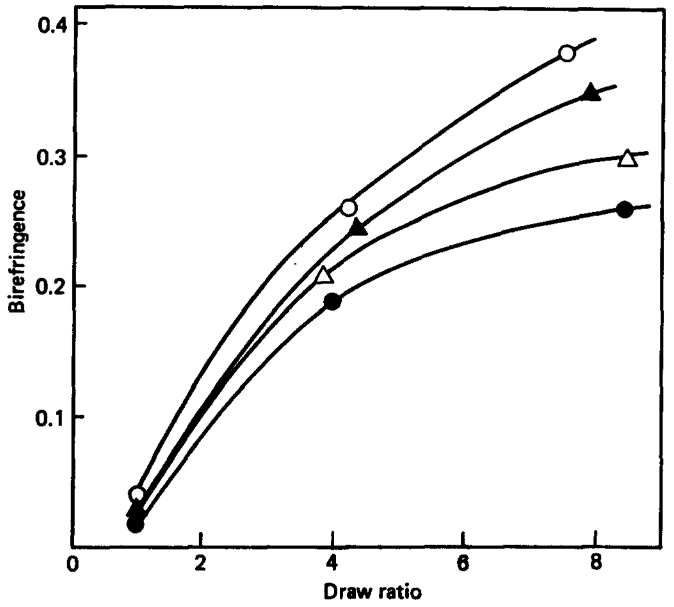

Figure 5 Birefringence as a function of draw ratio: (●) PET; (△) LC-10; (▲) LC-30; (○) LC-50. The drawing conditions were shown in *Table 1* and the caption of *Figure 3*

Birefringence measurements

The birefringences of drawn and undrawn samples were investigated. The observed total birefringences (Δn) are shown in *Figure 5* as a function of draw ratio. Each birefringence value is obtained at the optimum conditions (see figure captions) for the maximum E_s at the draw ratio. Δn increases with draw ratio and with PET–POB fraction. The difference between the birefringence values of blend samples and those of pure PET increases with increase of draw ratio, and it is thought that the orientation of PET–POB fraction increases with increase of draw ratio.

Dynamic mechanical behaviour

Storage (E') and loss (E'') moduli of two-stage drawn samples are shown in *Figure 6*. The drawing conditions of these samples are listed in *Table 1*. The contributions of PET and PET–POB to the mechanical absorptions were confirmed. It is well known that there are two absorptions

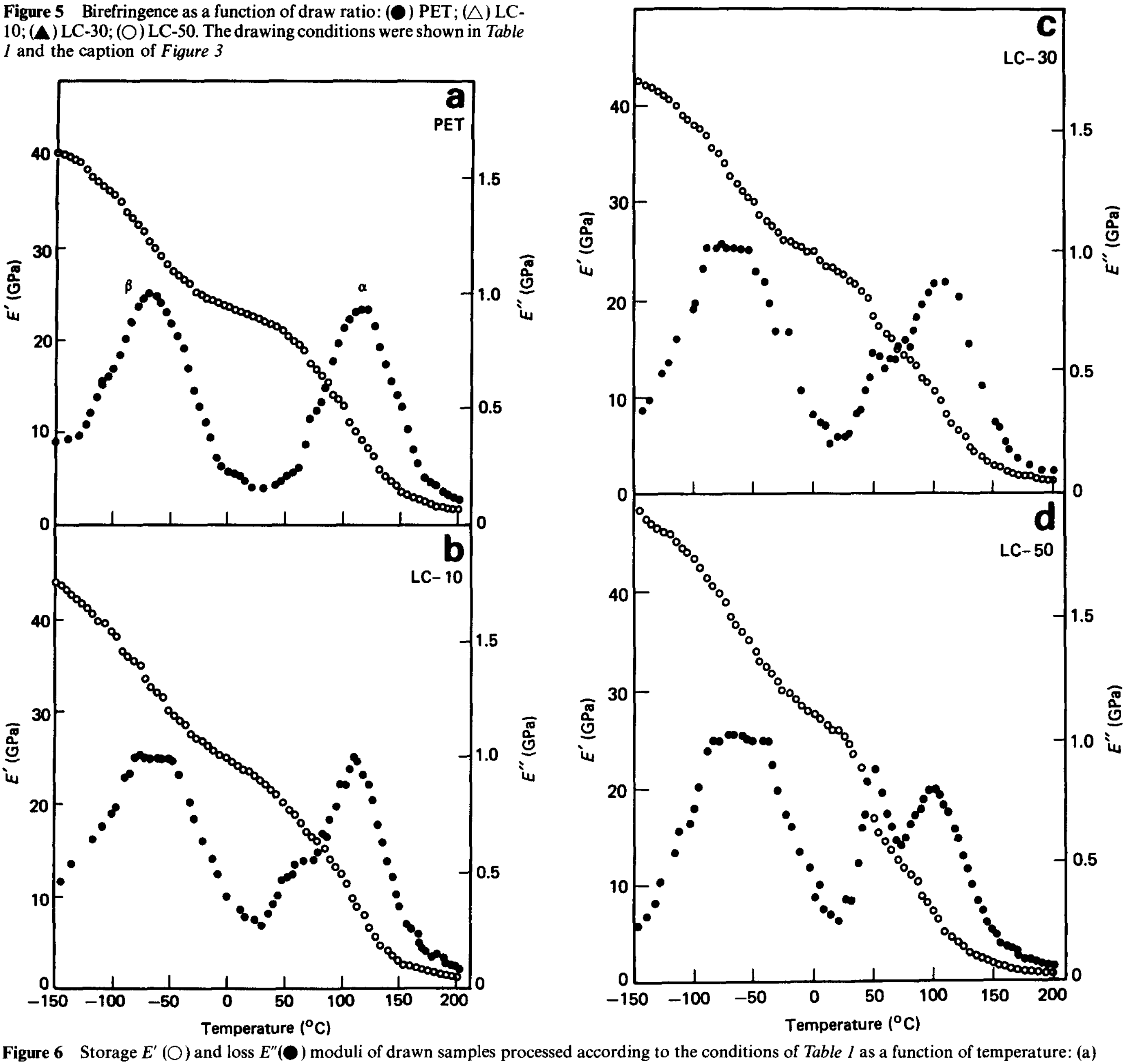

Figure 6 Storage E' (○) and loss E''(●) moduli of drawn samples processed according to the conditions of *Table 1* as a function of temperature: (a) PET; (b) LC-10; (c) LC-30; and (d) LC-50

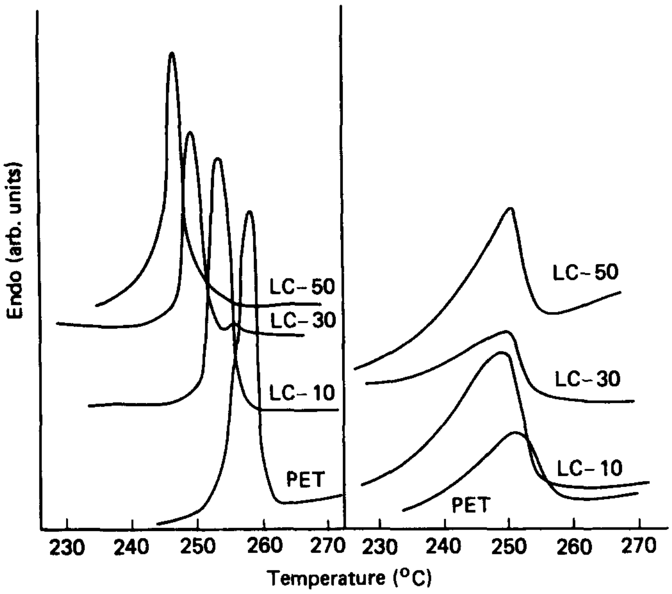

Figure 7 D.s.c. curves of drawn samples processed according to the conditions of *Table 1* (left) and undrawn samples (right)

(α and β) in PET[17]. These were observed for PET in *Figure 6a* at −70°C and at 120°C, respectively. The α and β absorptions are ascribed to micro-Brownian motion of the main chain and to local molecular motion, respectively[17]. When the PET–POB fraction is higher, other absorptions (around −50°C and 50°C) were observed. The absorption around −50°C was not clearly identifiable by comparison with the absorption of PET. The absorption around 50°C, which has been reported to correspond to the α absorption of the PET component in PET–POB[18], increased with increase in the PET–POB fraction. The polymer blend absorptions seem to appear only as an addition to those for PET and PET–POB, and no united absorption was observed, which suggests that there is incompatibility between the two components. As for E', the E values at lower temperature were higher with increase of the PET–POB fraction, and the highest attained E' value of LC-50 reached 48 GPa at −147°C.

Differential scanning calorimetry

Samples drawn under the optimum conditions for highest E_s (see *Table 1*) and undrawn ones were assessed by d.s.c. The d.s.c. curves are shown in *Figure 7*. Endothermal single peaks were observed for all the samples over the temperature range 230–260°C, and these peaks cannot be divided into a component from the PET fraction and that from the PET–POB fraction. These melting peaks are thought to be derived from the PET fraction and also from the PET component of the PET–POB fraction[19]. For undrawn samples, the melting behaviour of pure PET and blend samples shows no difference. However, for drawn samples, the widths of the curves were narrower than for undrawn ones, and a decrease of the peak temperature with increase in the PET–POB fraction was observed.

Fracture surface observation

Figure 8 shows the fracture surfaces of the undrawn samples examined by s.e.m. The surfaces of LC-10 and LC-30 look smooth; however, non-homogeneous structures on the fracture surfaces were observed for LC-50. It is thought that the two components were not well mixed for LC-50. The polymer blends between PET and PET–POB (60% POB) exhibited non-uniform fracture surfaces, and their incompatibility was shown[14]. The PET–POB samples used here (50 mol% POB) were also incompatible with PET at 50% PET–POB fraction. However, the surfaces of blended samples are smoother, as the PET–POB fraction is lower, and PET and PET–

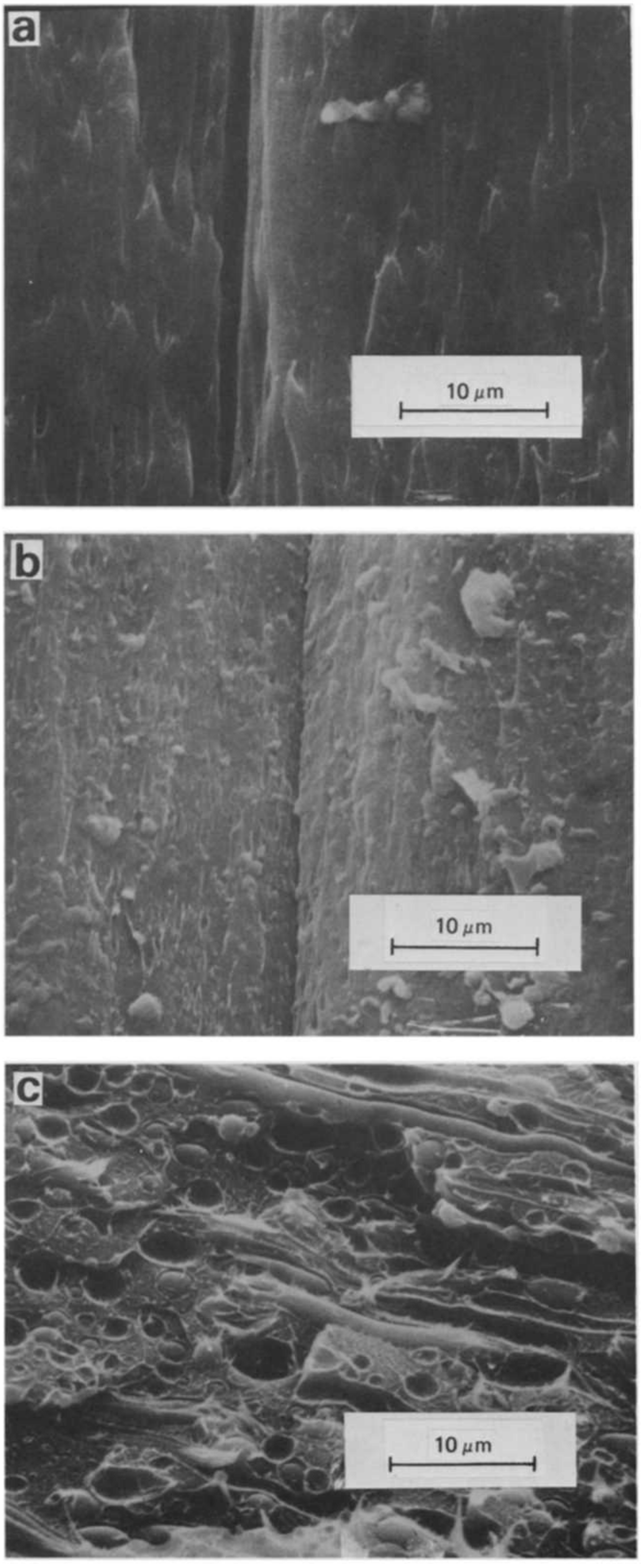

Figure 8 Fracture surface of undrawn samples: (a) LC-10; (b) LC-30; and (c) LC-50

POB are thought to be compatible for low PET–POB fractions.

CONCLUSIONS

The drawing behaviour and its assessment for drawn samples of polymer blends based on PET and a liquid crystalline copolyester (PET–POB) were investigated. Higher moduli were obtained, and drawn rod samples of the blends were produced under lower tensions and temperatures than for pure PET. The increase in orientation of the PET–POB fraction along with the PET fraction was confirmed. However, an incomplete mixing was suggested by dynamic mechanical measurement, and was found for the 50% PET–POB sample by s.e.m. observation.

ACKNOWLEDGEMENTS

We express our appreciation to H. Takata, N. Inagaki and S. Yamakawa for their continuous encouragement throughout this work.

REFERENCES

1 Hope, P. S., Gibson, A. G. and Ward, I. M. *J. Polym. Sci., Polym. Phys. Edn.* 1980, **18**, 1243

2 Mead, W. T., Desper, C. R. and Porter, R. S. *J. Polym. Sci., Polym. Phys. Edn.* 1979, **17**, 859

3 Kelb, B. and Pennings, A. J. *J. Mater. Sci.* 1980, **15**, 2584

4 Smith, P., Lemstra, P. J. and Booij, H. C. *J. Polym. Sci., Phys. Polym. Edn.* 1981, **19**, 877

5 Kwolek, S. L., Morgan, P. W., Schaefgan, J. R. and Gulrich, L. W. *Macromolecules* 1977, **10**, 1390

6 Ciferri, A. and Ward, I. M. 'Ultra-High Modulus Polymers', Applied Science, London, 1979, Ch. 5–8

7 Jackson, Jr, W. J. and Kuhfuss, H. F. *J. Polym. Sci., Polym. Chem. Edn.* 1976, **14**, 2043

8 Kunugi, T., Suzuki, A. and Hashimoto, M. *J. Appl. Polym. Sci.* 1981, **26**, 213

9 Pereira, J. R. C. and Porter, R. S. *J. Polym. Sci., Polym. Phys. Edn.* 1983, **21**, 1133, 1147

10 Ito, M., Kanamoto, T. and Tanaka, K. *Rep. Prog. Polym. Phys. Jpn.* 1984, **27**, 307

11 Amano, M. and Nakagawa, K. *Polymer* in press

12 Sakurada, I. and Kaji, K. *J. Polym. Sci. C* 1970, **31**, 57

13 Takeuchi, Y., Yamamoto, F. and Yamakawa, S. *Polym. J.* 1984, **16**, 579

14 Joseph, E. G., Wilkes, G. L. and Baird, D. G. 'Polymeric Liquid Crystals', (Ed. A. Blumstein), Plenum Press, New York, 1985, p. 197

15 Nakagawa, K., Konaka, T. and Yamakawa, S. *Polymer* 1985, **26**, 84

16 Acierno, D., La Mantia, F. P., Polizzoti, G., Ciferri, A. and Valenti, B. *Macromolecules* 1982, **15**, 1455

17 McCrum, N. G., Read, B. E. and Williams, G. 'Anelastic and Dielectric Effects in Polymeric Solids', Wiley, London, 1967, p. 504

18 Ciferri, A. and Ward, I. M. 'Ultra-High Modulus Polymers', Applied Science, London, 1979, p. 239

19 Meesili, W., Menczel, J., Gaur, U. and Wunderlich, B. *J. Polym. Sci., Polym. Phys. Edn.* 1982, **20**, 719