# Effect of pre-drawn morphology induced by treatment with mixtures of dimethylformamide and water on drawing of poly(ethylene terephthalate) fibres*

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The effects of pre-drawn morphology of melt-spun poly(ethylene terephthalate) (PET) fibres, induced by treatment at room temperature with mixtures of dimethylformamide (DMF) and water, on the two-stage drawing behaviour have been studied. The maximum achievable draw ratio ($DR_{max}$) in the first-stage cold drawing was dependent on the treatment time and the fraction of water in the mixtures. The fibres treated by $\leqslant 91/9$ (vol) DMF/water mixtures showed depression of the glass transition temperature. However, the $DR_{max}$ of the treated fibres was not improved appreciably. When the fibres were treated by a 95/5 mixture for 3 min, the fibres could be cold drawn up to a significantly higher draw ratio of 7. The value was about 30% higher than that for untreated fibres. The improved cold drawability of the treated fibres was explained by the presence of small and/or less perfect crystals induced by the mixture. With decreasing fraction of water and increasing treatment time, the treated fibres became brittle, which reduced the deformability at room temperature. This was primarily due to increased crystal perfection and surface roughening appeared on the fibre surface. By the second-stage hot drawing at 230°C, the initially cold-drawn fibres with the highest $DR_{max}$ of 7 could be drawn up to a total draw ratio of 11.5. These highly drawn fibres showed tensile moduli and strengths of $\leqslant 225$ and $\leqslant 10$ g/d, respectively.

**(Keywords: poly(ethylene terephthalate); pre-drawn morphology; fibres; liquid treatment; mixture of dimethylformamide and water; drawing; mechanical properties)**

## INTRODUCTION

It is well known that poly(ethylene terephthalate) (PET) interacts strongly with certain organic liquids, which lowers the glass transition temperature and induces crystallization, and in some cases leads to partial dissolution of low-molecular-weight PET. Much attention has thus been given to the diffusion mechanism of the liquids[1,2], the crystallization kinetics[3] and the properties and structure of the liquid-treated PET[4–6]. We reported[7] that PET fibres having high modulus and high tenacity could be obtained by drawing of fibres that had been treated with acetone. The highest modulus and strength values for the treated drawn fibres with the highest draw ratio of 11.5 were about 20% higher than those for the untreated drawn fibres with the highest draw ratio of 9.5. The improved ductility and enhanced mechanical properties of the treated drawn fibres were explained by the existence of small and/or less perfect crystals induced by acetone and by plasticization with the residual acetone trapped within amorphous regions. Fakirov *et al.*[8] also suggested that a low-crystallinity and very imperfect crystalline structure was the most proper initial structure for obtaining highly drawn nylon and polyesters. In this work, we found that the degree of plasticization, solvent-induced crystallization and partial dissolution of PET that occurred during treatment of PET fibres could be controlled by changing the fraction of water in dimethylformamide (DMF) and the treatment time. Thus, the purpose of this paper is to discuss the effects of plasticization and solvent-induced crystallization of PET fibres induced by mixtures of DMF and water on the drawing behaviour and properties of the resultant drawn fibres. Further, the preparation of high-modulus and high-strength PET fibres with various surface morphologies was examined by controlling the conditions of the liquid treatments. These fibres are suitable for use as a rubber reinforcing material as well as for textile fabrics with an improved dyeing property.

## EXPERIMENTAL

### *Samples*

Unoriented PET fibres with a diameter of about 65 $\mu$m were kindly supplied by Toyobo. The intrinsic viscosity of the fibre was 0.9 dl g$^{-1}$ and its crystallinity as revealed in a density gradient column was less than 5%. The dimethylformamide (DMF) was of analytical reagent quality. As-received fibres were dried at 50°C for 24 h under vacuum, and then they were immersed in mixtures of DMF and water at room temperature for varying lengths of time. The mixing ratios of DMF and water

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(DMF/water, v/v) were 100/0, 97/3, 95/5 and 91/9. Following the liquid treatments, the fibres were blotted twice on filter paper to remove excess liquid from the sample surface. A two-stage drawing technique was utilized for both treated and untreated original fibres. The fibres were drawn by tensile force at room temperature (cold drawing), followed by tensile drawing at 230°C (hot drawing).

### *Measurements*

The tensile properties of drawn fibres along the fibre axis were measured at room temperature and strain rate of $1 \times 10^{-3}\ \mathrm{s}^{-1}$. The gauge length was 100 mm. The modulus was determined from the tangent to the stress–strain curve at a low strain (0.1%). The intrinsic viscosity of the sample was measured in a mixed solvent of trifluoroacetic acid and dichloromethane (50/50, v/v) at 30°C. Wide-angle X-ray measurements were carried out on a Rigaku RAD-III diffraction unit with Ni-filtered Cu K$\alpha$ radiation generated at 40 kV and 25 mA with a fine-focus tube. Thermal analysis was carried out on a Seiko Denshi DSC 10 differential scanning calorimeter at a heating rate of 5°C min$^{-1}$.

## RESULTS AND DISCUSSION

### *Morphology of the treated fibres*

The liquid treatments induced a lowering of the glass transition temperature ($T_g$), solvent-induced crystallization and, in some cases, partial dissolution of PET from the fibre surface, all of which could be controlled by changing the fraction of water in the mixtures and the treatment time. Also, the ductility of the treated fibres was dependent on the extent of these variations.

*Figure 1* shows scanning electron micrographs (SEM) for the untreated and treated fibres. The treated samples were prepared by using mixtures with various water fractions. A constant immersion time of 3 min was utilized for the treatments. The fibre treated by a 91/9 mixture exhibits a smooth surface, which is similar to that for an untreated fibre. The fibres treated by the mixtures with lower water fractions (95/5, 100/0) show a significant surface roughening, which increases on decreasing the fraction of water. Jameel *et al.*[3] also reported a similar surface morphology of drawn PET films treated by DMF. They suggested that the roughening reflected dissolution of the polymer from the surface as in an etching process. As techniques of PET etching, treatments using alkali, amine and plasma are well established. However, all of these techniques involve molecular degradation, and hence a lowering of the mechanical properties of the treated films and fibres. In order to evaluate the change in molecular weight by the present liquid treatments, the intrinsic viscosity (*IV*) was measured for the samples treated by DMF for varying lengths of time; the results are shown in *Figure 2*. Although the DMF (water fraction 0) induced the highest degree of surface roughening among the mixtures studied, the *IV* retained by the treated fibres is almost 100% even after 1 h of treatment. The results indicate that etching is not accompanied by noticeable molecular degradation. A detailed molecular-weight characterization by g.p.c. was not carried out for

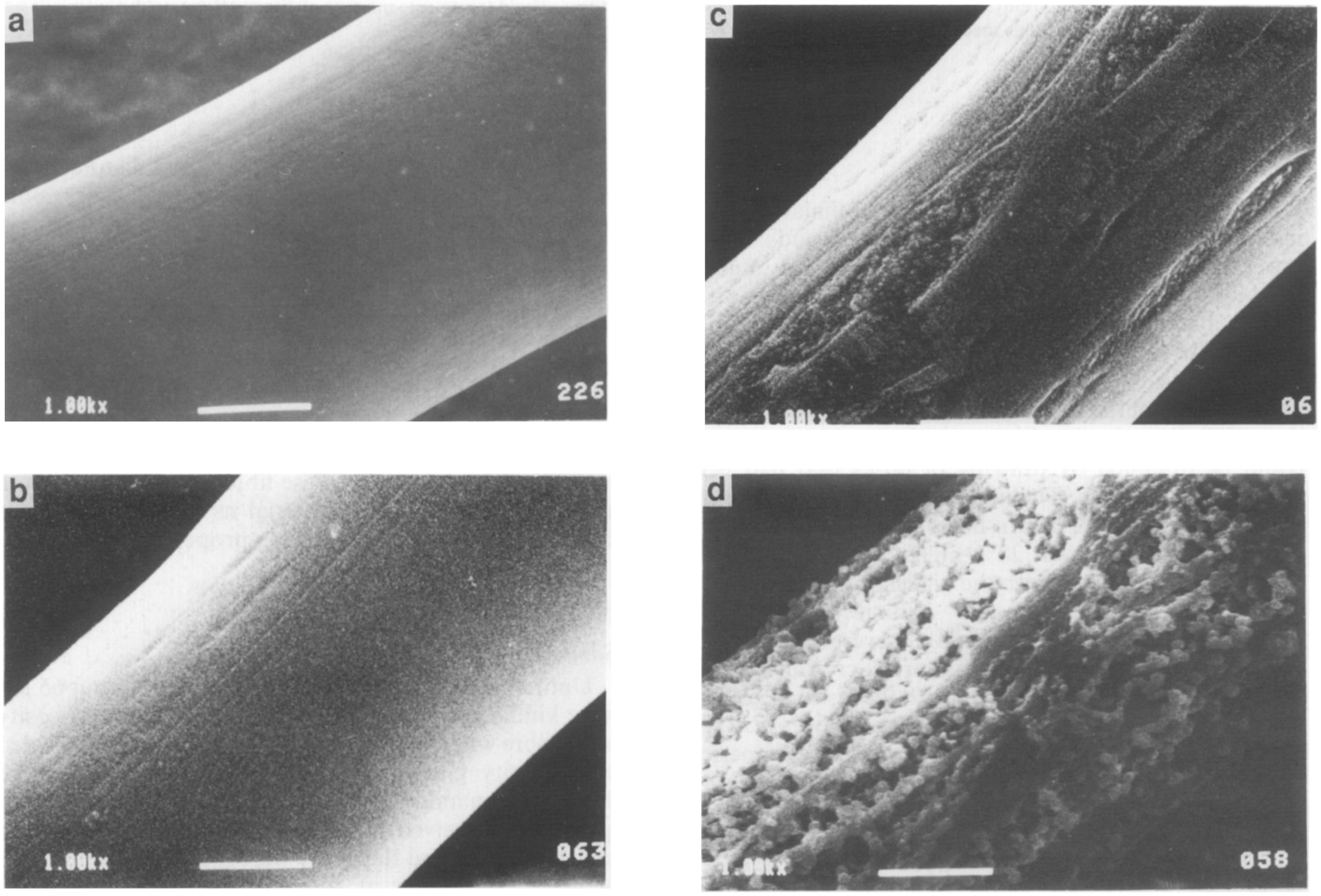

**Figure 1** Scanning electron micrographs of untreated and treated fibres: (a) untreated, (b) 91/9, (c) 95/5, (d) 100/0; bar = 20 $\mu$m

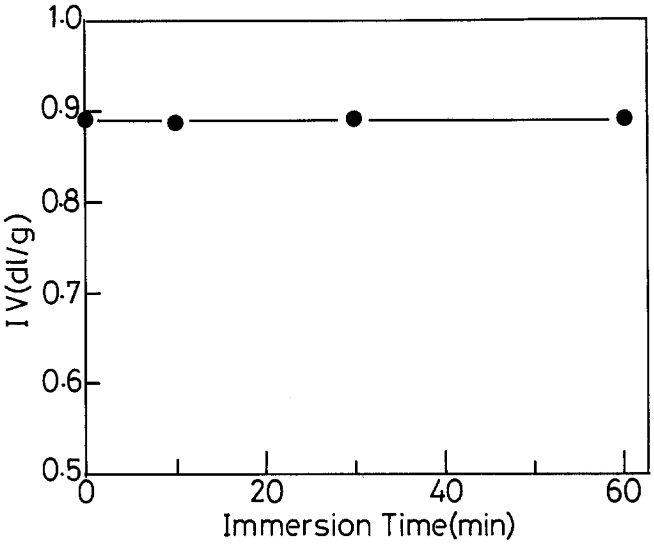

**Figure 2** Intrinsic viscosity of the treated fibres as a function of immersion time

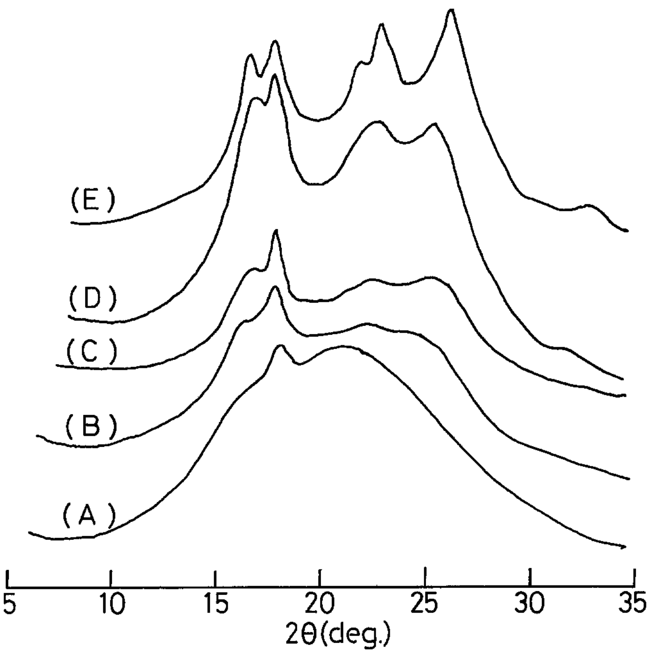

**Figure 3** Wide-angle X-ray diffraction patterns of the samples: (A) untreated, (B) 91/9, (C) 95/5, (D) 97/3, (E) annealed

the treated samples. However, the weight loss for the sample that had been treated by DMF for 1 h was about 10%. These results suggest that surface roughening is caused by partial dissolution of PET at the surface.

*Figure 3* shows wide-angle X-ray diffraction (WAXD) patterns of untreated and treated fibres. The samples used were similar to those for the SEM observations. In addition to these samples, the pattern of heat-treated fibres is also shown for comparison. The thermal treatment of untreated fibres was carried out at 200°C for 2 h. Untreated original fibres give a typical WAXD pattern of unoriented and nearly amorphous PET. A similar pattern is also observed for the fibres treated by a mixture with a high water fraction (91/9). In contrast, the fibres treated by mixtures with lower water fractions (97/3, 95/5) show clear crystalline reflections, although each diffraction is broad and diffuse compared with that for the heat-treated sample. Further, the broadness increases on increasing the fraction of water. The results indicate that the liquid-induced crystals are less perfect and/or that their sizes are very small, with this tendency more prominent with increasing fraction of water in the mixtures.

*Figure 4* shows d.s.c. thermograms of untreated and treated fibres. The treatments were carried out by using a 91/9 mixture for varying lengths of immersion time. At an initial stage of immersion (immersion time 1 min), the depressions of $T_g$ and cold crystallization temperature ($T_c$) were remarkable. The depressions of $T_g$ and $T_c$ are about 50 and 70°C, respectively. These results are clear evidence of plasticization by the treatment. The temperature shifts remained almost constant even after a longer treatment. Instead, the shape of the exotherm due to cold crystallization during the d.s.c. scan changed with treatment time. Initially double exothermic peaks became a single one for a treatment time of 5 min. The double crystallization peaks arose from heterogeneous plasticization at the initial stage of immersion. In this study, the kinetics of liquid penetration into fibres was not investigated. However, the d.s.c. results imply that it takes about 5 min to achieve a uniform distribution of 91/9 mixture within a fibre.

Sample B showed a large endotherm with a peak temperature ~145°C, just below the boiling point of DMF. However, the endotherm was not observed in sample C despite the fact that sample C also involved the same mixture. The size of the endotherm changed with time required for sample preparation for d.s.c. measurements owing to the rapid evaporation rate of the mixture. Taking all this into consideration, it is inferred that the endotherm arose from the evaporation of the mixture (91/9). However, the details are uncertain.

D.s.c. measurements were also carried out for fibres treated with mixtures with lower water fractions. However, the samples showed no detectable change in specific heat corresponding to the glass transition and cold crystallization. With decreasing fraction of water in the mixtures, the interaction between PET and liquids increased, which enhanced the solvent-induced crystallization as revealed in *Figure 3*. A high sample crystallinity might suppress cold crystallization during a

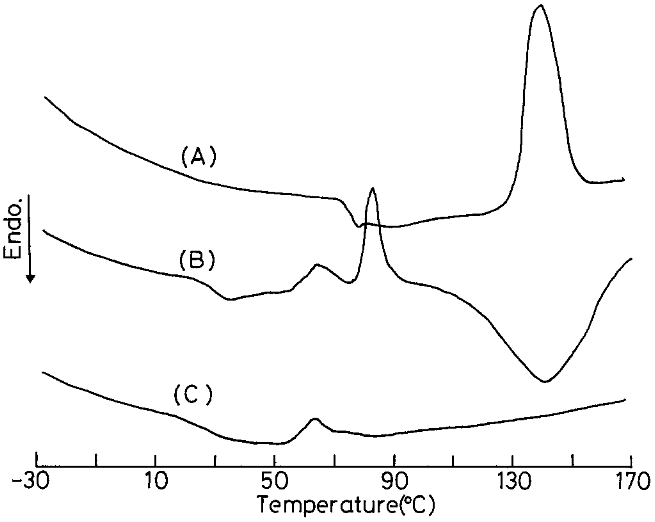

**Figure 4** D.s.c. thermograms of samples: (A) untreated, (B) treatment time 1 min, (C) treatment time 5 min

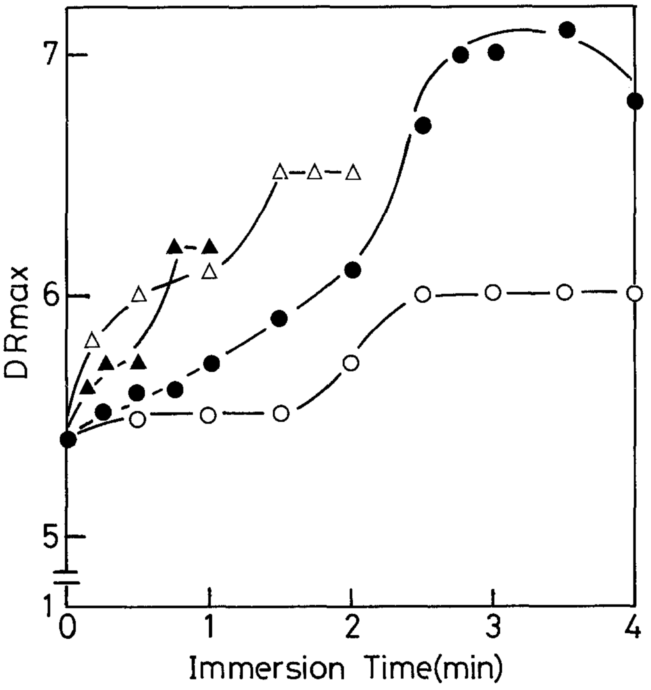

**Figure 5** $DR_{\max}$ at cold drawing as a function of immersion time and fraction of water in mixtures: (○) 91/9, (●) 95/5, (△) 97/3, (▲) 100/0

d.s.c. scan and prevent a large change in the specific heat around $T_g$, which made it difficult to detect $T_g$ and $T_c$ by d.s.c. Combined with the WAXD (*Figure 3*) and the d.s.c. (*Figure 4*) results described above, it is concluded that significant plasticization occurs in the fibres treated by a 91/9 mixture, but the degree of plasticization is not enough to induce the solvent-induced crystallization. On the other hand, the plasticization effects of the mixtures with lower water fractions ($<95/5$) are strong enough to enhance the crystallization.

The capability of liquid absorption on the fibres changes with the fraction of water in the mixtures, which might also influence the degree of plasticization mentioned above. In this study, the exact amounts of liquid uptake could not be determined owing to the partial dissolution of PET, which hampered further discussion on the plasticization behaviour of the treated fibres.

### *Ductility of the treated fibres*

*Figure 5* shows the effects of immersion time and fraction of water in the mixtures on the maximum achievable draw ratio ($DR_{\max}$) in the first-stage cold drawing. It is seen that $DR_{\max}$ is dependent on the immersion time and the fraction of water. The highest $DR_{\max}$ of 7 could be attained when the fibres were treated with a 95/5 mixture for 3 min. This value is about 30% higher than that for untreated fibres, and is comparable to that for acetone-treated fibres[7]. The fibres treated by mixtures with lower water fractions (97/3, 100/0) show high values of $DR_{\max}$ compared with that of untreated fibres. However, they lose ductility after a short immersion time of 1–2 min. As was shown in *Figure 1*, the degree of surface roughening in the treated fibres increased with decreasing fraction of water. On increasing the degree of surface roughening, the stress distribution on drawing might become inhomogeneous, leading to the loss of ductility of the treated fibres. Further, it was reported that isotropic and highly crystalline PET could not be cold drawn by tensile force, since fracture occurs at an early stage of deformation[9]. As was revealed by the WAXD patterns shown in *Figure 3*, the crystal perfection and/or crystal sizes in the treated fibres increased with decreasing fraction of water in the mixture. This might also reduce the ductility of the treated fibres owing to a corresponding increase in the draw stress. It should be noted that the fibres treated by a 91/9 mixture show the lowest improvement in ductility among the treated fibres studied. As described in the previous section, a considerable degree of plasticization occurred in the fibres treated by a 91/9 mixture. This means that the deformability of PET cannot be improved appreciably by the plasticizing effect alone.

*Figure 6* shows nominal stress *versus* strain curves for the untreated and treated fibres with a length of 3 cm recorded at a constant temperature ($T_e$) at 25°C and at a constant crosshead speed of 100 mm min$^{-1}$. The samples were prepared by using mixtures with various water fractions at a constant immersion time of 3 min. The yield stress for all the treated fibres was lower than that for the untreated fibre. This is due to the plasticizing effect of the liquid. With decreasing fractions of water in the mixtures, the stress increases. The increased stress is primarily due to the existence of solvent-induced crystals. It should be noted that the deformability of the sample treated with a 95/5 mixture is higher than that of the sample treated with a 91/9 mixture, despite the fact that the drawing stress for the former is higher than that for the latter. That is, the drawing stress is not directly related to the deformability of PET. For the samples treated by a 91/9 mixture and the untreated one, the stress on drawing begins to increase abruptly at a strain of 180–270%. The sharp increase in the stress arises due to the well known stress-induced crystallization of PET. On the other hand, for the samples treated by a 95/5 mixture, a rapid increase in the stress starts at a strain around 350%. However, the slope is not so steep as in drawing of the untreated fibres. The most crucial effect of the solvent-induced crystals on drawing PET fibres is

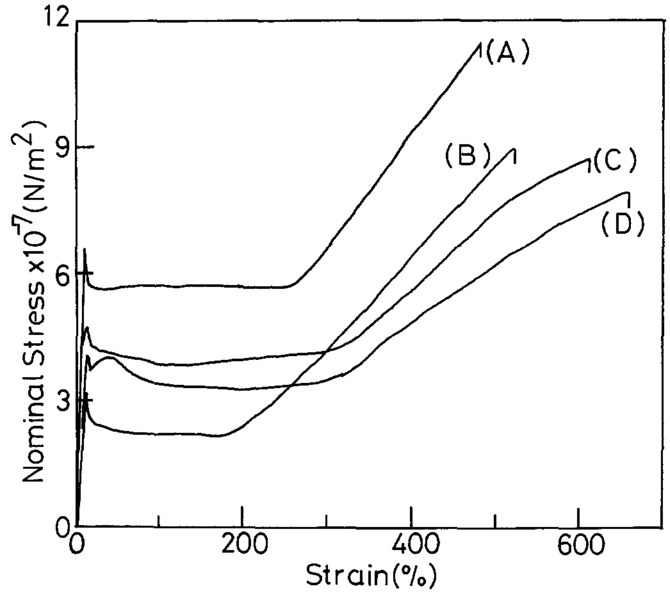

**Figure 6** Nominal stress *versus* strain curves for the samples: (A) untreated, (B) 91/9, (C) 97/3, (D) 95/5

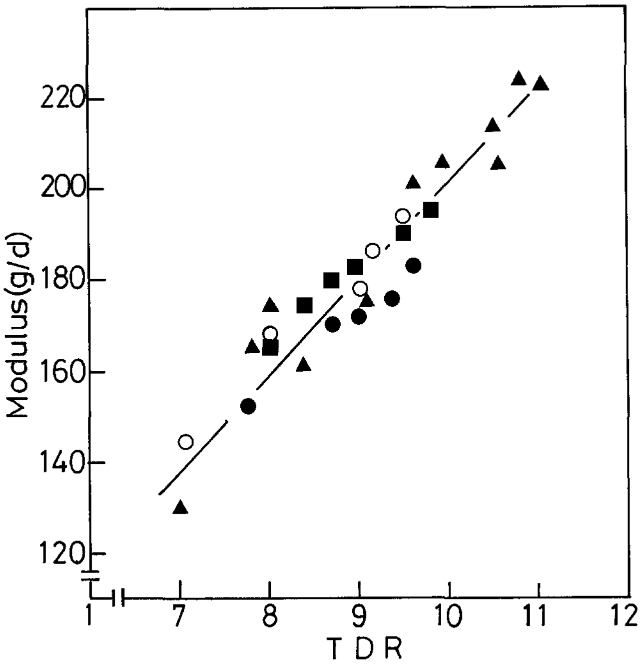

**Figure 7** *TDR* dependence of the tensile modulus for the two-stage drawn samples: (○) untreated, (■) 91/9, (▲) 95/5, (●) 97/3

to reduce strain hardening. As discussed in the previous section, the superstructure of treated fibres is extremely complex. The mobility of amorphous segments is markedly increased by liquids that are preferentially dissolved in the amorphous regions. The plasticization increases the deformability of only the amorphous regions. Further, the small and less perfect crystallites induced by the liquid might be deformed more easily than the well developed crystals that are usually formed by heat treatment. Thus, the less perfect crystals act as deformable network points. These combined effects might suppress strain hardening, leading to the higher deformability of fibres treated by a 95/5 mixture.

In a previous paper[10], we emphasized the importance of two-stage drawing (combination of cold drawing and hot drawing) in obtaining high-modulus and high-strength PET fibres. In this study, the same technique was utilized for both treated and untreated fibres. Both treated and untreated fibres were drawn by tensile force to the $DR_{max}$ at room temperature, followed by drawing samples in a tensile tester at 230°C. Although the fibres treated with DMF (100/0) could be drawn up to ~6 at room temperature, the ductility of the drawn fibres at 230°C was quite low, probably due to high crystallinity and significant surface roughening. Therefore, the second-stage draw was not carried out for the first-stage drawn fibres treated with DMF. The tensile properties of the resultant drawn fibres were dependent on several parameters, including the total draw ratio ($TDR = DR_{max} \times DR$ for the hot drawing), and the load applied to the samples during cooling after hot drawing. The higher the load and *TDR*, the higher were the mechanical properties of the drawn fibres that could be achieved. In this study, the hot drawing was carried out under a draw stress ~50 kg mm$^{-2}$ by controlling the crosshead speed. After the hot drawing, the samples were cooled to room temperature under a constant sample length. Thus, the load applied to the samples increased from ~50 kg mm$^{-2}$ at the draw temperature of 230°C to ~65 kg mm$^{-2}$ at room temperature. The maximum achievable draw ratio in the second-stage draw was 1.6–1.9, independent of $DR_{max}$ that was obtained by the first-stage draw. Thus, the maximum achievable *TDR* for the treated fibres with $DR_{max}$ of 7 and the untreated one with $DR_{max}$ of 5.5 were 11.5 and 9.5, respectively. During the hot drawing at 230°C, the residual liquid was removed, and simultaneously the solvent-induced crystals increased in their perfection and sizes and stress-induced crystallization proceeded; all of which might reduce the ductility of the treated fibres.

In *Figures 7* and *8*, tensile moduli and strengths of the samples are plotted against *TDR*. Both the tensile modulus and strength increase with increasing *TDR*. The highest modulus and strength of 225 and 10 g/d, respectively, were obtained for the treated fibres with the highest *TDR*. These values were about 20% higher than those obtained for the untreated drawn fibres with the highest *TDR*. Also, it can be seen in *Figures 7* and *8* that the liquid treatments have no effect on the tensile modulus, and the values are primarily determined by the *TDR*. On the other hand, fibres treated by a 97/3 mixture show the lowest value of tensile strength at any *TDR* among the samples studied. This can be closely related to the inhomogeneous structure of the fibre surface.

Finally, the effects of surface morphology on the dyeing behaviour of the treated fibres is discussed in a qualitative way. As mentioned in the previous section, the surface morphology of the treated fibres could be controlled from smooth to rough structure by changing the fraction of water in the mixtures. Although the deformability of the treated fibres with high degree of surface roughening was poor, the fibres with moderate surface roughening were drawable (see *Figure 5*). *Figure 9* shows SEM photographs of treated undrawn, cold-drawn and two-stage drawn fibres. The treatment was carried out by using a 97/3 mixture for 3 min. $DR_{max}$ and *TDR* for

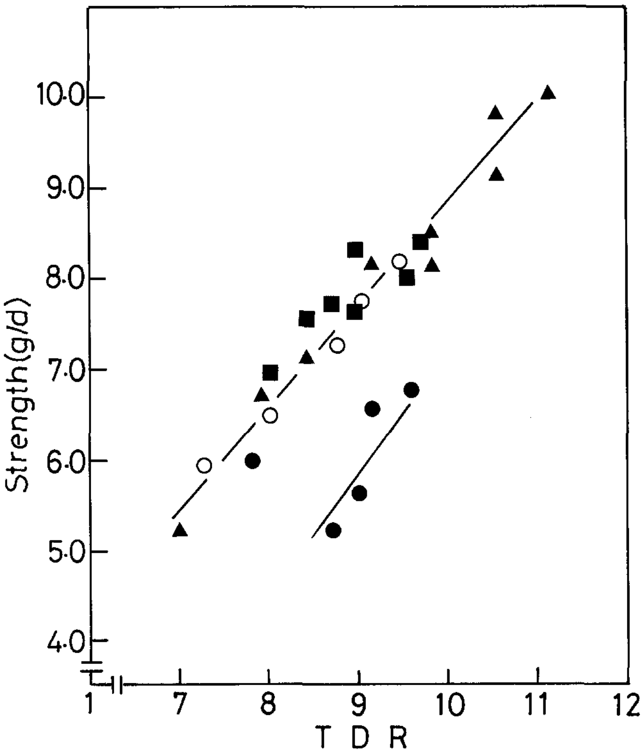

**Figure 8** *TDR* dependence of the tensile strength for the two-stage drawn samples: (○) untreated, (■) 91/9, (▲) 95/5, (●) 97/3

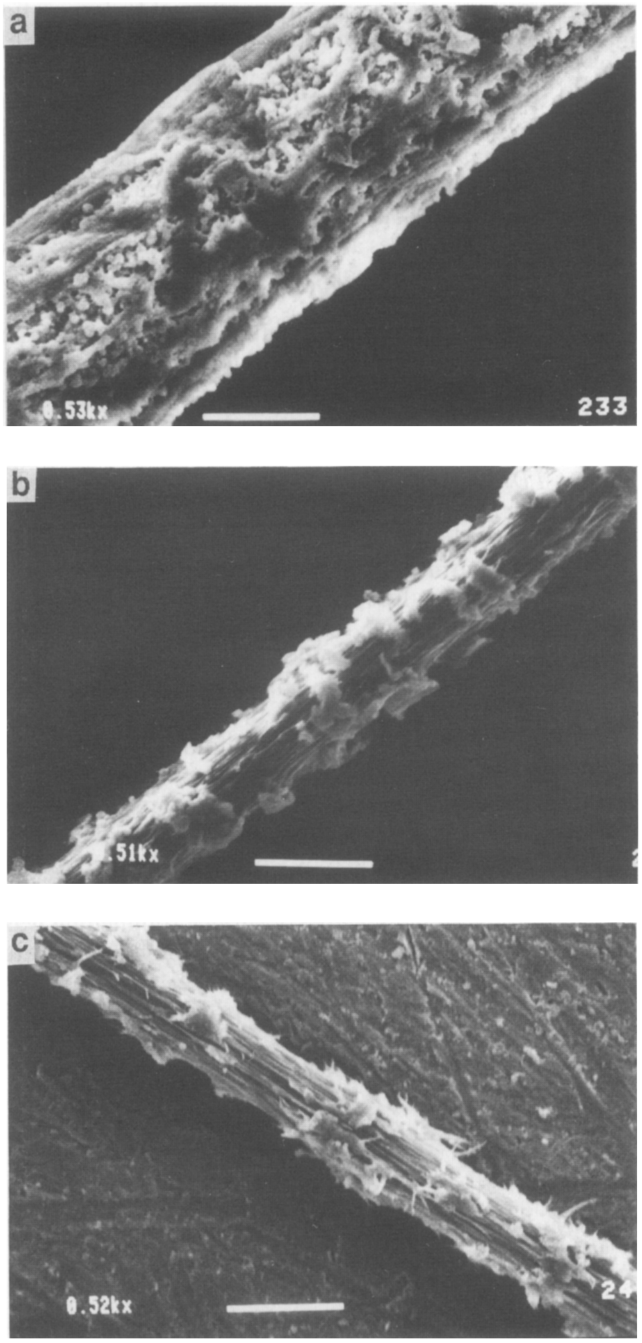

**Figure 9** Scanning electron micrographs of treated samples: (a) undrawn, (b) cold drawn, (c) two-stage drawn; bar = 40 $\mu$m

these fibres were 6 and 9.5, respectively. The tensile modulus and strength of the two-stage drawn fibres were 180 and 6.8 g/d, respectively. It is clearly seen from the photographs that surface roughening still exists in the two-stage drawn fibres. These results indicate that high-modulus and high-strength PET fibres with a rough surface can be obtained by two-stage drawing of PET. These fibres are suitable for use as a rubber reinforcing material as well as for clothing. For example, a deep-coloured dyeing was possible for the fibres shown in *Figure 9C*. This was not due to increased dye uptake but to increased surface roughness, since no difference in dye uptake was observed between the untreated and treated drawn fibres. With increasing surface roughening, the ratio of degree of mirror reflection at the surface to internal reflection decreases. As a result, we can observe a deep-coloured light.

## CONCLUSION

When PET fibres were treated by a mixture of DMF and water, plasticization, solvent-induced crystallization and partial dissolution of PET occurred in the treated fibres. Further, the extents could be controlled by changing the amount of water in DMF and the treatment time. The ductility of the treated fibres was dependent on the extent of these variations. The deformability of PET at room temperature was not improved appreciably by the plasticizing effect alone. But the deformability increased owing to the formation of small and/or less perfect crystallites induced by the liquid treatments. The small and less perfect crystallites induced by the liquid are likely to be deformed more easily than the well developed crystals that are usually formed by heat. That is, the less perfect crystals act as deformable network points. These combined effects might improve the deformability of PET. When the cold-drawn fibres with the highest draw ratio of 7 that had been treated by a 95/5 mixture were drawn further by a tensile force at 230°C, the fibres could be elongated to 11.5 times the original length. The tensile modulus of the drawn fibres with the highest draw ratio of 11.5 was 225 g/d, which was about 20% higher than that which could be achieved by drawing of the untreated original fibres. The difference in the tensile modulus was explained by the difference in the achievable draw ratio by the two-stage draw. Finally, surface roughening induced by treatment with the mixtures remains after drawing of the fibres. This endows the PET fibres with a deep-coloured dyeing ability.

## REFERENCES

1 Makarewicz, P. J. and Wilkes, G. L. *J. Polym. Sci., Polym. Phys. Edn.*1978, **16**, 1529
2 Jameel, H., Waldman, J. and Rebenfeld, L. *J. Appl. Polym. Sci.* 1981, **26**, 1795
3 Jameel, H., Noether, H. D. and Rebenfeld, L. *J. Appl. Polym. Sci.* 1982, **27**, 773
4 Makarewicz, P. J., Wilkes, G. L. and Budnitky, Y. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 1545
5 Know, B. H., Scott, M. G., Weigmann, H. H. and Rebenfeld, L. *Text. Res. J.* 1981, **51**, 549
6 Vicini, L., Seves, A., Canetti, M., Sadocco, P. and Galli, R. *Polymer* 1984, **25**, 1774
7 Ito, M., Miya, H., Watanabe, M. and Kanamoto, T. *J. Appl. Polym. Sci.* 1990, **40**, 543
8 Fakirov, S., Evstatiev, M. and Schultz, J. M. *J. Appl. Polym. Sci.* 1991, **42**, 575
9 Newman, S. *J. Polym. Sci.* 1958, **27**, 563
10 Ito, M., Takahashi, K. and Kanamoto, T. *Polymer* 1990, **31**, 58