Structural and morphological studies of aminolysed poly(ethylene terephthalate) fibre

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The aminolysis of poly(ethylene terephthalate) fibres with four draw ratios (2.65, 3.00, 4.00 and 5.00) drawn at three temperatures (36, 170 and 200°C), i.e. one below and two above the glass transition temperature, was studied using 40% methylamine solution. The changes in the structural properties were studied using X-ray diffraction, infra-red spectroscopy and scanning electron microscopy. It was observed that the crystallinity initially decreases for treatment of 3 h and then increases for treatments of 6 and 8 h. The electron microscopic study showed that treatment of 3 h reveals little about the morphological changes, whereas treatments of 6 and 8 h showed stress cracking perpendicular to the fibre axis for all the samples. Fibres drawn at 170°C, in addition, showed longitudinal cracking.

(Keywords: poly(ethylene terephthalate); aminolysis; morphology; structural studies; stress cracking; chemical degradation)

INTRODUCTION

The degradation of oriented poly(ethylene terephthalate) (PET) fibre by different amines is of considerable interest from the points of view of morphological features and ageing.

A degradative technique for PET was developed by Baker[1] using n-propylamine. He studied the etching of one-way and two-way stretched films, solvent crystallized films and mechanically damaged films. The etching studies of these various films showed that the etched patterns appeared to be a measure of the direction and extent of orientation. He observed that directional lines parallel to the stretch direction are etched into one-way stretched film. On the other hand, the two-way stretched films revealed a lamellar composition, each layer possessing a brick-wall-like structure. Attempts have been made in the past by several workers[2-4] to study the chain folding of unoriented and oriented PET. The first investigators in this field, Farrow, Revens and Ward[5], studied the infra-red spectroscopy and low-angle X-ray scattering of aminolysed PET. They concluded that 'there is a rapid degradation of the amorphous regions, extensive degradation leads to attack on both crystalline and amorphous regions'. Tucker *et al.*[6,7] also studied the structure and morphology of n-propylamine treated PET fibres and films.

The aminolysis of the esters takes place according to the following chemical reaction:

$$R'COOR + H_2NR'' \rightarrow R'\text{–}CONHR'' + ROH$$

Here

$$R' = C_6H_4 \qquad R = CH_2\text{–}CH_2\text{–}O, \qquad R'' = \text{–}CH_3$$

Kurita[8] suggested that the aminolysis reaction is selective, and that high crystallinity values can be obtained in the aminolysed samples. He concluded that the amorphous regions are steadily degraded in the initial stage of treatment, corresponding to a rapid weight loss in the polymer. This stage is then followed by chemical attack on the crystalline regions, resulting in the very slow degradation rates. Mehta and Bell[4] have also suggested that the aminolysis procedure effectively removes the amorphous material. The characterization of oriented PET samples after degradation has been reported by Mocheria and Bell[3].

Sweet and Bell[9] studied aminolysis using 40% methylamine solution. They have shown that residual or internal stresses remaining in commercially drawn fibres are sufficient to cause stress cracking without the need for an applied load. In spite of these attempts to study aminolysis of PET, no definite study has been carried out to evaluate the effect of drawing the fibres at various temperatures. In the present paper, therefore, we report the infra-red spectroscopic, X-ray diffraction and scanning electron microscopic studies of PET fibres drawn at three different temperatures with four different draw ratios.

EXPERIMENTAL

Materials

In the present investigation, poly(ethylene terephthalate) (PET) continuous filament yarns drawn at three different drawing temperatures, 36, 170 and 200°C (viz. one below the glass transition temperature T_g and two above T_g), have been studied. At each temperature, fibres were drawn at four different draw ratios (2.65, 3.00, 4.00 and 5.00). The molecular weight of these fibres was determined by a viscosity method using an Ubbelohde viscometer at

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25±0.2°C by dissolving the fibre in *o*-chlorophenol. The values thus obtained are tabulated in *Table 1*.

All these fibres had an average denier of 1.4 and birefringence of 0.008 before drawing. The residence time on the heated surface was 11.765 s.

Chemical degradation

All degradation experiments were carried out at room temperature (24°C) using approximately 0.5 g of PET fibres in 200 ml of 40% methylamine solution. Degradation experiments were carried out in sealed flasks to prevent the loss of gaseous methylamine from solution. Experiments were carried out with and without mild agitation, both of which produced the same results.

After the degradation experiment was over, the PET samples were washed with distilled water and carefully dried under vacuum at 30°C for 3 h. In order to ensure the complete removal of water and methylamine solution, one of the samples was dried in vacuum for 24 h. No additional loss in weight was observed. It was therefore concluded that the initial drying of 3 h was sufficient. The weight loss of the material was found by recording the weight before and after amine treatment.

Infra-red spectroscopy

The infra-red spectra were recorded on a Perkin–Elmer model 397 spectrophotometer using the KBr pellet technique. A blank KBr pellet was always used in the reference beam to avoid scattering due to KBr. Fibres were cut into fine powder and sieved through a 300 mesh to reduce the effect of orientation.

X-ray diffraction

X-ray diffractograms of the samples were recorded on a Philips 1009 unit fitted with texture attachment and vertical goniometer, operated at 35 kV and 20 mA. Monochromatic radiation from a copper target was obtained by means of a nickel filter. The fibres were cut into fine powder and sieved through a 300 mesh to ensure that there was randomization and disorientation of the crystallites. A pellet of 1 cm diameter was prepared for the X-ray diffractometric studies. The radial scans were taken in the 2θ range from 10 to 30°. The speed of the strip chart recorder was 2 cm min^{-1}.

Table 1 Sample specifications (initial denier = 1.4, initial birefringence = 0.008, residence time on heated surface = 11.765 s)

Draw ratio	Temperature of drawing (°C)	Viscosity-average molecular weight	Roller steam pressure (kg m^{-2})
2.65	36	16700	0/0
3.00	36	16300	0/0
4.00	36	15350	0/0
5.00	36	14150	0/0
2.65	170	13800	8/8
3.00	170	12600	8/8
4.00	170	11200	8/8
5.00	170	10300	8/8
2.65	200	13700	15/15
3.00	200	12900	15/15
4.00	200	11700	15/15
5.00	200	9900	15/15

Scanning electron microscopy

Aminolysed filaments were examined, in the secondary mode, in a Cambridge 'Stereoscan' model S4-10 scanning electron microscope (SEM), with an acceleration voltage of 5 kV and scanning rate of 0.04 s/line and 40 s/frame. Occasionally an ISI DS-130 scanning electron microscope was employed to photograph the fibres.

All filaments were mounted on specimen holders (SEM mounts) using silver paint and coated with gold in a thermal evaporation unit. Samples were rotated during the coating operation to achieve gold coatings of uniform thickness.

RESULTS AND DISCUSSION

Loss in weight

The process of aminolysis is mainly due to the degradation phenomenon and dissolving out of some disordered portions. Therefore, all the aminolysed samples showed decrease in weight subsequent to amine treatment.

Figures 1, 2 and *3* represent graphs of weight loss *versus* time of treatment for three different sets of samples drawn at 36, 170 and 200°C. It can be seen from these three figures that the percentage weight loss increases with increase in time of treatment for fibres of different histories (draw ratio and drawing temperature). However, the rates of increase of weight loss are different for different intervals of time. For example, fibres having draw ratio 4.0 and drawn at 36°C have a rate of increase the same as that of fibres of draw ratio 2.65 during the period of treatment up to 6 h; but during the period of treatment between 6 and 8 h, the rate of increase of the weight loss for fibres having draw ratio 4.0 slows down to some extent. Therefore, this curve meets the curve drawn for the sample of draw ratio 2.65. Such differences in the rates of weight

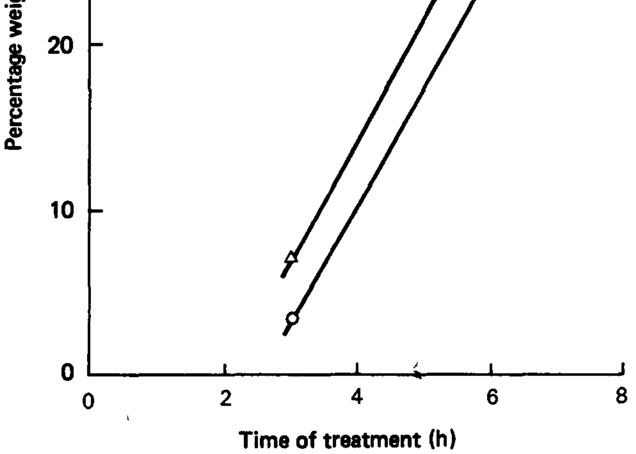

Figure 1 Loss in weight of PET fibres (drawn at 36°C) treated with 40% methylamine solution

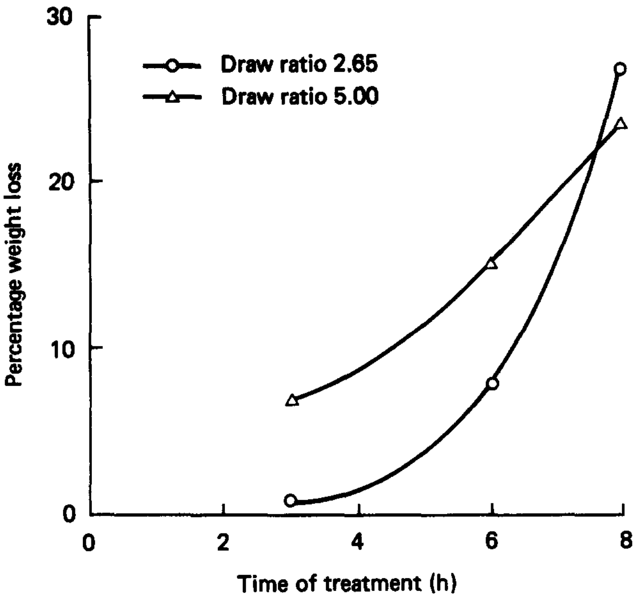

Figure 2 Loss in weight of PET fibres (drawn at 170°C) treated with 40% methylamine solution

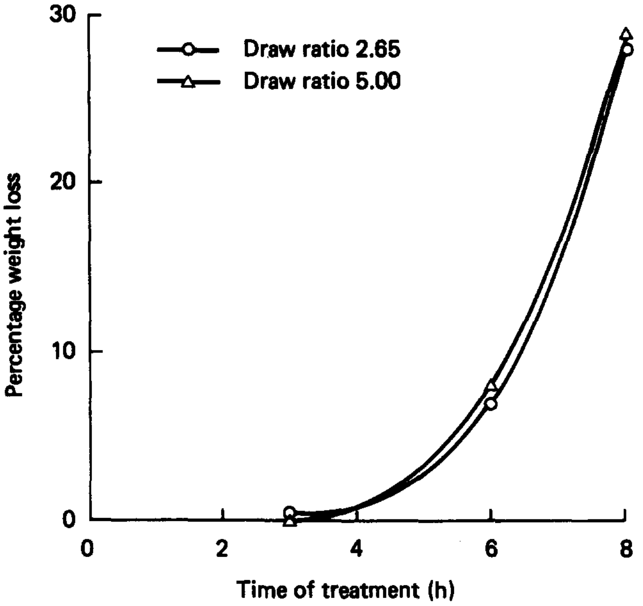

Figure 3 Loss in weight of PET fibres (drawn at 200°C) treated with 40% methylamine solution

loss over different durations of time were also observed in the case of two other sets of samples drawn at 170 and 200°C (*Figures 2* and *3*).

Figure 1 shows that the same amount of weight loss may occur for fibres having the draw ratio of 2.65 and 4.00 drawn at 36°C if the aminolysis is carried out for 7.75 h. Similarly, in the case of fibres drawn at 170 and 200°C (*Figures 2* and *3*), the curves corresponding to the draw ratio of 2.65 and 5.00 cross each other at 7.5 and 4.0 h, respectively. On the basis of the above results, it can be supposed that the fibres having higher draw ratio may show a higher amount of etching during the period up to 6 h and decrease later on.

Crystallinty measurement

Infra-red spectroscopy. In the infra-red spectrum of PET, several bands change their intensity on crystallization during processing or chemical treatment. Some bands become stronger and others weaker, viz, 973, 895, 1453 and 1370 cm^{-1}. Correlation of the intensities of these bands with crystallinity has been investigated by Cobbs and Burton[10], using the crystalline band 972 cm^{-1} to follow the crystallization as the polymer is heated. There are also bands that do not change their intensity on crystallization during processing or treatment, viz the bands at 1410, 1018 and 874 cm^{-1}. Therefore, the crystallinity index of the PET fibres was calculated by using the band at 1410 cm^{-1} as an internal standard and 868 cm^{-1} as crystalline band. The formula used was

$$\text{crystallinity index, } CI = A_{868}/A_{1410} \qquad (1)$$

where A_{868} and A_{1410} are the absorbances at 868 and 1410 cm^{-1} respectively.

X-ray diffraction. The measurement of crystallinity by X-ray diffraction methods has always posed problems to workers in the field. It involves the assumption of a two-phase model. Experimental methods to measure the crystallinity by separating the contribution due to different crystalline phases have been reported by several workers[11,12]. In all these methods, the separation of intensity of crystalline scattering from that of total scattering involved many assumptions. Hence, in the present work, it was though interesting to calculate the order factor in the sample by a relatively simple but reproducible method. The change in the lateral order was followed by the change in resolution of the peaks in the equatorial scan by using the method of Manjunath *et al.*[13].

The resolution factor, *RF*, of three peaks for PET was calculated from the formula:

$$RF = \frac{m_1 + 2m_2}{h_1 + h_2 + h_3} \qquad (2)$$

where h_1, h_2 and h_3 are the heights of the maxima from the appropriate baseline drawn between $2\theta = 10°$ and $2\theta = 30°$, and m_1 and m_2 are the heights of the minima between these two peaks.

When the resolution is completely lost, *RF* tends to 1, and conversely *RF* tends to 0 when the resolution is maximum. Thus *RF* is inversely related to the lateral order. Hence the value $1 - RF$, which is referred to as the crystallinity index, is found to be directly proportional to the lateral order of the sample.

The crystallinity index values calculated from infra-red spectroscopy and X-ray diffraction methods for some of the samples studied in the present investigation are tabulated in *Table 2*. It is evident from the table that crystallinity values initially decrease for 3 h of amine treatment for fibres of all draw ratios and drawn at different temperatures. However, when the time of amine treatment was increased, the crystallinity values increased rapidly for 6 and 8 h of treatment for all fibres. Similarly, the comparison for fibres having the same draw ratio and same time of amine treatment revealed that crystallinity was lower when the temperature of drawing was higher.

The initial decrease in the crystallinity value for the treatment of 3 h indicates that, as a result of swelling, there is considerable destruction of crystallites or that the smaller crystallites have been partially dissolved. An increase in the time of treatment leads to more and more dissolution of disordered regions, leaving the larger

Table 2 Crystallinity in PET fibres treated with 40% methylamine solution

Draw ratio	Temperature of drawing (°C)	Time of treatment (h)	Crystallinity index	
			Infra-red	X-ray
2.65	36	–	0.27	0.46
2.65	36	3	0.23	0.25
2.65	36	6	0.69	0.88
2.65	36	8	0.94	0.97
4.00	36	–	0.35	0.50
4.00	36	3	0.24	0.31
4.00	36	6	0.36	0.68
4.00	36	8	0.64	0.95
2.65	170	–	0.27	0.42
2.65	170	3	0.23	0.24
2.65	170	6	0.28	0.45
2.65	170	8	0.51	0.98
5.00	170	–	0.38	0.48
5.00	170	3	0.29	0.25
5.00	170	6	0.39	0.33
5.00	170	8	0.43	0.75
2.65	200	–	0.30	0.54
2.65	200	3	0.16	0.22
2.65	200	6	0.33	0.40
2.65	200	8	0.35	0.74

crystallites unaffected, and thereby yielding a larger value for overall crystallinity. Investigation using infra-red spectroscopy also leads to similar conclusions.

Crystallite size

The size of the crystallites in a polymer system plays a key role in determining the structural properties and morphology. Therefore, in the present work, it was thought interesting to gain more information about the degradation phenomenon of PET due to methylamine by measuring the crystallite size. Such measurement is based on the fact that a highly ordered region possesses the characteristics of an optical diffraction grating[14]. The average crystallite dimension was determined by the Sherrer formula

$$D=\frac{K\lambda}{\beta\cos\theta}$$

where D is the crystallite size in direction perpendicular to the plane corresponding to the measured reflection, λ is the wavelength of radiation used (1.542 Å), K is a constant, β is the half maximum breadth in radians and θ is the Bragg's angle. K varies between 0.9 and 1.1 and a value of 1.0 has been used for these calculations.

The values obtained for the crystallite size using the Sherrer formula are given in *Table 3*. It is interesting to note that, for all the fibres under investigation, there is a sudden drop in the average crystallite size after degradation for 3 h. However, the crystallite size does increase when treatment was carried out for 6 and 8 h. Since the values of crystallite size observed experimentally represent an average for the entire material, it can be presumed that the initial swelling at 3 h and partial dissolution leads to a much smaller average crystallite size. But when the time of treatment is increased, the smaller crystallites and disordered regions are completely dissolved, giving a higher average. At the treatment time of 8 h the crystallite size has a maximum value because all the smaller crystallites are completely attacked and the fibre crumbles to powder. If we recall the results of crystallinity by X-ray and infra-red methods, a similar trend of a sudden drop at 3 h was observed. In addition to the increase in the value of crystallinity and crystallite size due to dissolution, it is also likely that some solvent-induced crystallization or disorientation takes place.

Further, it is interesting to note that the crystallite size increases in the directions perpendicular to the planes (110) and (100) for all the samples under investigation. However, the crystallite size calculated from the reflection (010) shows an increase for fibres drawn at 36°C but reveals a decrease for fibres drawn at 170 and 200°C.

Typical X-ray diffractograms for some of the samples are depicted in *Figures 4*, *5* and *6*. It can be seen that an additional reflection occurs at an angle of $2\theta=12.5°$ for all the samples treated for 8 h. The presence of this extra peak was suspected to be due to reflection from planes (001). Therefore, calculation of d for this plane, using the values of the unit cell reported in the literature[15], was carried out. The value thus obtained was 8.7 Å, whereas the value of d obtained for $2\theta=12.5°$ was found to be 7.1 Å. The discrepancy appears to be rather large but possibly could occur due to lattice distortions and orientation as a result of drawing and heat treatment during fibre manufacturing.

Scanning electron microscopy

The morphology of the aminolysed PET fibres was investigated using scanning electron microscopy. The aminolysis carried out for 3 h for all the samples does not alter the morphology of the fibre significantly. From two such photographs (*Figures 7* and *8*), it appears that the fibre surface is not modified, though slight weight loss (~5%) was observed. Indirectly, it means that the weight loss could be due to the removal of oligomers.

When the samples were treated for 6 h, a large amount of cracking was noticed as shown in *Figures 9*, *10* and *11*,

Table 3 Crystallite size in PET fibres treated with 40% methylamine solution

Draw ratio	Temperature of drawing (°C)	Time of treatment (h)	Crystallite size (Å)		
			$D_{(010)}$	$D_{(110)}$	$D_{(100)}$
2.65	36	–	30	27	37
2.65	36	3	17	19	20
2.65	36	6	32	53	64
2.65	36	8	112	100	114
4.00	36	–	35	41	45
4.00	36	3	28	23	30
4.00	36	6	24	29	67
4.00	36	8	163	90	114
2.65	170	–	53	26	34
2.65	170	3	28	22	29
2.65	170	6	22	41	34
2.65	170	8	49	90	101
5.00	170	–	45	34	34
5.00	170	3	32	19	25
5.00	170	6	30	23	30
5.00	170	8	32	77	101
2.65	200	–	48	38	56
2.65	200	3	29	27	27
2.65	200	6	28	28	38
2.65	200	8	38	58	113

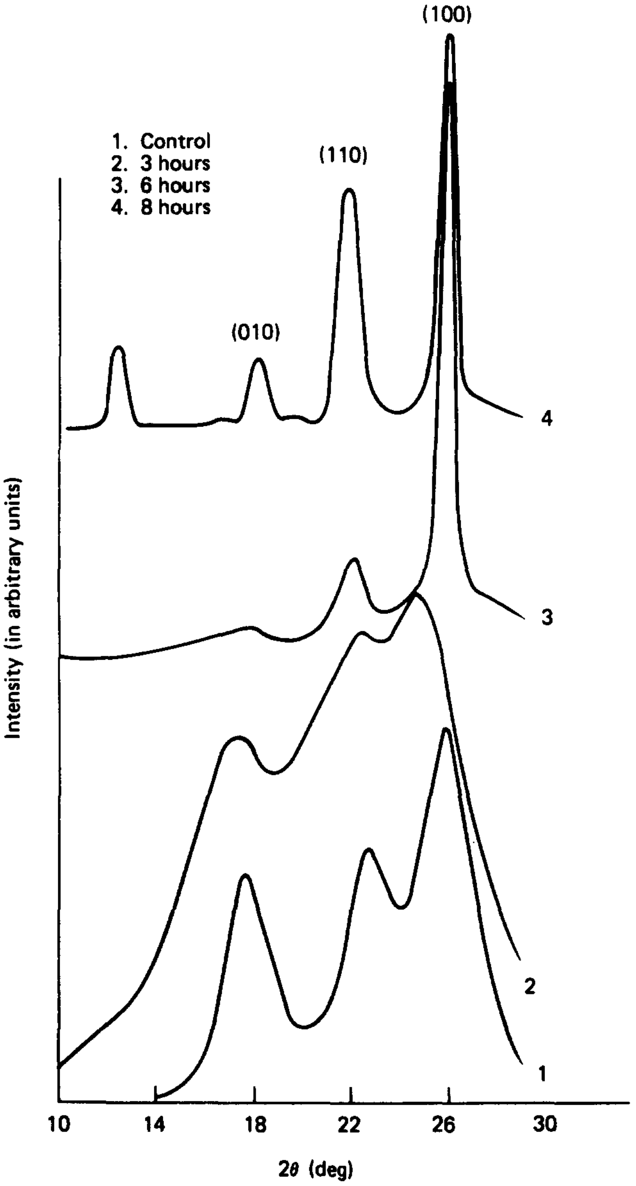

Figure 4 X-ray diffractograms of PET fibres (draw ratio 2.65, drawing temperature 36°C) treated with 40% methylamine solution

the effect being a maximum at the lower draw ratios. *Figure 9* reveals the type of cracks and striated structures observed subsequent to treatment. In general, these cracks propagate perpendicular to the fibre axis and in some cases follow a helical path along the cylindrical filament. It can also be seen that cracking does not appear for fibres having a higher draw ratio. Similarly, fibres having the same draw ratio but drawn at different temperatures show some variation in the pitch (average distance between consecutive cracks) of the spiral. These values, which are tabulated in *Table 4*, show that the distance between two cracks increases with draw ratio. It may also be noted from the table that the average distance between two cracks for fibres drawn at 170°C show comparatively higher values. For these fibres, longitudinal cracks were also noticed, which are quite distinct from those seen in fibres drawn at 36 and 200°C (*Figures 12* and *13*). The above results of aminolysis for 3, 6 and 8 h duration indicate that there may be an induction time of about 3 to 4 h before cracking develops. With increase in time of treatment, larger number of cracks developed; and finally after treatment for 8 h, the fibre was converted into powder (*Figure 14*). The cracking loosens the material and some loose discs are seen in the photograph.

A larger separation between two cracks at a higher draw ratio and non-occurrence of cracks at higher draw ratio of 5.0 indicate that the highly drawn PET fibre has an increased resistance to chemical degradation as well as cracking.

The cracking patterns seen in the present investigation indicate that the mechanism of cracking may not be only due to attack on the disordered portion by the amine. The regularity and mode of cracking remind one of chemical stress cracking phenomena. It was established from the studies of Baker[1] that the cracking could be correlated with the orientation of the film. In the PET fibres, some residual or internal stress remains. When such fibres come into contact with solvent, relaxation occurs, which would cause stress cracking without application of any load. However, the phenomena may not be due only to environmental stress cracking, as a large amount of weight loss also occurs. Thus, the combination of degradative phenomena due to amine and the presence of built-in stresses bring about enhanced cracking and

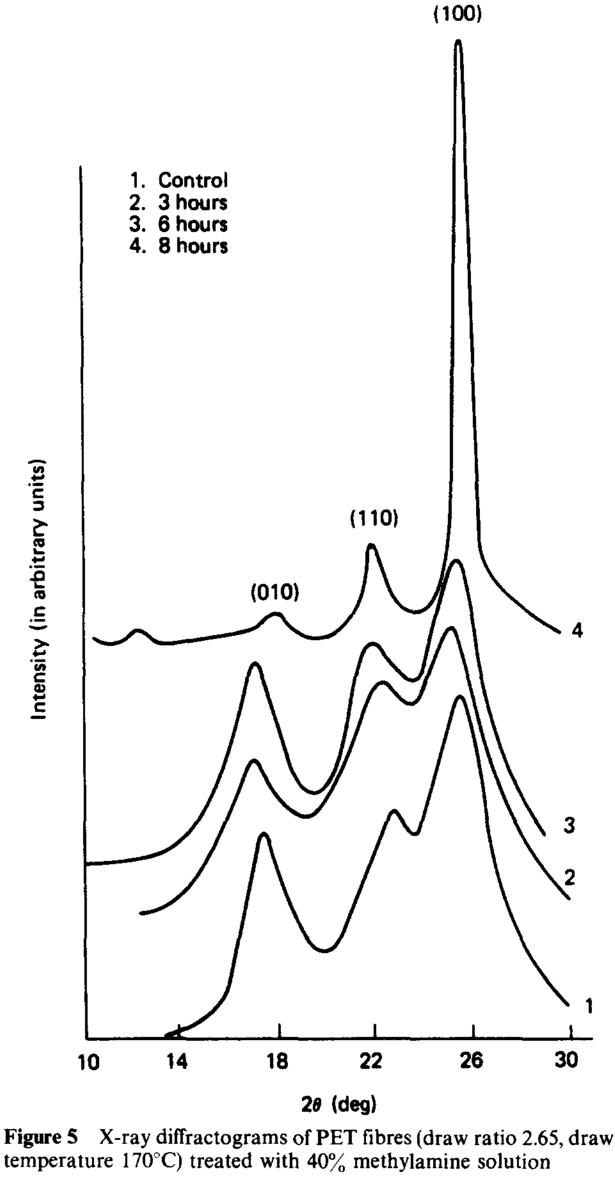

Figure 5 X-ray diffractograms of PET fibres (draw ratio 2.65, drawing temperature 170°C) treated with 40% methylamine solution

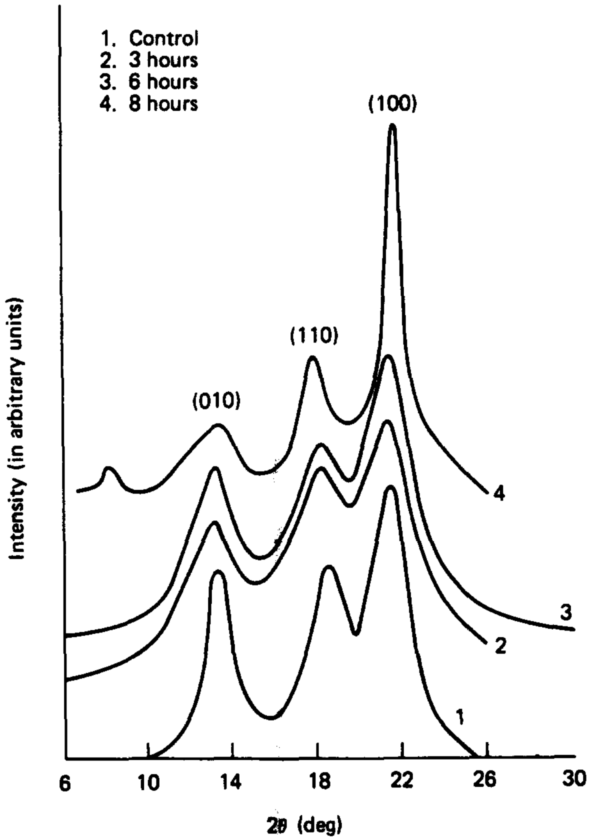

Figure 6 X-ray diffractograms of PET fibres (draw ratio 2.65, drawing temperature 200°C) treated with 40% methylamine solution

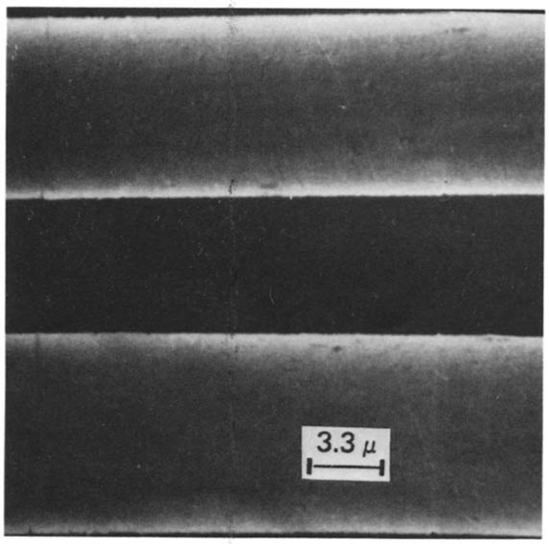

Figure 7 Electron micrograph of PET (draw ratio 2.65, drawing temperature 36°C) treated with methylamine for 3 h (3000 x)

degradation. It may be noted from *Table 4* that the average distance between two cracks for the fibres drawn at 170°C is much larger than for the fibres drawn at 36 and 200°C. It has been shown by earlier workers[16] as well as established from our previous results[17] that PET undergoes rapid structural changes particularly in the range 100–170°C (above T_g). Therefore, a large crystallite size and higher orientation[18] seem to resist the degradation by methylamine. However, unfortunately the distance between two cracks (2–5 μm) has no direct correlation with a structural parameter.

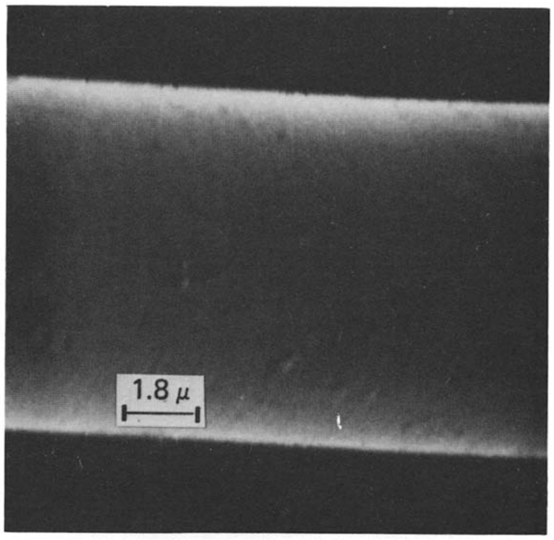

Figure 8 Electron micrograph of PET (draw ratio 4.00, drawing temperature 36°C) treated with methylamine for 3 h (5500 x)

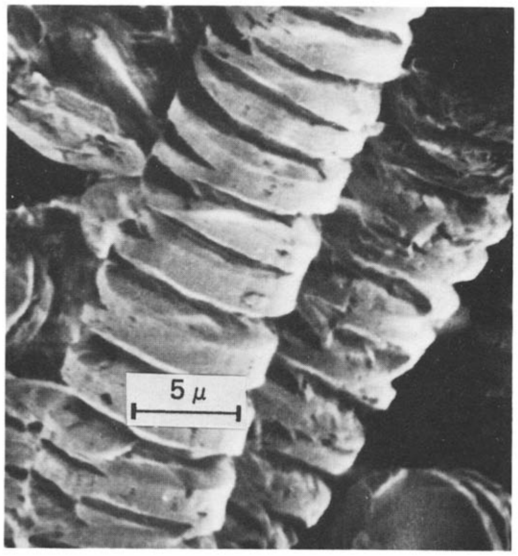

Figure 9 Electron micrograph of PET (draw ratio 2.65, drawing temperature 36°C) treated with methylamine for 6 h (3000 x)

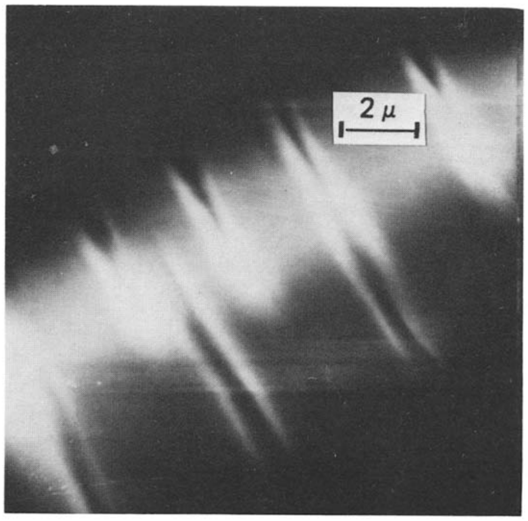

Figure 10 Electron micrograph of PET (draw ratio 4.00, drawing temperature 36°C) treated with methylamine for 6 h (5000 x)

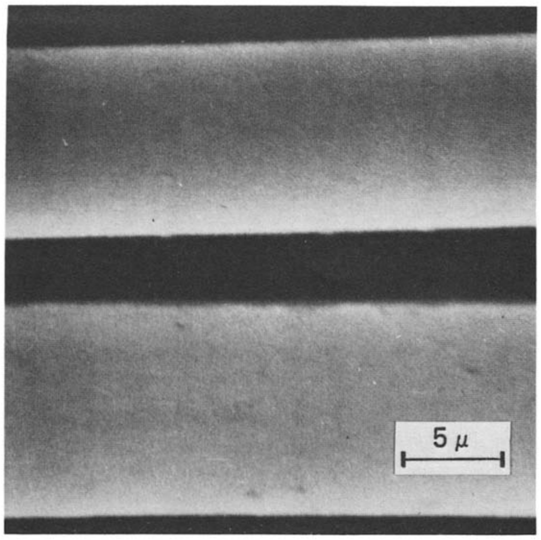

Figure 11 Electron micrograph of PET (draw ratio 5.00, drawing temperature 36°C) treated with methylamine for 6 h (3000×)

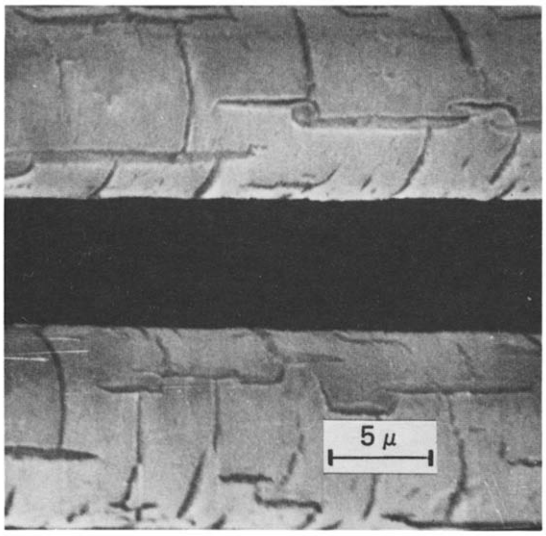

Figure 12 Electron micrograph of PET (draw ratio 2.65, drawing temperature 170°C) treated with methylamine for 6 h (2900×)

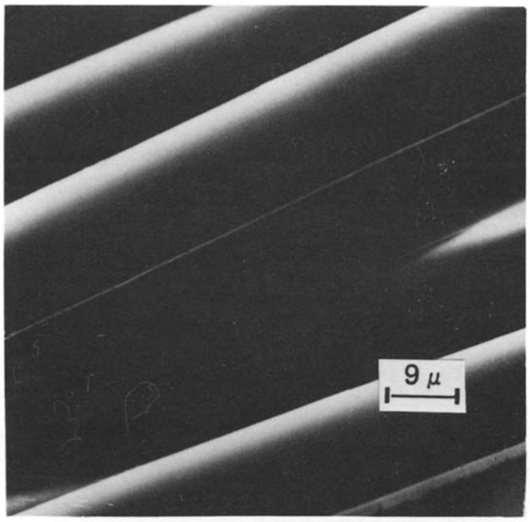

Figure 13 Electron micrograph of PET (draw ratio 5.0, drawing temperature 170°C) treated with methylamine for 6 h (1100×)

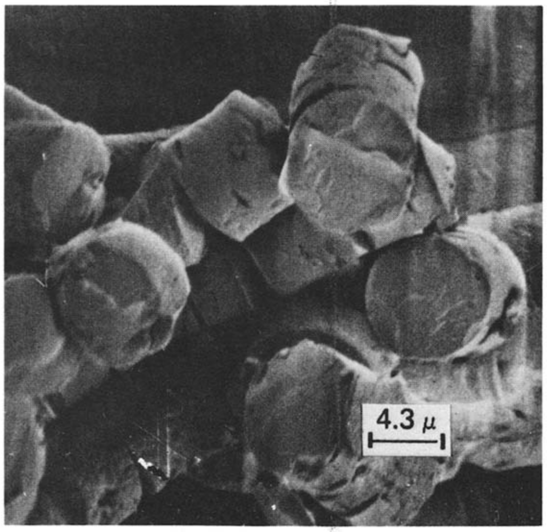

Figure 14 Electron micrograph of PET (draw ratio 2.65, drawing temperature 200°C) treated with methylamine for 8 h (2300×)

Table 4 Average distance between two consecutive cracks (pitch of spiral) for various PET fibres treated with 40% methylamine solution for 6 h

Draw ratio	Temperature of drawing (°C)	Average distance (μm)
2.65	36	1.97
3.00	36	2.11
4.00	36	2.21
2.65	170	3.88
3.00	170	5.15
2.65	200	2.72
3.00	200	5.40

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REFERENCES

1 Baker, W. P. *J. Polym. Sci., Polym. Phys. Edn.* 1962, **57**, 993
2 Dumbleton, J. H. *J. Polym. Sci. (A-2)* 1969, **7**, 667
3 Mocheria, K. K. and Bell, J. P. *J. Polym. Sci., Polym. Phys. Edn.* 1973, **11**, 1779
4 Mehta, R. E. and Bell, J. P. *J. Polym. Sci., Polym. Phys. Edn.* 1973, **11**, 1793
5 Farrow, G., Revens, D. A. S. and Ward, I. M. *Polymer* 1962, **3**, 17
6 Murray, R., Davis, H. A. and Tucker, P. *J. Appl. Polym. Sci.; Appl. Polym. Symp.* 1978, **33**, 177
7 Tucker, P. and Murray, R. 'Proc. Electron Microscopy Society of America', 1975, p. 82
8 Kurita, T. *Kobunshi Kagaku* 1969, **26**, 571
9 Sweet, G. E. and Bell, J. P. *J. Polym. Sci., Polym. Phys. Edn.* 1978, **16**, 2057

10 Cobbs, W. H. and Burton, R. L. *J. Polym. Sci.* 1953, **10**, 275

11 Roldan, C. G., Rahl, R. and Paterson, A. R. *J. Polym. Sci.* 1965, **8**, 145

12 Heuvel, H. M., Huisman, R. and Lind, K. C. J. B. *J. Polym. Sci., Polym. Phys. Edn.* 1976, **14**, 921

13 Manjunath, B. R., Venkatraman, A. and Stephan, T. *J. Appl. Polym. Sci.* 1973, **17**, 1091

14 Housman, J. A. and Walter, N. M. 'Physical Methods in Chemical Analysis', Academic Press, New York, Vol. I, 1960

15 Daubney, R. de and Bunn, C. W. *Proc. R. Soc. Lond. A* 1954, **226**, 331

16 Weigmann, H. D., Scott, M. G., Ribnick, A. S. and Rebenfield, L. *Text. Res. J.* 1976, **46**, 574

17 Patel, V. H., M.Sc. (Tech.) Thesis, University of Bombay, Bombay, 1984

18 Bhat, N. V. and Naik, S. G. *Text. Res. J.* 1984, **54**, 868