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High modulus/high strength poly-(*p*-phenylene benzobisthiazole) fibres

Part 2 *Structure–property investigations*

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Wide-angle X-ray diffraction studies of poly-(*p*-phenylene benzobisthiazole) fibres from Part 1 of this work were undertaken to examine fibre structural changes associated with the heat treatment process and which contribute to the observed significant enhancement of mechanical properties. Crystallite size perpendicular to the fibre axis increases from approximately 2 nm in as-spun fibres to 10 to 12 nm in fibres heat treated at temperatures above 600° C. Fibre tensile strength was found to increase with this increase in the extent of the lateral molecular order. However, tensile modulus and tensile strength did not depend directly on heat treatment parameters but rather indirectly through the effect of applied tension during heat treatment on the overall axial orientation. Higher values of fibre tensile modulus and tensile strength were exhibited by the more highly oriented fibres.

1. Introduction

Investigations of structure–property relationships for high performance materials based on extended chain macromolecules are few in number owing to the relative infancy of this class of materials. The present availability of high modulus/high strength fibres of poly(*p*-phenylene benzobisthiazole) (PBT) in conjunction with the means of altering structure and properties of these fibres through heat treatment processing [1] provides for an excellent opportunity in which to pursue structure–property relationships of extended chain polymers. In Part 1 of this work [1] the mechanical property enhancement resulting from heat treatment processing of as-spun PBT fibres was discussed; fibres possessing tensile moduli as high as 300 GPa with tensile strengths of 3 GPa were being produced. Part 2 of this work is concerned with PBT fibre morphological changes resulting from such heat treatment and the relationship between fibre structural characteristics and mechanical properties.

Structural investigations of PBT fibres morphology have been carried out by a number of authors [2–7]. Initial X-ray diffraction work by Adams *et al.* [2] on as-spun PBT fibres suggested a simple hexagonal packing of axially staggered periodic cylinders (the rod-like PBT molecules) to describe the structural organization. Upon heat treatment, the lateral molecular order in PBT fibres is significantly enhanced [3–7]. Structural models for heat treated PBT fibres consider the stiff PBT molecules to be laterally well ordered but still with translational shifts along the chain axis such that a true three-dimensional crystalline order is absent. Based on electron diffraction and dark-field electron microscopy studies of fibre fragments by Roche *et al.* [3], Minter *et al.* [6] and Shimamura *et al.* [7] an apparent "crystallite" size of 8 to 12 nm in width and approximately 1.5 to 5 times as long may be

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taken as a measure of the extent of the local lateral molecular order in typical heat treated PBT fibres. Additionally, Roche *et al.* [3] proposed from their electron microscopy observations that the lath-shaped ribbons of the PBT fibre are composed of finer microfibrils which consist of a succession of these narrow "crystallites" embedded in a somewhat less ordered, but highly oriented, matrix of PBT.

While these structural studies have indicated a substantial improvement in structural perfection resulting from heat treatment, the limited number of fibre samples examined precluded any correlation of structural characteristics with mechanical properties or with processing conditions. Additionally, the majority of these works have been concerned with electron microscopy techniques where only localized structural information may be examined. Recently we employed wide-angle X-ray diffraction to examine PBT fibre structural characteristics in fibres possessing differences in mechanical properties resulting from heat treatment variations [8]. These results have indicated the importance of overall axial molecular orientation and the degree of lateral molecular ordering on PBT fibre properties, particularly the tensile modulus and tensile and shear strengths of the fibres. The present work is concerned with the results of X-ray diffraction investigations of heat treated PBT fibres where a more systematic comparison between structure, properties and processing is provided from the heat treated fibres generated as reported in Part 1 of this work [1].

2. Experimental details

Wide-angle X-ray diffraction studies were carried out employing both diffractometric and flat film techniques on a representative number of fibres taken from the heat treatment studies discussed in Part 1 of this work [1]. Fibre samples were prepared by carefully winding a length (~ 30 cm) of yarn (20 filaments) around cardboard mounts to provide a bundle of fibres roughly 8 mm × 1.5 mm over the hole in the mount. Flat film fibre patterns were obtained with a Warhus (Statton) camera employing pinhole (0.2 mm) collimation and a sample to film distance of 18 mm. Diffractometer (2θ) scans of equatorial reflections were obtained on a Siemens D-500 diffractometer employing line focus collimation. Incident beam diffractometer slits of 0.3° (2θ) with a final slit of either 0.05° or 0.15° (2θ) were used for a scan rate of 0.2° ($2\theta\,\mathrm{min}^{-1}$). Azimuthal breadths of major equatorial reflections (measured as the full width at half maximum intensity (FWHM)) were also obtained from intensity scans with rotation of the fibre sample about a direction perpendicular to the incident beam (Huber pole figure device). Cu$K\alpha$ tubes operated at 40 kV and 30 mA were used for both the Warhus camera and Siemens diffractometer. A lead aperture was placed over the fibres to prevent spurious scattering from the cardboard mount.

Selected single filament flat film patterns were recorded on a Phillips microfocus camera with an Elliot rotating anode generator (Cu$K\alpha$, 45 kV, 40 mA), at the Air Force Materials Laboratory [9]. Tensile mechanical properties reported here are taken from Part 1 of this work [1].

3. Results and discussion

Fig. 1 illustrates typical equatorial diffractometer traces observed for both as-spun and heat treated PBT fibres and presents the peak designation convention employed (e_1, e_2). The precursor as-spun PBT fibre [1, 10] used for this study exhibits two major equatorial reflections (e_1, e_2) corresponding to *d*-spacing values of 0.554 and 0.345 nm. The ratio (e_1/e_2) of these *d*-spacing values is 1.6, close to the value of $\sqrt{3}$ suggested by Adams *et al.* [2] for hexagonal packing of cylinders as a means of interpreting diffraction data of as-spun PBT fibres. Considering that the molecular cross-section of PBT is more elliptical than circular and that only two broad reflections are available for structural analysis it seems reasonable that a near hexagonal packing arrangement of the rod-like molecules is sufficient to describe the structure of as-spun PBT fibres. The azimuthal spreads (FWHM, $\Delta\mu$) of the equatorial reflections e_1 and e_2 for this as-spun fibre are fairly small (15° to 18°) indicating that the rod-like PBT molecules are highly aligned in the fibre direction (i.e. Hermans orientation factor $f \simeq 0.87$). The tensile properties of this as-spun fibre (150 GPa modulus, 1.7 GPa strength) are impressive, illustrating the relative ease of obtaining high performance properties from a highly aligned array of rod-like molecules.

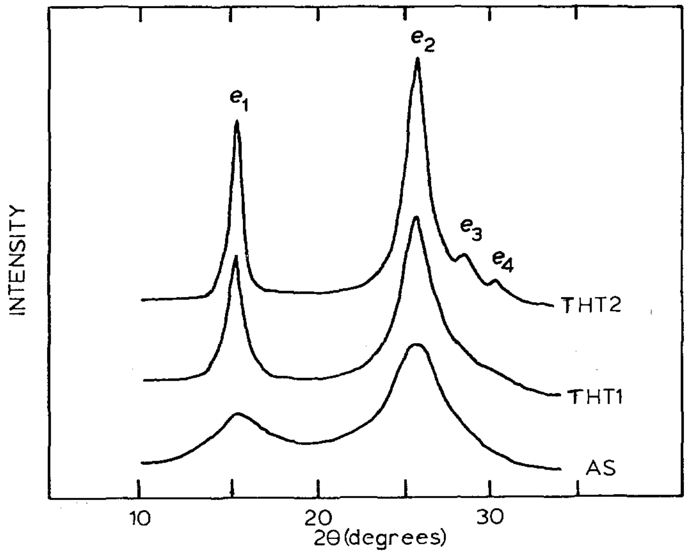

Figure 1 Typical equatorial 2θ scans of PBT fibres. AS, as-spun fibre; THT1, 400° C heat treated fibre; THT2, 600° C heat treated fibre.

Table I summarizes diffraction results and mechanical properties of fibres heat treated for 8 to 10 sec under an applied tension of approximately 130 MPa for heat treatment temperatures of 450 to 715° C. In the range of 10° to 35° scattering angle (2θ) all of these heat treated fibres exhibited four equatorial reflections (e_1 to e_4) corresponding to d-spacing values of 0.585, 0.351, 0.315 and 0.295 nm (see for example Fig. 1: THT2). The emergence of additional equatorial reflections (e_3, e_4) in the case of heat treated PBT fibres along with a shift of the spacing of e_1 and e_2 (with respect to as-spun values) indicates the existence of a higher degree of perfection of the lateral molecular order as well as of an increase in fibre density [3]. The d-spacing values and relative peak intensities of the four equatorial reflections (e_1 to e_4) correspond fairly well with the monoclinic packing arrangement proposed by Roche *et al.* [3].

TABLE I Comparison of PBT fibres heat treated at various temperatures

Heat treatment temperature (° C)	(Gaussian) lateral coherence size (nm)		Tensile modulus (GPa)	Tensile strength (GPa)
	e_1	e_2		
450	8.5	6.1	330	2.0
550	8.8	6.4	315	2.3
600	11.3	7.2	270	2.2
640	10.0	6.6	305	2.7
665	10.7	7.0	335	3.1
690	11.8	6.8	320	3.1
715	10.2	7.0	225	2.3
As-spun	1.8	1.9	150	1.6

8 to 10 sec residence times, 130 MPa tension.

Assuming that the peak widths are solely determined by the size of the lateral, coherently scattering regions, the Scherrer Equation 1 permits an estimate of the extent (L) of the lateral coherence. In Equation 1,

$$L_{hkl} = \frac{K\lambda}{(\mathrm{FWHM})_s \cos\theta_{hkl}} \qquad (1)$$

K is a constant usually assigned a value of 1, and λ and θ have their usual meaning for scattering. The value of FWHM to be used in Equation 1, however, should be corrected for any instrumental peak broadening. Instrumental broadening was evaluated, for the operating conditions used, by measuring the FWHM of the 0.4968 nm spacing diffraction peak ($2\theta = 17.84°$) of hexamthylenetetramine, which, due to its large crystal size should have negligible size broadening.

In addition to an increase in the perfection of the local lateral molecular order, increases in the extent of the lateral order are also observed as a result of heat treatment. As shown in Table I, the lateral coherence size (Gaussian corrected) associated with e_1 and e_2 increases with increasing heat treatment temperature. The local extent of the lateral molecular order (based on e_1) is roughly 2 nm in the as-spun fibre increasing to roughly 8 nm for a 450° C heat treatment and to 10 to 12 nm in fibres heat treated above 600° C. The 10 to 12 nm coherence sizes reported in Table I were based on a Gaussian profile correction. For Cauchy peak profiles, lateral coherence sizes of 11 to 13 nm are calculated. Secondly, these lateral coherence sizes should be considered as lower bounds due to the neglect of any peak broadening associated with paracrystallinity or other lattice distortions, correction for which would increase the size values reported here.

The Roche packing model suggests that the planes giving rise to e_1 and e_2 are approximately perpendicular ($\gamma = 95.2^\circ$) so that a comparison of *d*-spacing value with lateral coherence size for both e_1 and e_2 provides an estimation of the number of chains (unit cells) comprising the lateral coherence size. For the as-spun fibre such a comparison indicates bundles of approximately 20 chains comprise the coherence size whereas bundles of approximately 400 chains are calculated for fibres heat treated above 600° C. It is also interesting to note that the lateral coherence size (L) evaluated for reflections e_1 and e_2 differ in value. The ratio Le_1/Le_2 is approximately 1.5 based on the values in Table I. This size ratio indicates that the cross-section of a PBT "crystallite" is approximately rectangular with a ratio of side lengths of roughly 1 : 1.5.

Increases in the extent and degree of perfection of lateral molecular order (with respect to the as-spun fibre) are common to all of the heat treated fibres examined, with higher heat treatment temperatures providing greater increases. Table I shows that associated with higher heat treatment temperatures, higher tensile strengths are obtained as lateral molecular order is increased. However, this factor alone is not sufficient to explain the increases in strength and modulus as a result of heat treatment.

Table II compares PBT fibres which were heat treated at 640° C for various amounts of applied tension during heat treatment. A comparison of the fibre heat treated without tension with the tensioned heat treated fibres shows that while the local structure is highly developed for all fibres, significant differences in tensile strength and tensile modulus exist. Measurement of the azimuthal spread of the major equatorial reflections (e_1, e_2) of the fibres in Table II gave values of 12° to 14° for the fibre heat treated without tension, decreasing to 8° to 10° for the fibre heat treated with an applied tension of 190 MPa. This decrease in the azimuthal spread of the equatorial reflections is indicative of an increase in the overall molecular orientation as a result of the applied tension during heat treatment. The axial orientation is therefore seen as one of the main structural factors affecting mechanical properties of heat treated PBT fibres. Table II shows that higher tensile modulus and tensile strength results from higher applied tension during heat treatment which would be associated with higher degrees of axial molecular orientation in the tensioned heat treated fibres.

TABLE II Comparison of PBT fibres heat treated under various tensions

H.T. applied tension (MPa)	Lateral coherence size (nm)		Tensile modulus (GPa)	Tensile strength (GPa)
	e_1	e_2		
0	10.7	6.1	200	1.9
32	9.6	6.8	225	1.6
74	10.5	7.2	285	2.4
135	10.0	6.6	305	2.7
190	10.0	7.0	300	3.0
As-spun	1.8	1.9	150	1.6

640° C, 8 sec.

While the values of azimuthal spread of the equatorial reflections (e_1, e_2) measured by diffractometry indicate a trend of increased axial orientation with applied heat treatment tension (or equivalently resulting fibre modulus and strength), the actual values obtained (8° to 10°) are not truly representative of the actual axial orientation in a single PBT fibre. The relatively small degree of misorientation present in a PBT fibre causes some experimental difficulty in its precise measurement. The sample preparation procedure for X-ray diffraction of the fibres (wrapping a twenty-filament yarn around a cardboard mount) involves misorientation from slight wrap angle, filament splay within the yarn and wrap looseness which may contribute to the observed azimuthal breadths. Fig. 2 compares flat film X-ray diffraction patterns of a typical wrapped bundle of heat treated PBT fibres with that of a single fibre taken from the bundle. The effect of bundle misorientation on the observed azimuthal spreading of equatorial reflections (FWHM of 8.0° compared to 5.5°) is clearly indicated.

Fig. 3 compares flat film, single fibre patterns of several PBT fibres heat treated with 0, 32 and 190 MPa applied tension. It is evident from this

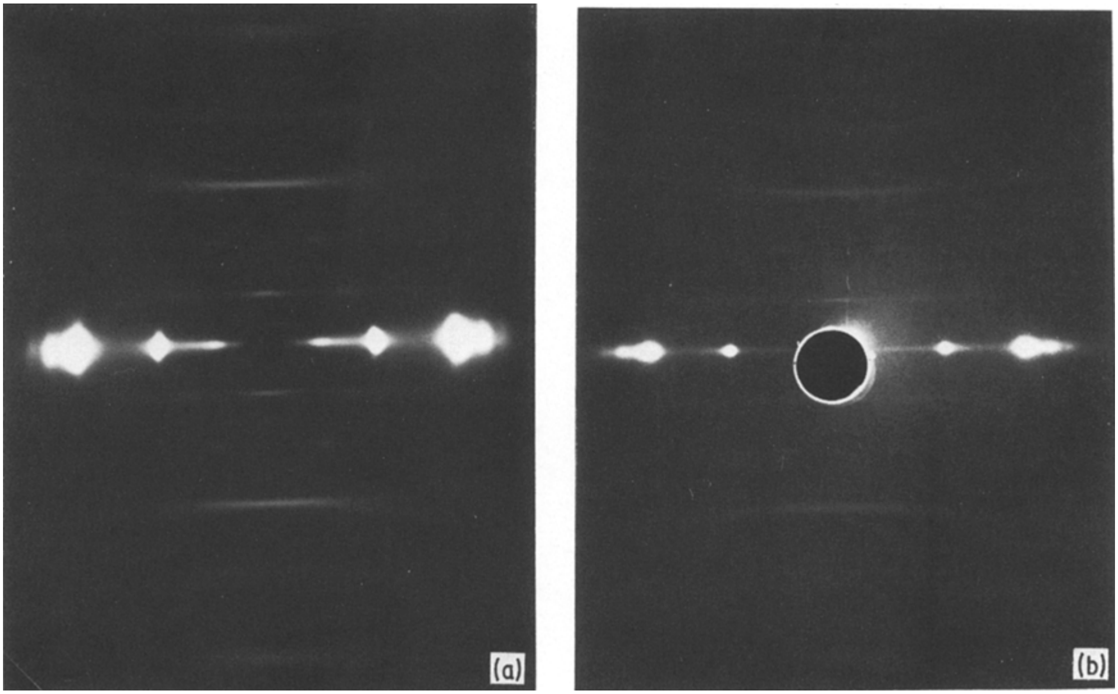

Figure 2 Comparison of (a) fibre bundle, and (b) single filament flat film X-ray diffraction patterns.

figure that higher applied tensions during heat treatment lead to higher overall molecular orientation with respect to the fibre axis. The azimuthal spreads of the two major equatorial reflections for the three fibres of Fig. 3 are 12.5°, 7.3° and 5.5°, respectively, for the 0, 32 and 190 MPa tension heat treatments (corresponding to $f = 0.93, 0.98$ and 0.99). Correspondingly, this increase in axial orientation is associated with significant increases in both tensile modulus and tensile strength as summarized in Table II. The increase of overall axial molecular orientation combined with increases in the extent and perfection of lateral molecular order are therefore seen as the primary factors affecting the tensile properties exhibited by heat treated PBT fibres. Tensile modulus and tensile strength of heat treated PBT fibres are not directly dependent upon the degree of heat treatment but indirectly as the heat treatment affects the overall molecular ordering.

Previous electron diffraction studies have shown that, *locally*, axial molecular orientation is high in as-spun PBT fibres (and films) and does not change substantially upon heat treatment [4, 6, 11]. The enhancement of axial orientation resulting from tensioned heat treatment observed in the fibre X-ray diffraction studies (Fig. 3) is suspected to be mainly associated with an enhancement of the overall axial alignment of the fibrillar morphology. Optical microscopy as well as scanning electron microscopy (SEM) investigation [10, 12] of as-spun PBT fibres has revealed the existence of a wavy or wrinkled fibrillar morphology of varying severity. Fibre deformation studies [10, 12] have shown a straightening out of the wrinkled morphology can result in an enhancement of the axial tensile modulus of as-spun PBT fibres (for example see Figs. 4a and b). SEM observations of the as-spun fibre used in the present study also indicate an initial non-uniform fibrillar organization which, after tensioned heat treatment, is observed to be highly oriented in the fibre direction with a more uniform fibre appearance. The tensioned, heat treatment processes therefore, perfects not only the local molecular organization, but also the *overall* fibrillar morphology.

Other investigations of high modulus/high strength fibres have suggested the use of relatively simple correlations between measures of axial molecular orientation and axial modulus. Northolt and van Aartsen [13, 14] have correlated

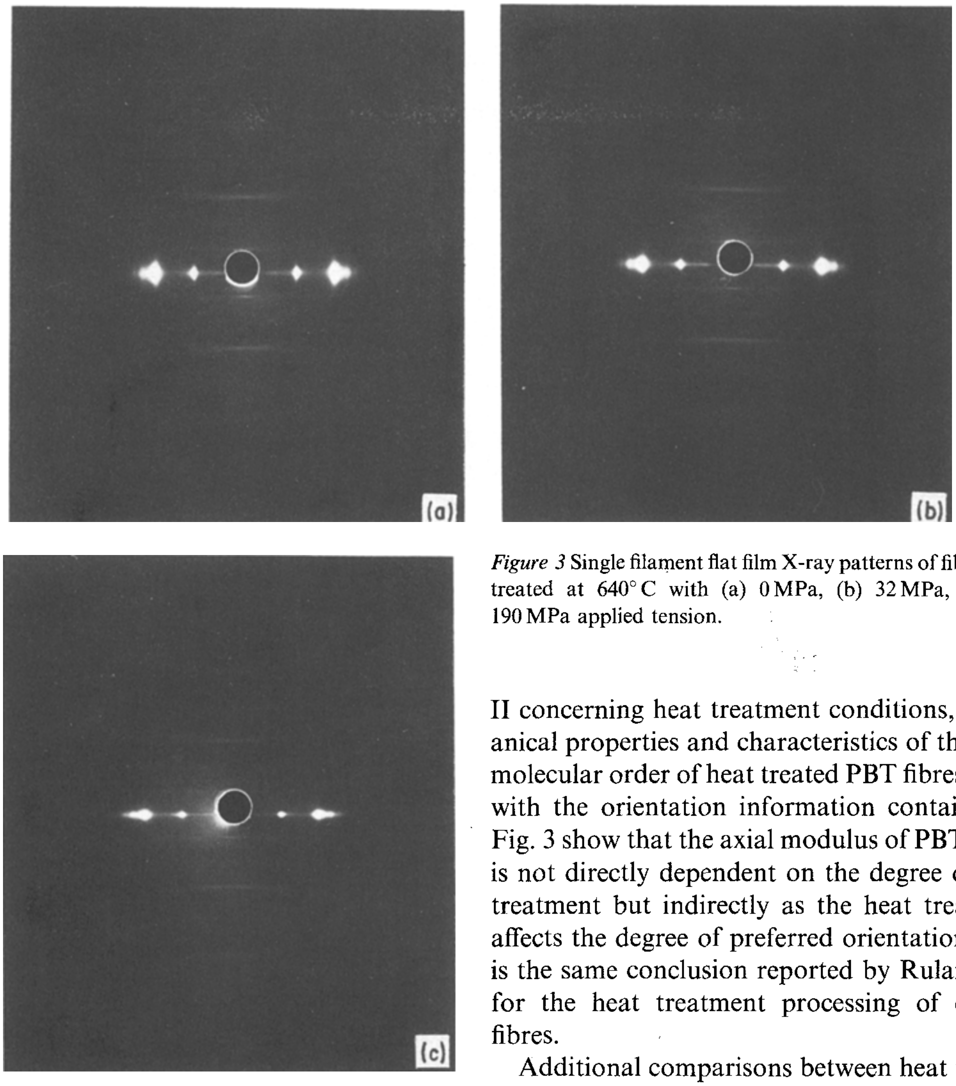

Figure 3 Single filament flat film X-ray patterns of fibres heat treated at 640° C with (a) 0 MPa, (b) 32 MPa, and (c) 190 MPa applied tension.

orientation with axial modulus for fibres of the extended chain polymer poly-(p-phenylene terephthalamide) [PPTA]. Similar correlations have been made by Ruland for carbon fibres [15]. The correlations observed between orientation and axial modulus for extended-chain PPTA fibres and for carbon fibres strongly suggest similar correlations may be usefully applied to heat treated PBT fibres which possess a similar fibrillar morphology. However, at present, due to the difficulties encountered in measuring axial orientation of heat treated PBT yarns and the lack of quantitative single fibre orientation studies, insufficient data exists for possible correlations to be examined in any detail. The findings summarized in Tables I and II concerning heat treatment conditions, mechanical properties and characteristics of the local molecular order of heat treated PBT fibres along with the orientation information contained in Fig. 3 show that the axial modulus of PBT fibres is not directly dependent on the degree of heat treatment but indirectly as the heat treatment affects the degree of preferred orientation. This is the same conclusion reported by Ruland [15] for the heat treatment processing of carbon fibres.

Additional comparisons between heat treated PBT fibres and carbon fibres are useful for a consideration of fibre strength characteristics. While material strength is sensitive to structural imperfections such as voids, inclusions or other flaws, strength variations are observed in similar carbon fibres whose fibrillar character differ in terms of perfection. Observations made by Bacon [16] indicate that of two carbon fibres possessing the same degree of preferred orientation and hence modulus, the fibre possessing the more pronounced fibrillar structure is weaker. Fracture in high modulus graphite fibres is believed to occur along interfibrillar boundaries preceded by plastic deformation including slippage between fibrils (and basal plane shear within microfibrils). These types of deformations are certainly more likely the more pronounced the fibrillar structure, i.e. longer

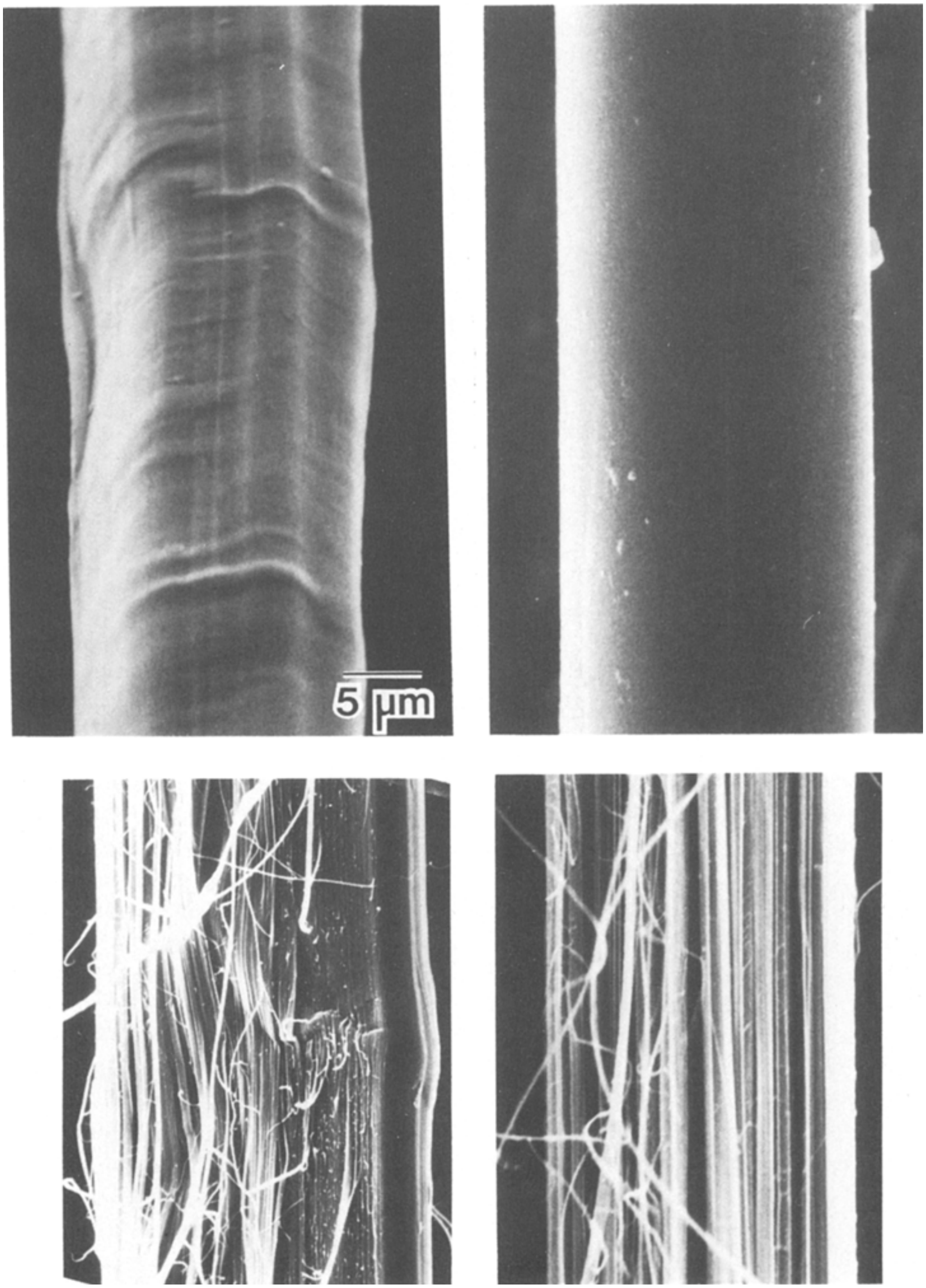

Figure 4 Comparison of surface undulations and interior fibrillar alignment in (a) as-spun, and (b) tensioned heat treated PBT fibres.

and straighter microfibrils, less inter-connectivity, more highly aligned and structurally more perfect fibrils [16].

If the tensile fracture of PBT fibres is associated with fibrillar boundaries, as suspected for carbon fibres [16], the nature of lateral molecular interactions is an important structural factor. In fact, because of the finite length of a PBT molecule, or of a fibril in a PBT fibre, tensile stresses in the fibrils are transferred through shear interactions which are directly dependent on the nature of the intermolecular forces. Lateral and/or shear stresses present in a highly aligned fibrillar structure of a fibre experiencing a tensile stress would be dependent on the preferred orientation of the fibre. If these shear or

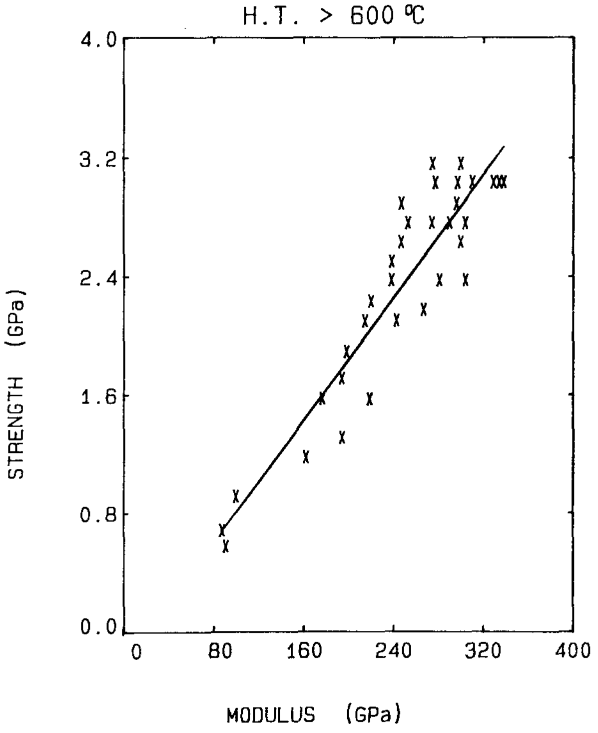

Figure 5 Strength and modulus of PBT fibres heat treated above 600° C.

transverse stresses are important in determining failure along fibrillar boundaries, then the tensile strength of the fibre should be sensitive to the preferred orientation.

The experimental difficulties encountered in measuring such high axial orientation in PBT fibres have been discussed earlier. However, if it is assumed that a simple relationship between preferred orientation and tensile modulus exists for PBT fibres as exists for PPTA and carbon fibres, then modulus values may be considered to provide a measure of orientation. Fig. 5 compares the tensile strength of PBT fibres heat treated above 600° C with their corresponding tensile modulus. With the assumption made above, it may then be inferred that the tensile strength of heat treated PBT fibres is dependent on the overall fibre orientation. The fact that the tensile failure of PBT fibres is associated with orientation and lateral interactions is evidenced in the large axial splitting observed for tensile fractured specimens. Fig. 6 shows a scanning electron micrograph montage of a typical PBT fibre tensile fracture exhibiting axial splitting. Additionally, the stronger, more highly oriented fibres would be expected to exhibit longer axial split tensile failures. Fig. 7 summarizes some preliminary measurements of tensile failure split lengths (length/fibre diameter ratio) and associated tensile strengths for some heat treated PBT filaments. Even with the high degree of scatter of such measurements a trend of larger split *L*/*D* ratios for higher tensile strengths is clearly indicated. The correspondence between longer fibre split length (or equivalently a smaller angle between the fibre axis and the fracture plane) and higher fibre strength is also consistent with simple models for the angular dependence of tensile strength in unidirectional composites (see [17]) and with models proposed by Papkov [18, 19] for the angular dependence of strength in anisotropic materials.

4. Conclusions

The heat treatment processing of as-spun PBT fibres results in a significant enhancement of the lateral molecular order of the rod-like PBT molecules. The breadths of equatorial reflections in as-spun PBT fibres suggest that the extent of individual ordered regions is quite small (2 nm), involving bundles of roughly twenty chains. In heat treated PBT fibres the local order is more highly developed and the extent of the laterally ordered regions (10 to 12 nm) involved bundles of approximately four hundred chains. The extent and perfection of laterally ordered

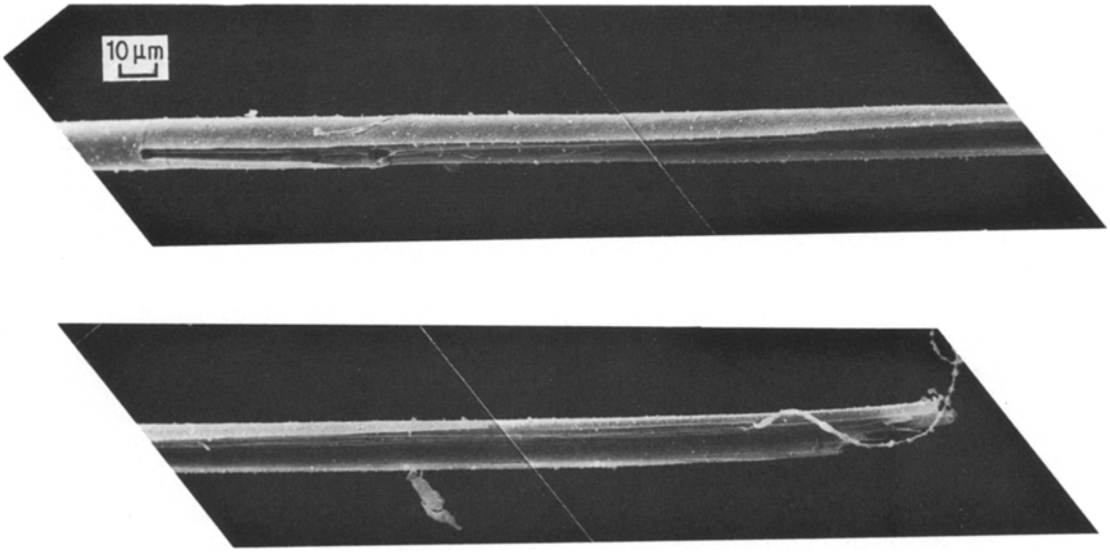

Figure 6 Scanning electron micrograph montage of typical heat treated PBT fibre tensile failure exhibiting axial splitting.

regions increases for increasing heat treatment temperatures. Tensile modulus and strength are observed not to directly depend on heat treatment conditions but indirectly as heat treatment affects the overall fibre orientation. The application of tension during heat treatment serves to enhance the overall orientation and hence significantly affects resulting heat treated fibre modulus and strength. The tensile strength of heat treated PBT fibres is sensitive to both the extent of the lateral molecular order and to the overall axial orientation. Higher heat treatment temperatures produce greater increases in the extent of the lateral molecular order (as measured by equatorial peak breadths) and improved lateral order is associated with increases in tensile strength (i.e. Table II). Additionally, higher tensile strength is observed for fibres possessing higher tensile modulus and for fibres exhibiting longer axial split tensile

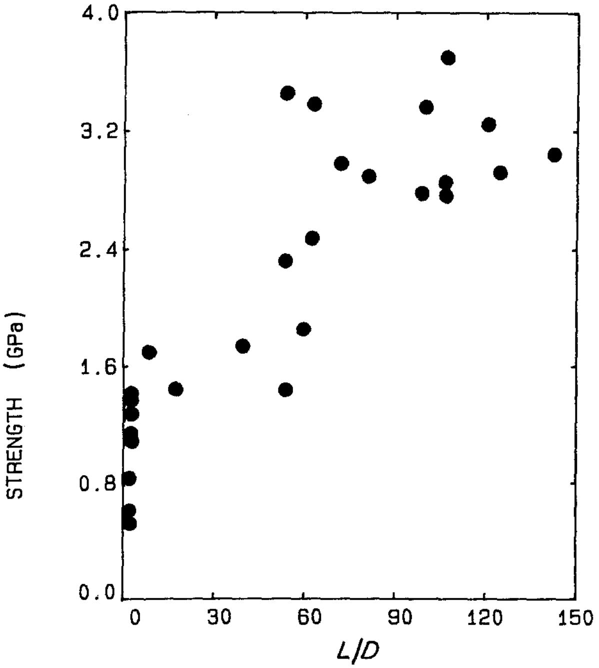

Figure 7 Tensile strength plotted against relative tensile fracture split lengths (L/D) of heat treated PBT single filaments.

failures, higher values of which represent higher overall axial orientation.

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