

# Processing/property relationships of a thermotropic copolyester: 2. Correlations between tensile properties and orientation

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The relationships between tensile properties and macromolecular orientation of a thermotropic copolyester of hydroxybenzoic acid and hydroxynaphthoic acid are investigated with respect to their differing processing histories. A correlation between modulus and orientation is described using simplified aggregate models and is shown to be independent of the method of sample preparation. Tensile strength also depends on the sample preparation conditions of extrusion temperature, deformation rate and the method of orientation. Tensile yield behaviour is predominant in samples of low orientation. Yielding can be characterized by a single strain level of 0.7%, similar in magnitude to values reported for lyotropic liquid crystalline polymers.

(Keywords: liquid crystalline polymers; tensile modulus; tensile strength; yield; molecular orientation; aggregate model)

## INTRODUCTION

In our previous paper<sup>1</sup> the properties of a thermotropic liquid crystalline polymer (TLCP) were correlated with variations in the deformational and thermal histories. In this paper, the relationships between tensile behaviour and macromolecular orientation are studied with consideration to these processing differences. The tensile parameters of modulus, strength and yield are investigated. Orientation parameters are determined from wide-angle X-ray diffraction (WAXD).

Samples of varying degrees of orientation were prepared using three different processing regimes. Material was oriented either by the use of variable length extrusion dies or the imposition of varying spinline take-up velocities. Samples were collected in the former case at extrusion temperatures of 290 and 300°C and in the latter case at 290°C.

This study has been facilitated by previous work that developed simple and direct procedures for the evaluation of the degree of molecular alignment<sup>2</sup>. Experimental results have been interpreted in accordance with techniques applied to earlier lyotropic liquid crystalline polymer (LLCP) systems<sup>3-5</sup> and with the results of earlier studies of TLCPs<sup>6-10</sup>.

## EXPERIMENTAL

Monofilament specimens of a thermotropic copolyester of 73 mol% hydroxybenzoic acid (HBA) and 27 mol% hydroxynaphthoic acid (HNA) (Hoechst-Celanese VECTRA<sup>®</sup> A950) were prepared by extrusion from an

Instron 3211 capillary rheometer and subsequent spinline extension by a variable speed take-up apparatus. Details of the experimental conditions employed in sample preparation and in the characterization of tensile properties and orientation are reported elsewhere<sup>1</sup>.

In this study  $\langle P_2 \rangle$ , orientation angle and  $\langle \sin^2 \theta \rangle$  are used to quantify the degree of macromolecular orientation present in the solidified extrudate. The second-order spherical harmonic coefficient  $\langle P_2 \rangle$  (Hermans' orientation factor) is defined as

$$\langle P_2 \rangle = \frac{3\langle \cos^2 \theta \rangle - 1}{2} \quad (1)$$

where  $\theta$  is the angle between the molecular axis of the mesogenic moiety and the filament axis (direction of extrusion). The limiting values of 1.0 and -0.5 for  $\langle P_2 \rangle$  indicate perfect axial and transverse orientation, respectively. This parameter is estimated from azimuthal intensity traces, as detailed elsewhere<sup>1</sup>.

The orientation angle represents the azimuthal breadth of the WAXD intensity trace at half peak height<sup>11</sup>. Smaller angles are indicative of higher orientations.

The orientation parameter  $\langle \sin^2 \theta \rangle$  is calculated from the azimuthal intensity profile using the expressions<sup>12,13</sup>

$$\langle \sin^2 \alpha \rangle = \frac{\int_0^{\pi/2} I(\alpha) \sin^2 \alpha \cos \alpha \, d\alpha}{\int_0^{\pi/2} I(\alpha) \cos \alpha \, d\alpha} \quad (2)$$

$$\langle \sin^2 \theta \rangle = 2\langle \sin^2 \alpha \rangle \quad (3)$$

where  $\alpha$  is the angle between the plane normal and the equator ( $\alpha=0^\circ$ ) and  $I(\alpha)$  is the azimuthal intensity distribution. In equation (3), random lateral texture in the fibre cross-section is assumed.

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## RESULTS AND DISCUSSION

## Modulus

Using data reported in our previous paper<sup>1</sup> and in other studies<sup>14,15</sup>, the relationship between initial modulus and macromolecular orientation is plotted in Figure 1. In earlier work<sup>1</sup>, samples were prepared by: (i) extrusion through dies of various  $L/D$  at 290°C and at a constant take-up velocity (draw ratio of 4); (ii) extrusion through dies of  $L/D$  10 and 133 at 290°C at various take-up velocities ( $3 < \text{draw ratio} < 12$ ); and (iii) extrusion through dies of various  $L/D$  at 300°C and at a constant take-up velocity (draw ratio of 4). In the first and third cases, differences in properties result from variations in die flow history only, while in the second case the differences result from changes in the spinline process. The agreement between these data and those published by Kenig<sup>14</sup> and Calundann *et al.*<sup>15</sup> validates the modulus–orientation dependency shown in Figure 1. In these other studies, the primary difference in orientation levels results from the imposition of a varied amount of extension applied in the post-extrusion spinline (similar to the second condition above). Kenig<sup>14</sup> investigated an HBA/HNA thermotropic copolyester (comonomer concentrations not reported) using a capillary rheometer at a melt temperature of 300°C. Dies of diameter 0.76 mm and lengths 25.4 and 101.6 mm were employed. Draw ratios between 3 and 9 were applied. Calundann *et al.*<sup>15</sup> present a tensile modulus and orientation dependency representative of an entire class of naphthoic acid based TLCPs.

No significant differences are apparent when the modulus–orientation angle relationships of samples prepared using the three methods here are compared. This indicates that the tensile modulus of extrudate prepared at the two different temperatures and orientated by either extrusion die dominated or spinline-dominated flow is solely a function of the level of orientation present

in the solidified extrudate. The stiffness of the sample produced is independent of the method of preparation. Clearly this demonstrates that the degree of molecular orientation is the primary factor in determining the modulus. High stiffness extrudates can be prepared by using either short dies with a small level of post-extrusion extension or poorly orienting, long dies with a higher degree of applied spinline extension.

It is appropriate to extend this analysis by the application of theoretical relationships that relate orientation distribution to tensile modulus. Ward's<sup>16</sup> aggregate model considers that the polymer consists of an aggregate of highly oriented units that differ in overall orientation. The resulting tensile modulus is determined by either a constant stress (Reuss average) or strain average (Voigt average) over the orientation distribution of these units within the material. In the case of fibre symmetry, mechanical anisotropy is characterized by five independent elastic constants. Where a high degree of molecular alignment exists, the prediction of tensile compliance can be further simplified<sup>9</sup> to

$$\frac{1}{E} = \frac{1}{E_c} + \frac{1}{G} \langle \sin^2 \theta \rangle \quad (4)$$

where  $E$ ,  $E_c$  and  $G$  are the tensile modulus, apparent chain modulus and shear modulus, respectively. This model has been used<sup>7</sup> to estimate the degree of disorientation  $\langle \sin^2 \theta \rangle$ , knowing the parameters  $E$ ,  $E_c$  and  $G$ , and has been examined<sup>8</sup> to explain an observed sensitivity to  $G$  for an HBA/HNA TLCP. Northolt<sup>4</sup> has presented an alternative relationship, based on oblong rather than cubic aggregates

$$\frac{1}{E} = \frac{1}{E_c} + \frac{1}{2G} \langle \sin^2 \theta \rangle \quad (5)$$

The predictions of this model agree well with the experimental data for medium and highly oriented poly(*p*-phenylene terephthalamide) (PpPTA) LLCP fibres<sup>4</sup>. This relationship differs from the previous in that it predicts a different value of shear modulus when the orientation distribution and tensile modulus are known.

From a plot of tensile compliance against  $\langle \sin^2 \theta \rangle$  (Figure 2) the values of  $E_c$  and  $G$  can be determined using linear regression. The data shown represent samples prepared in an earlier study<sup>1</sup> at the various temperatures and methods of primary orientation. The compliance has been approximated by the inverse of the filament modulus, which is valid for stiff materials away from major molecular transitions<sup>17</sup>. The intercept of the best-fit line predicts a value of  $122 \pm 35$  GPa (95% confidence limit) for the apparent chain modulus. This compares to an X-ray determined stiffness of  $97 \pm 9$  GPa calculated from the shift in the meridional pattern under stress<sup>6</sup>. Given the variability in the values reported here, a good agreement exists. From the slope of the best-fit line, shear modulus values of  $3.4 \pm 0.3$  and  $1.7 \pm 0.15$  GPa are predicted using equations (4) and (5), respectively. Based on torsional oscillation measurements, differing values of the dynamic/complex shear modulus of approximately 0.9 GPa<sup>7</sup> and 2.0 GPa<sup>8</sup> have been reported. Recently, Choy and coworkers<sup>18</sup> determined (using an ultrasonic technique) the shear modulus to be 1.47 GPa for a related material. Although it is difficult to make a valid comparison with dynamic and ultrasonic measurements, the lower value of 1.7 GPa

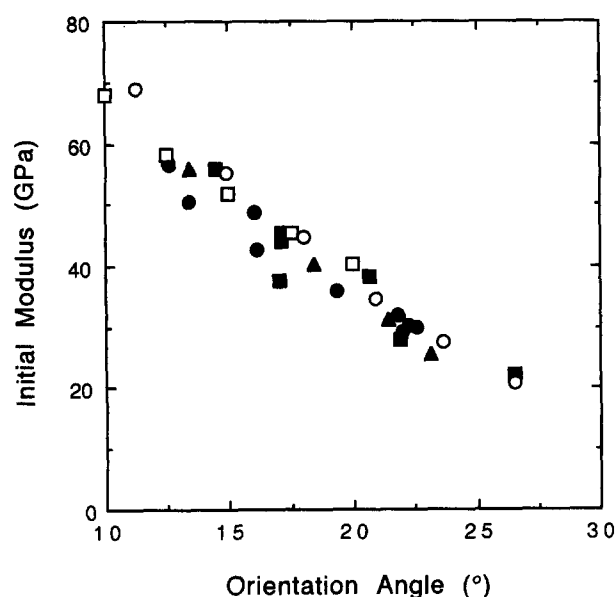


Figure 1 Relationship between initial modulus and X-ray orientation angle for an HBA/HNA TLCP. Filled symbols represent data from an earlier study<sup>1</sup> for samples having orientation differences developed either in the die (by varying die  $L/D$ ) or in the spinline (by varying draw ratio) at various extrusion temperatures: die 290°C (●); spinline 290°C (■); and die 300°C (▲). Data of Kenig<sup>14</sup> (○) and Calundann *et al.*<sup>15</sup> (□) are plotted for comparison

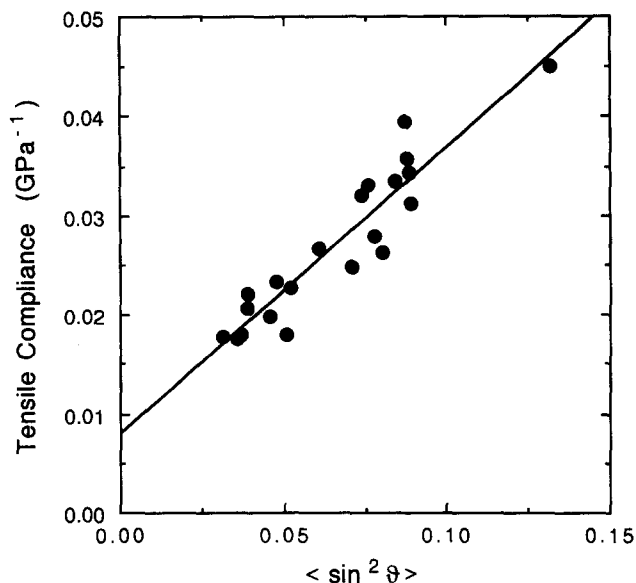


Figure 2 Application of the aggregate model (equations (4) and (5)) to the combined data of the earlier study<sup>1</sup> described in Figure 1

predicted using Northolt's derivation, which assumes oblong symmetry, is in good agreement.

This independent assessment of shear modulus confirms that this value is small compared to the tensile modulus. This results in a large sensitivity of axial stiffness to the degree of molecular orientation present (equations (4) and (5)). Where a stress is applied at a small angle relative to the chain direction, chain slippage and local rotation is favoured over chain stretching. This is related to the fibril structure of the oriented TLCP that is held together by weak, transverse van der Waals forces. In aramid fibres, such as PpPTA, the larger shear modulus results from the presence of stronger hydrogen bonds. For a given chain orientation distribution, aramid fibres exhibit a greater tensile modulus than thermotropic copolyesters due to stiffer interchain interactions<sup>15</sup>.

#### Tensile strength

The tensile strength of oriented polymers is less well understood than stiffness. It is influenced by a number of factors including molecular-weight distribution, chain disorientation with respect to the fibre axis, the presence of non-uniformities such as voids and impurities, and the microstructure of the cross-section<sup>19</sup>. In TLCPs the presence of a domain structure is an additional complicating factor. Commercial TLCP fibres are heat treated to increase the breaking strength. This process has been ascribed to an increase in molecular weight through solid-state polymerization and a refinement of the nematic structure, which does not affect the chain orientation distribution and, hence, the fibre stiffness. The heat treatment of an HBA/HNA TLCP<sup>8</sup> was reported to be associated with the conversion of a pseudo-hexagonal arrangement of polymer chains to a well-defined orthorhombic nematic structure resulting in a three-fold increase in strength. The fact that no significant change in modulus was observed confirms that tensile strength can be modified independently of stiffness and, hence, orientation. Yoon<sup>10</sup> has presented a theory of the strength of highly oriented LCP fibres based on the premise that load transfer occurs between polymer chains through intermolecular interactions and is governed primarily by intermolecular adhesion.

Figure 3 depicts the relationship between tensile strength (tenacity) and the degree of orientation for the specimens prepared using the three different processing conditions discussed earlier. The scatter in the data, resulting from the variability associated with both the measurement of tensile strength and orientation, makes conclusions difficult. It would appear, however, that tenacity is influenced by both the level of orientation and by the method of preparation. Tensile strength increases with increased orientation but the sensitivity of tenacity to changes in orientation differs depending on the extrusion conditions. This difference is most clearly seen in the more highly anisotropic specimens (i.e.  $\langle P_2 \rangle$  greater than 0.925). The highly oriented samples produced using the short dies and a low level of fixed spinline extension at 290°C (solid circles) are associated with lower tensile strength values. The corresponding tenacity values for the materials extruded at the higher temperature under the same conditions and under the condition where orientation was developed primarily by spinline-applied extension are greater. This dependence on sample preparation technique agrees with a previous result where it was observed<sup>1</sup> that the tenacity can vary independently of the initial modulus and, therefore, orientation. In the region of  $\langle P_2 \rangle$  equal to 0.9, the effect of preparation method is less significant.

The differences in tenacity at equivalent levels of anisotropy result from changes in extrudate microstructure (e.g. variation in chain-end free volume and defects), since no change in molecular weight is expected between samples. Conceivably, a defect structure developed in extrusion exists in the highly oriented samples prepared using the short dies at 290°C. Extrusion pressure has been identified previously<sup>1</sup> as a potential factor acting to influence tenacity and may offer an explanation. The lower temperature of 290°C is closer to the melting temperature and, given the broad melting behaviour of these materials, unmelted crystalline regions may still exist. The presence of these regions, although orientable

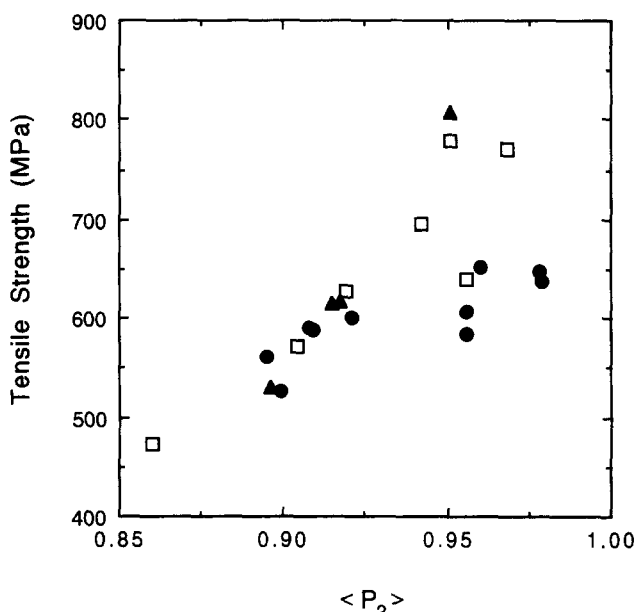
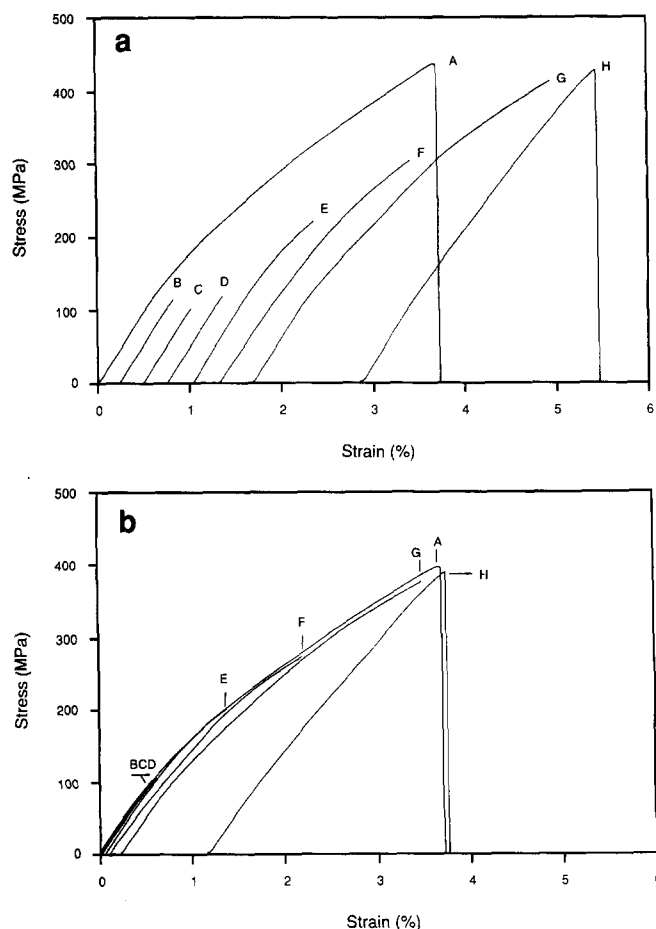


Figure 3 Relationship between tensile strength and orientation parameter  $\langle P_2 \rangle$  employing data from an earlier study<sup>1</sup> for samples having orientation differences developed either in the die (by varying die  $L/D$ ) or in the spinline (by varying draw ratio) at various extrusion temperatures: die 290°C (●); spinline 290°C (□); and die 300°C (▲)

in the die, may result in reduced tenacity through an imperfectly developed microstructure.

### Yield

As discussed in an earlier paper<sup>1</sup>, tensile tests reveal a change in slope detracting from the initial linear stress-strain behaviour at a critical stress or strain level. This effect is most pronounced in materials exhibiting comparatively poor tensile properties. The yield stress for a material can be defined as the level of stress at which irreversible strain occurs upon loading, and is associated with the commencement of permanent sample deformation. As shown in *Figures 4a* and *b* the multiple strain loadings of an extruded filament (lightly drawn sample produced using die *L/D* 133) at stress levels above and below this critical value suggest that this point is indicative of yield behaviour. Curve A represents the stress-strain behaviour of a single filament tested until failure and curves B-H represent the behaviour from multiple loadings of an identical single filament. In the latter case, the material was quickly unloaded (i.e. the sample grips were returned to their initial separation) after each maximum load was obtained. For clarity, the curves are shifted along the strain axis in *Figure 4a* and appear unshifted in *Figure 4b*.



**Figure 4** (a) Stress-strain curves of a lightly oriented extrudate tested until failure (curve A) and a second sample tested under the conditions of repeated strain before failure (B-H), illustrating yield behaviour. Curves shifted along the strain axis for clarity. (b) Curves of *Figure 4a* plotted unshifted, indicating: (i) the amount of slack or irreversible extension generated in the previous elongation; and (ii) the similarity between tensile strength and elongation at break for the continuously (curve A) and previously (curve H) extended samples

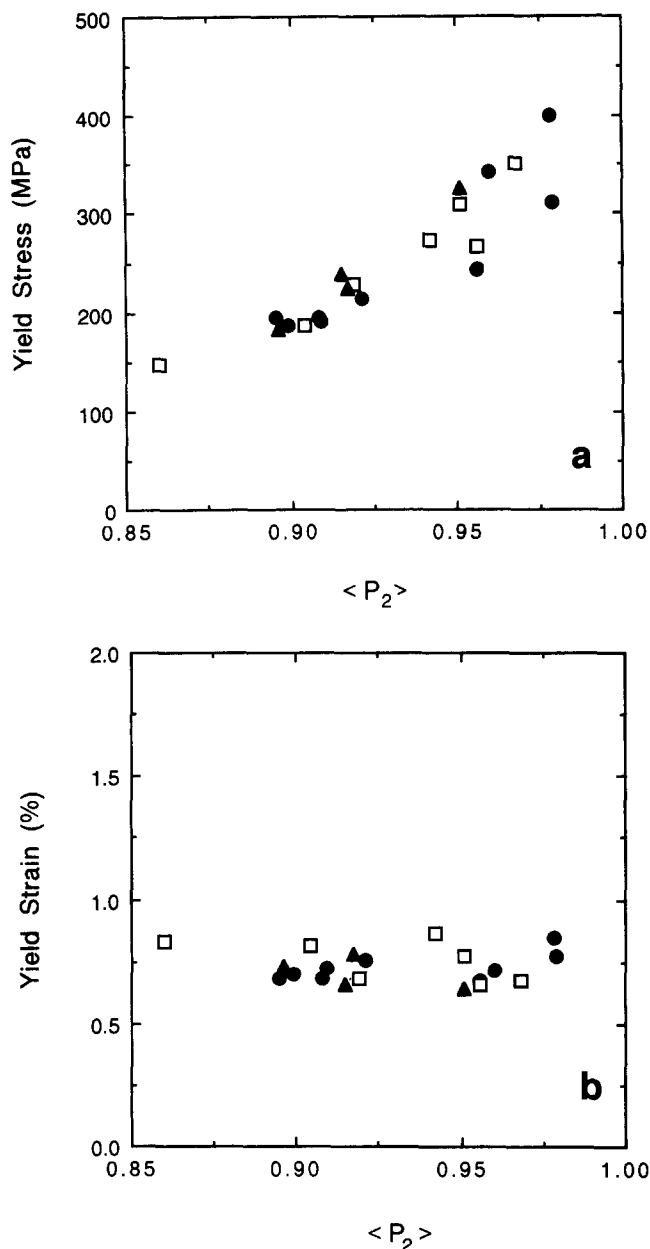
In curve A, a linear relationship between tensile stress and strain is observed up to critical stress and strain values of approximately 120 MPa and 0.7%, respectively. Beyond this value, the material elongates more easily under load until fracture occurs at 420 MPa stress or 3.8% strain. In curves B-D the fresh second sample is repeatedly strained to a level corresponding to the point of deviation from linearity observed in curve A. The similarity of curves B-D (see overlap in *Figure 4b*) indicates that no significant irreversible extension occurs. In curve E, the sample is strained to a stress level above the critical value and the change in curve shape at approximately 120 MPa is seen. Further extension of the same sample, curves F-H, shows similar behaviour to occur at 120 MPa. Additionally, another very slight change in curve shape can be detected at the level of the previous extension or maximum stress. This is apparent in curves F, G, and H at strain values of 1.4, 2.2 and 3.6% and corresponding stress values of 220, 300 and 400 MPa. Beyond these values, the individual stress-strain curves appear to follow the shape of the original stress-strain curve (curve A), indicating that the stress-strain behaviour at levels beyond previous loadings/extensions does not reflect the previous deformational history. Finally, curve H is tested until failure, which occurs at the same overall elongation and stress as in curve A (*Figure 4b*).

The displacement of the point of initial load measurement along the strain axis, observed for curves E-H in *Figure 4b*, indicates the amount of pre-irreversible extension or slack that must be taken up in successive loadings. This was not observed in curves B-D. This confirms that the material elongates irreversibly in extension where stress and strain levels exceed a critical value. This demonstrates that the initial linear stress-strain region corresponds to Hookean or elastic behaviour and the onset of irreversible extension is marked by the point of deviation from this linearity. It is valid, therefore, to define initial modulus as the slope of the initial linear stress-strain region and the point of deviation from linearity as the yield stress or yield strain value.

Comparing curve A, where the material was tested as extruded, to curve H, where the material had been strained previously, no change in the initial modulus is detected. However, a marked reduction in the amount of extension under load for the latter is observed. This suggests that the deformation of the material to failure can be broken up into separate deformation steps. Modulus, strength and total extensibility remain unchanged.

Yield behaviour in TLCPs has not to our knowledge been examined in detail. Northolt and Sikkema<sup>5</sup> discuss yielding of a PpPTA LLCP which is related to rupturing of the interfibril hydrogen bonds, thus allowing for a straightening of the fibrils. They note that yielding is most pronounced in lower modulus fibres and that the phenomenon disappears with increasing modulus.

More information on the yield behaviour of this TLCP can be obtained by plotting the yield stress (*Figure 5a*) and yield strain (*Figure 5b*) against the degree of orientation present in the extrudates prepared under three different processing conditions. In the case of yield stress, a strong correlation with orientation is apparent. The value of the yield stress is independent of the method of sample preparation and solely dependent on



**Figure 5** Relationship between (a) yield stress and (b) yield strain and the orientation parameter  $\langle P_2 \rangle$ . Data used from an earlier study<sup>1</sup> for samples having orientation differences developed either in the die (by varying die  $L/D$ ) or in the spinline (by varying draw ratio) at various extrusion temperatures: die 290°C (●); spinline 290°C (□); and die 300°C (▲)

the orientation of the molecules, as was observed for the modulus. Interestingly, the strain at yield is a constant value of approximately  $0.73 \pm 0.07\%$  (compliance corrected value<sup>20</sup>), independent of sample preparation and orientation. This shows that the level of the yield stress is simply the stress that results from elastic extension of the tensile specimen to 0.73% strain. Yield behaviour is less predominant in more highly oriented fibres because the correspondingly greater stiffness results in a lower extensibility under load.

This critical yield strain value is very similar to reported LLCPC yield strain values of 0.7% for a poly(*p*-phenylene benzobisthiazole) (PBT) fibre, 0.8% for a poly(*p*-phenylene benzobisoxazole) (PBO) fibre, and 0.5% for a PpPTA<sup>5</sup> fibre. The similarity in these values suggests that these materials are governed by a common deformation process. This supports the application of the

aggregate model, derived for crystalline fibres, to describe the elastic extension of this less crystalline TLCP.

For this TLCP material, a critical strain value exists that defines the limit of elastic deformation, i.e. the change from linear stress-strain behaviour. It is proposed that yielding occurs when the material is extended beyond this initial strain level by a mechanism of intermolecular slip. This slip may occur with localized chain rotation, given the zig-zag nature of the packed chains. The restraining intermolecular interactions result from dispersion forces which are governed by the limiting mobility. Global rotation of molecular segments in the direction of extension is not expected as the filament modulus remains unchanged in subsequent extension. In samples of increased orientation, the level of strain required for yielding is practically unchanged, but the level of stress will increase due to greater attractive forces. With further increases in tensile strain beyond yield, additional strain-sensitive or stress-sensitive yielding occurs. This explains the second shift in curve shape at the level of the previous extension/load.

## CONCLUSIONS

For TLCP samples prepared under various processing conditions, the macroscopic tensile modulus is solely a function of flow-induced orientation. The relationship between filament stiffness and orientation can be described by existing aggregate models. The strong sensitivity of tensile properties to orientation is explained by the relatively low value of the shear modulus.

Tenacity, however, can be influenced by factors other than degree of anisotropy. Lower than expected tensile strength values of extrudate were produced using the more highly orienting short dies at 290°C than were achieved where stronger post-extrusion orienting spinline extension was applied. As this difference was not apparent at the higher extrusion temperature, the difference in tenacity at equivalent levels of orientation is explained by the presence of a die flow induced defect structure.

TLCPs demonstrate a yield behaviour in tensile testing similar to that which has been observed previously in LLCPCs. Unlike LLCPCs, a reduction in slope of the stress-strain curve at the yield point and the similarity of the modulus with repeated specimen extension suggest that yielding is not associated with contraction of the chain orientation distribution. It is proposed that plastic deformation occurs by chain slippage at strain levels beyond the level of chain extensibility. Up to this level, elastic extension occurs without exceeding the strain-limited interchain forces. A characteristic yield strain value of 0.7%, similar to values reported for several LLCPCs, describes the onset of irreversible extension. Correlations between levels of yield strain and yield stress and orientation demonstrate that yield is a strain-determined phenomenon.

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