Processing/property relationships of a thermotropic copolyester: 1. Effect of capillary die aspect ratio

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This study investigates the mechanisms involved in the orientation development of thermotropic liquid crystalline polymers (TLCPs). It demonstrates the complementary effect of extensional flow in the die entrance with that in the spinline on molecular orientation. The tensile properties and microstructure of a thermotropic copolyester of hydroxybenzoic acid and hydroxynaphthoic acid are related to changes in the deformation history associated with flow through capillary dies of different aspect ratios. The presence of extensional flow within the convergent die entrance section is shown to be associated with increased tensile modulus, strength, yield stress and orientation (based on tensile tests, scanning electron microscopy and wide-angle X-ray diffraction). Flow in the varied length capillary section permits relaxation of the highly oriented morphology developed in the die entry. Modelling indicates a characteristic average relaxation time of approximately 0.5 s which corresponds to a die length to diameter ratio (*L*/*D*) of 37. Samples of differing orientations were prepared with varied die *L*/*D* ratios, spinline draw ratios, extrusion temperatures and deformation rates.

(Keywords: liquid crystalline polymers; mechanical properties; molecular orientation; relaxation; elongational flow; shear flow)

INTRODUCTION

Thermotropic liquid crystalline polymers (TLCPs) are a recent class of materials that exhibit complex behaviour, have exceptional physical properties, and are of significant commercial and academic interest. Their anisotropic properties are dependent on the microstructure developed during processing. Unlike conventional thermoplastic materials, a high degree of molecular order is retained in the melt. Rigid molecules exist in localized domains of parallel orientations described by directors. In the quiescent state, these directors are randomly spatially distributed throughout the system. Under the conditions of shear and extension during processing these domains are broken up and the material reorientates itself within the flow. The degree of orientation that exists in the solidified material is a product of the flow type, intensity and duration, as well as molecular relaxation effects. TLCPs exhibit long relaxation times relative to isotropic polymers because of their rigid molecular structure. Thus, the properties of TLCP injection mouldings, extrusions and fibres reflect the deformational and thermal histories of the TLCP in processing. A heightened understanding of these effects is fundamental to exploit fully the unique properties of these materials.

This paper develops an improved understanding of the effects of die geometry on the flow-induced tensile properties and morphological structure of a TLCP. Tensile testing and microstructural characterization of extrudates produced under various processing conditions using a large number of extrusion dies of different length to diameter ratios (*L*/*D*) have been undertaken. In the accompanying paper[1] the relationships between orientation and tensile properties of the samples prepared here are investigated further. The effect of die geometry on the behaviour of the rheological parameters viscosity and die swell is detailed elsewhere[2].

PROCESSING HISTORY/PROPERTY RELATIONSHIPS

Several studies have investigated the relationships that exist between processing history, mechanical properties and structure of TLCPs. Before the results of these studies are discussed, a review of the nature of flow-induced molecular orientation and relaxation is presented.

Orientability and relaxation

The excellent mechanical properties of TLCPs are related to the high degree of orientation of the extended rigid chain molecules that can be resolved using conventional processing methods. To demonstrate the orientability of a TLCP molecule in both shear and extensional flow the effects of placing a rigid rod in simple shear and uniaxial extensional flow fields are illustrated in *Figure 1*. For simple shear flow, the difference in the velocities of the end-points produces a tumbling or rotational motion of the rod which does not lead to a permanent preferential orientation. In the extensional

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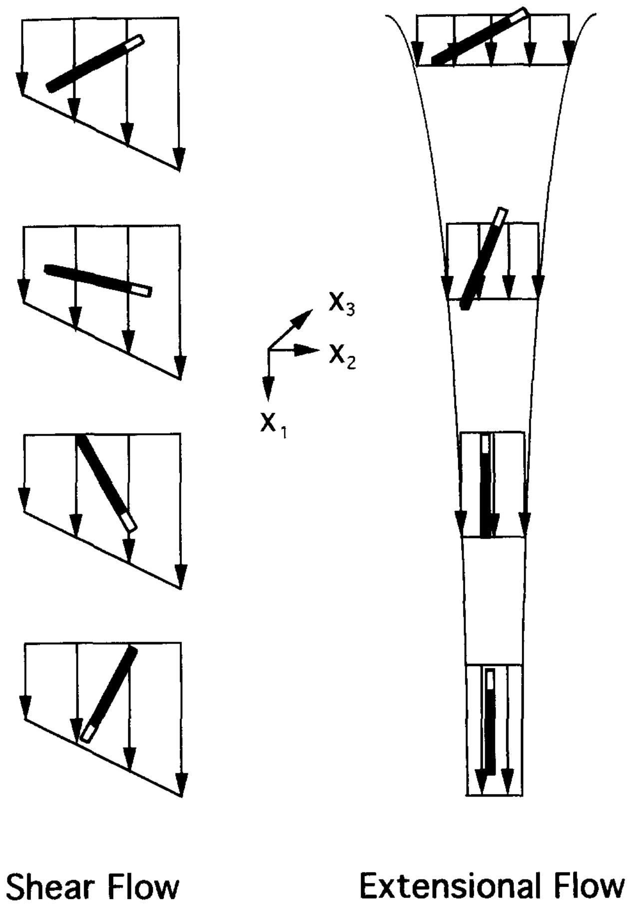

Figure 1 Orientability of a rigid rod in simple shear and uniaxial extensional flow fields

flow field, however, the velocity gradient in the x_1-direction causes the rod to align itself in the direction of flow. In this grossly simplified depiction, greater orientability is associated with extensional flow fields. This idealized behaviour is complicated by the interaction of neighbouring molecules and, in liquid crystal systems, the presence of a domain structure. Results of extrusion studies that have compared property development in the spinline with die extrusion (predominantly using long length shearing dies) and studies of injection mouldings are in agreement with this trend. Recently, Peuvrel and Navard[3] confirmed rheo-optically in the flow of a lyotropic liquid crystalline polymer (LLCP) around an obstacle that elongational flow is more effective than shear flow in causing LLCP orientation.

The relatively fast relaxation times associated with conventional, flexible coil polymer melts prevent the orientation developed during flow from being retained in the solidified material. Jackson[4] has shown, however, that TLCPs exhibit long relaxation times which increase with increasing molecular rigidity. For an LLCP Onogi and coworkers[5] demonstrated that the relaxation of stress and orientation are distinct and decoupled processes. In rheo-optic experiments, stress is observed to relax in the order of seconds, whereas orientation remains for minutes and hours. Baird[6] has demonstrated similar behaviour for a TLCP based on poly(hydroxybenzoic acid-*co*-ethylene terephthalate) (PHB/PET). The implication of this behaviour is that the orientation developed in the flow relaxes at a sufficiently slow rate so that a high degree of orientation remains in the solidified material. The relationship between chain linearity, orientation and the resulting tensile properties was investigated by Blundell and coworkers[7]. It was shown that the observed increased tensile modulus of mouldings produced from TLCPs of increased chain linearity is due to increased levels of macromolecular orientation resolved during processing, and not from compositional differences. Incorporating Jackson's work described above, we can extend this interpretation further. The higher degree of orientation of the more rigid chain compositions results from an expected increase in relaxation time, which preserves the orientation to a greater extent than in the less rigid compositions that have faster relaxation times.

Effect of processing history on mechanical properties and microstructure

Studies which deal with injection moulding are difficult to interpret because of the complex mixture of flow, solidification and relaxation that has occurred within the moulding die. It is clear from these studies that a multilayered structure is produced that reflects the mould-filling history. Up to nine main layers have been identified[7] and thin sections show that mechanical properties such as modulus are maximized at the surface and decrease in the core region[8,9]. These property differences are related to differences in orientation. More highly oriented material exists at the surface region which has undergone elongational flow from the spreading flow front and has solidified more rapidly. Less highly oriented material is found in the centre of the moulding where shear flow predominates and solidification occurs more slowly.

Because of their simpler flow geometries, studies of processes similar to commercial fibre production are of more value in determining the fundamental relationships involved in orientation development. This process involves extrusion through a capillary die and subsequent take-up of the extrudate in a spinline. The deformational history relating to orientation development is depicted in *Figure 2*. The process can be divided into the two areas of (i) extrusion through the die and (ii) flow outside the

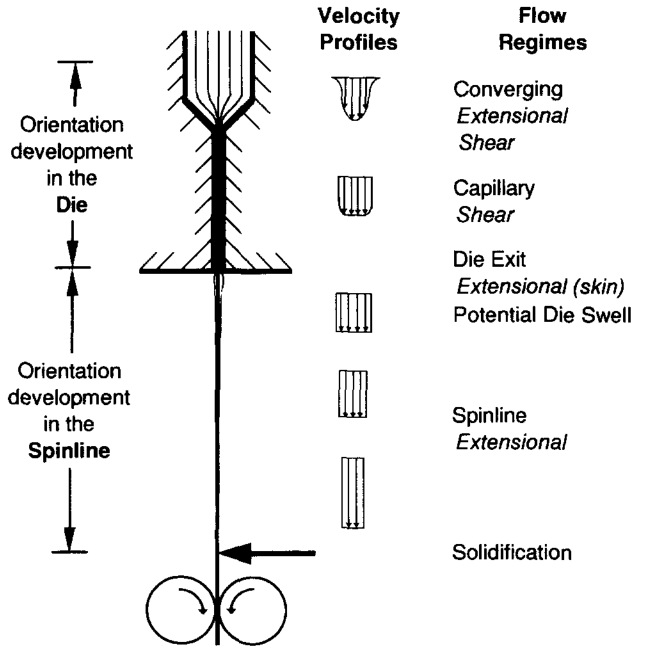

Figure 2 Flow history and orientation development in fibre extrusion and take-up

die in the spinline. Previous studies have concentrated mainly on the latter and this will be discussed first.

Effect of flow in the spinline

In the spinline a non-isothermal uniaxial elongational flow field predominates. This stretching flow results from the take-up velocity being greater than the average filament velocity exiting the die. The velocity in the axial direction changes with distance along the spinline away from the die until the point of solidification is reached prior to the take-up. The velocity profile across the diameter of the molten filament is assumed to be constant. The extensional strain rate (the instantaneous derivative of axial velocity with respect to distance) can be constant or vary along the spinline. The total extension applied to a particle within this flow regime is the integral of the extensional strain rate over the duration of the residence time. For a constant strain rate it can easily be shown that the total amount of extension is equivalent to the total drawdown ratio minus one. The drawdown ratio or spin stretch factor (draw ratio) is defined as the ratio of the filament velocity at the take-up to that at the die exit. Because of the constant flow rate, this can additionally be determined from the ratio of the cross-sectional areas of the die and the resulting filament. The orientation developed in the spinline of a TLCP is frozen into the filament upon solidification.

Studies involving TLCP materials based on PET/PHB[10,11] and random copolymers of hydroxybenzoic acid and hydroxynaphthoic acid (HBA/HNA)[12,13] have shown that orientation and tensile properties improve with the amount of applied extension. The relationship between draw ratio and orientation has been neatly demonstrated for a poly(ester amide) by Calundann *et al.*[14]. The shapes of plots of initial modulus *versus* draw ratio show that initially a high degree of sensitivity of modulus to imposed extension exists. In this region, the filament stiffness and strength vary linearly with the true or Hencky strain (the log of the draw ratio)[15]. This initial sensitivity decreases with increasing draw ratios above 10 to 100, depending on the material and test conditions. For these materials, the effect that the small initial amount of post-extrusion extension has on the orientation and tensile properties suggests that orientation is not developed fully during flow through the die. Kenig[13] discusses a material-dependent orientability parameter which relates changes in the degree of orientation to the amount of deformation imposed in the spinline. Using a lyotropic liquid crystalline polymer and four TLCP samples, a different orientability parameter was reported for each of the materials investigated. In some cases, such as with an amorphous TLCP[16,17], PHB/PET[18] and hydroxypropylcellulose[19], post-extrusion extension may provide no additional improvement in tensile properties, suggesting that maximum orientation can in some cases be developed in the die region. Ide and Ophir[15] studied the effects of extensional stress and strain rate by varying the temperature profile in the spinline and measuring take-up stress. By observing that no changes in the resulting filament stiffness occurred they were able to show that extensional stress and extensional strain rate do not influence the resulting stiffness and, hence, orientation. The total amount of applied extensional strain, or draw ratio, is the determining factor.

Superimposed on the flow regime in the spinline is the velocity rearrangement and swelling/contraction effects at the die exit. Velocity rearrangement occurs at the transition from shear flow to extensional flow, as shown in *Figure 2*. This change causes an acceleration of the outer filament layers which move at very low velocities in the shear flow within the die. It has been suggested[15] that the extensional flow history of the outer material at the die exit accounts for the observed skin/core structure in TLCP fibres. In addition, the material emerging from the die can undergo swelling or contraction. In conventional isotropic polymer melts swelling reflects the viscoelastic nature of the polymer as it recovers from the elastic deformation or orientation encountered with flow through a die. Its level is influenced by the restraining effect of the applied take-up stress. TLCPs exhibit unusual die shrinkage or expansion depending on flow conditions[2].

Effect of flow in the die

Few detailed studies of the effect of die geometry on the mechanical and morphological properties of TLCPs have been published in the open literature. The work that has been done suggests that the amount of orientation developed in the die is slight and reflects the poor orientability associated with shear flow[15]. In plots of an extrudate orientation parameter against applied draw ratio, Garg and Kenig[9] account for shifts of straight line relationships observed using different dies (varied diameter) as being indicative of initial orientations developed in the die.

The contribution of the orientation developed in the converging section of the die which involves both extensional and shear flow has not been examined in detail for these materials. Referring to *Figure 2*, polymer entering the die is forced to undergo a stretching as well as a shearing flow due to the change in flow cross-sectional area. Flow in contractions has been reviewed by Cogswell[20] and Gibson[21]. Han[22] experimentally determined a velocity profile in converging flow, confirming that the majority of extension occurs in the core regions and shear predominates in the outer regions of flow. The orientability of converging flows has been demonstrated for PET and is known to be important in the development of two-phase mixtures of conventional, flexible coil polymers[23] and TLCPs[24]. Once in the constant diameter region of the die, shear flow predominates wherein the flow velocity becomes constant in the axial direction and is rearranged into a modified parabolic profile in the radial direction. The highly non-Newtonian nature of a TLCP, quantified by its small power law index, causes this profile to be flat or plug-like (*Figure 2*). The material closest to the die wall is highly sheared while the remaining material in the core flows unsheared.

The orientation developed in the die region reflects the extensional and shear flow histories in the entrance zone and shear flow in the land region. The die aspect, or length to diameter ratio (L/D), is an important parameter as it describes the balance between extensional and shear flow history. Long dies of large L/D ratios produce material with substantially more shear flow history than shorter dies of small L/D. For a given material and die diameter the total amount of shear strain is directly related to the die L/D ratio[25]. In addition, dies with large L/D ratios permit greater relaxation of the morphology developed in the converging section. A zero length die ($L/D=0$) is one in which only the converging section is present and potentially represents the maximum ratio of extension to shear deformation history. A report by Ide and Ophir[15] using constant diameter dies of *L/D* 33, 66 and 132 showed marginal if any improvement in tensile properties with increasing *L/D*. Kenig[25] also investigated this effect using two dies of *L/D* 33 and 133, and concluded that the orientation and filament stiffness improved with shear strain (i.e. die length) and was independent of shear rate. It was further noted that orientation development by shear is much lower than by extension. Muramatsu and Krigbaum[10], using dies of equal length but different diameter with *L/D* ratios of 12, 26 and 50, correlated property improvements with larger *L/D*. The fact that both diameter and *L/D* change independently in their different dies makes meaningful comparative conclusions difficult. Studies of Isayev and coworkers[26,27] with dies of *L/D* 10 and 30 showed that the modulus and strength of an unblended HBA/HNA TLCP improved with decreasing *L/D* and increasing deformation rate. These differing results and the use of relatively long dies suggest a more comprehensive study is needed to understand fully the effect of flow history through the die on the development of mechanical properties and morphological structure.

EXPERIMENTAL

Materials

A random aromatic copolyester of 73 mol% HBA and 27 mol% HNA was studied. This material is a commercially available, main-chain TLCP manufactured by Hoechst–Celanese as VECTRA® A950. This material has been studied extensively. Its synthesis[28], structure[29], rheology[30], microstructure[31], spinnability[12,32] and mechanical properties[33,34] have been described elsewhere.

Specimen preparation

Monofilament (thick fibre) specimens were prepared by extrusion and subsequent controlled drawdown using an Instron 3211 capillary rheometer and a modified Göttfert RHEOTENS® apparatus, respectively. The rheometer was operated as both a processing device to extrude molten polymer at a controlled flow rate as well as to monitor rheological properties. Ten different extrusion dies were employed in this study. Four of these were standard tungsten carbide Instron dies of 25.4, 50.8, 76.2 and 101.6 mm land length and 0.76 mm diameter. Dies of land length 0.4, 1.9, 3.8, 7.6, 11.4 and 25.4 mm were fabricated from a high tensile steel (EN25, Eagle & Globe Steel Co. Ltd, Melbourne, Australia) to extend the study into the investigation of smaller die lengths. From microscopic measurements the diameters of these dies were determined to be in the range of 0.77 to 0.82 mm. Thus, approximate constant diameter dies of aspect ratio 0.5, 2.5, 5, 10, 15, 31, 33, 67, 100 and 133 were studied. A purposeful duplication in the region of a die *L/D* ratio of 33 was made so as to make a comparison between the effects of the different materials and construction methods possible. All dies had a 90° full angle (45° half angle), conical converging section that preceded the constant diameter land length section. Dimensioned drawings of the fabricated dies are available from the authors.

To study the effect of changes in die geometry, material was extruded at a constant flow rate through the different extrusion dies. A constant thermal and deformational history was imposed on the material exiting the die. In this way, observed changes in the properties of the extrudate were indicative of the influence of deformational and thermal history differences from extrusion through the die only. The shear rate at the die wall was 700 s^{-1} (Rabinowitsch corrected). The extrudate was collected at a low level, constant take-up speed sufficient to overcome the variable amount of drawdown associated with freely fallen extrudate only. Collected filament diameters were measured using a Nikon V-16 projection microscope equipped with a digital micrometer. The average specimen diameter of 0.38 mm in this test corresponds to a draw ratio of 4.0.

To study the effect of flow rate in the die, extrudate was also prepared at a variety of shear rates from the shortest and longest dies. The take-up speed of the extrudate was adjusted so as to maintain a constant level of post-extrusion extension, and hence a constant filament diameter. A higher draw ratio of 8 was employed.

The effect of post-extrusion extension on the mechanical properties of extrudate produced from three different die lengths was investigated. Using dies of *L/D* 0.5, 10 and 133 various draw ratios were imposed by varying the take-up speed. The total amount of extension was calculated from measurements of filament diameter. Additionally, to provide a more sensitive means of studying the effect of shear in the longer dies (*L/D* 33, 67, 100 and 133), extruded specimens were collected at three different imposed draw ratios.

Pellet samples were dried overnight under vacuum at 120°C and loaded directly from the oven into the rheometer barrel. Extrusion temperatures of 290°C and 300°C were employed. These temperatures were chosen based on the results of earlier studies that showed extrudate irregularity is observed at higher temperatures[12,16,32] and evidence of incomplete melting exists at lower temperatures[16]. The former phenomenon is associated with the requirement that a minimum shear stress is exceeded to obtain good quality extrudate. Increasing the temperature further results in a decrease in the shear stress and is accompanied by poor extrudate quality. In this study, extrusion was carried out at a sufficiently high shear stress to avoid this effect, and smooth monofilament specimens were produced.

Tensile testing

Tensile testing of extrudate was performed using an Instron 4505 testing machine. Filaments were gripped with an adhesive–paper composite system to avoid failure in the gripping section and thus allow for the calculation of breaking strength. This involved adhering the filament ends to a paper substrate using an appropriate adhesive (UHU® all-purpose adhesive, Lingner & Fischer GmbH, Germany) and gripping in emery paper lined flat plate grips. The presence of the cured adhesive appears to distribute better the clamping load, avoiding stress concentrations. Estimates of the initial tensile modulus were corrected for machine compliance[35]. The tensile strength and the yield stress (discussed later) were measured. A crosshead speed of 10 mm min^{-1} and a gauge length of 100 mm were employed. The cross-sectional area of each individual filament was calculated based on microscopic measurements of the filament diameter. The average and standard deviations of up to seven samples are reported.

Microstructure characterization

Scanning electron microscope (SEM) images were produced on a Jeol JSM-840 to investigate the textures of peeled and fractured samples. Peeled samples were prepared by notching the cross-sectional face of a cut extruded filament and peeling back to expose the surface along the length of a half section. Fracture surfaces of tensile test specimens that failed at a localized zone outside the gripping area were investigated. Failure occurred in some cases by separation of the filament into microfilaments that extended along the entire gauge length.

To quantify the preferred orientation, single filament specimens were evaluated by transmission X-ray diffraction. Wide-angle X-ray diffraction (WAXD) patterns were obtained using a Philips PW1030 flat plate camera employing monochromatic (nickel-filtered) CuKα radiation. An exposure time of 2 h was used. Azimuthal intensity traces of the strong $\langle 110 \rangle$ equatorial reflection (4.53 Å) were produced using a Joyce Loebl double beam recording microdensitometer Mk IICS and a rotational stage. The diffraction patterns arise from interchain interferences the directions of which correspond to planes normal to the chain axis[36].

The level of orientation can be quantified by the second-order spherical harmonic coefficient $\langle P_2 \rangle$ (Hermans' orientation factor) defined as

$$\langle P_2 \rangle = (3\langle \cos^2 \theta \rangle - 1)/2 \qquad (1)$$

where θ is the angle between the molecular axis of the mesogenic moiety and the filament axis (direction of extrusion). $\langle P_2 \rangle$ can vary from 1.0 to -0.5. Values of 1.0, 0 and -0.5 are indicative of perfect axial alignment, random orientation and orientation in the perpendicular direction, respectively. This parameter is estimated from the azimuthal intensity traces using a procedure discussed elsewhere[37]. Calculated values have been corrected for the intrinsic width of the reflection[38] by dividing by 0.97. The average of up to three specimens is reported. Greater variability was observed in the less-oriented specimens evaluated, possibly due to skin–core effects.

Differential scanning calorimetry (d.s.c.) has been used to identify any differences in the first-heating traces of the prepared filaments. Lengths of filament of approximately 2 mm were cut and placed in the d.s.c. pan. Sample mass varied from 7 to 12 mg. A Perkin–Elmer DSC-7 was employed and calibrated using indium and lead standards.

RESULTS AND DISCUSSION

The effects of die aspect ratio on the tensile properties and microstructures of extrudate produced are reported. In a later section, the observed property differences are related to the flow processes of orientability and relaxation. Moreover, the additional effects of varied deformation rate and extension applied in the spinline are investigated.

Effect of die L/D *on tensile properties*

Figure 3 shows some typical stress–strain behaviours of specimens prepared from dies of different *L/D* but with identical diameter and post-extrusion flow and thermal history. Lines drawn tangentially to the initial linear stress–strain relationships of the extrudates produced using three different dies (*L/D* 0.5, 10 and 33) are depicted.

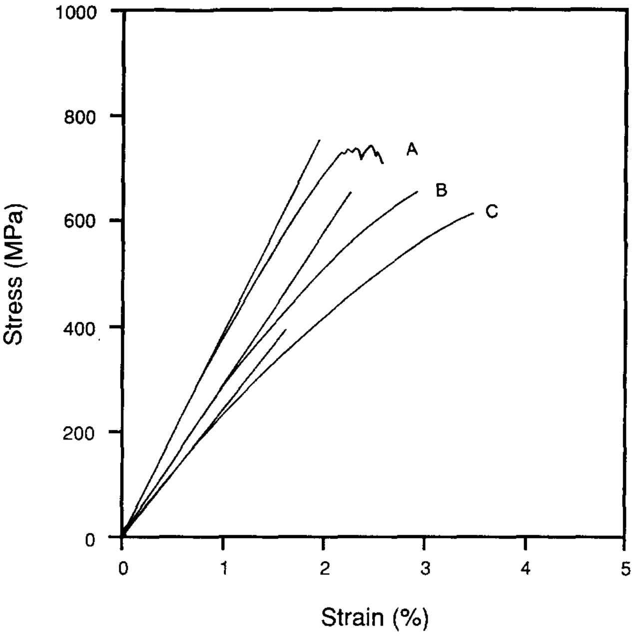

Figure 3 Stress–strain relationships of monofilaments produced using dies of aspect ratio 0.5 (curve A), 10 (curve B) and 33 (curve C)

There is a clear change in the tensile behaviour depending on the extrusion die employed. The material produced using the shorter die exhibits a higher stiffness, strength and a lower elongation to failure than those produced using the longer dies. This was also reflected in a marked difference in the fracture behaviour of the samples depending on the die employed. In the case of the higher modulus and strength extrudates, such as those produced from the die of *L/D* 0.5, failure occurred by an internal delamination or splintering/tearing process. The serrated shape of the stress–strain curve near the failure of the material produced using this die (*Figure 3*) reflects this mechanism.

In all tensile tests, there is a change in the slope of the stress–strain curve at a critical stress or strain level which causes a deviation from the initial linear behaviour (*Figure 3*). This effect is more pronounced in the materials exhibiting comparatively lower tensile properties. Yield stress for a material is defined here as the level of stress at which irreversible strain upon loading, associated with the onset of permanent sample deformation, commences. As seen in more detail in the accompanying paper[1], the onset of irreversible extension occurs at the point of deviation from this initial linear stress–strain relationship. Thus, it is appropriate to define the slope of this initial region as the initial tensile modulus of elasticity (initial modulus) and the level of stress at which deviation from the initial linearity occurs as the yield stress.

From curves of the form shown in *Figure 3*, the values of initial modulus, tensile strength, and yield stress of extrudate produced at 290 and 300°C were calculated. *Figure 4* illustrates the changes in these properties with die *L/D* and extrusion temperature.

The dramatic effect that die *L/D* has on the mechanical properties of the extrudate is demonstrated clearly. The highest stiffness (*Figure 4a*), strength (*Figure 4b*) and yield stress (*Figure 4c*) values are associated with extrusion through the shorter dies. The modulus of material produced using a short die is up to two times that produced using a long die. Beyond the die length

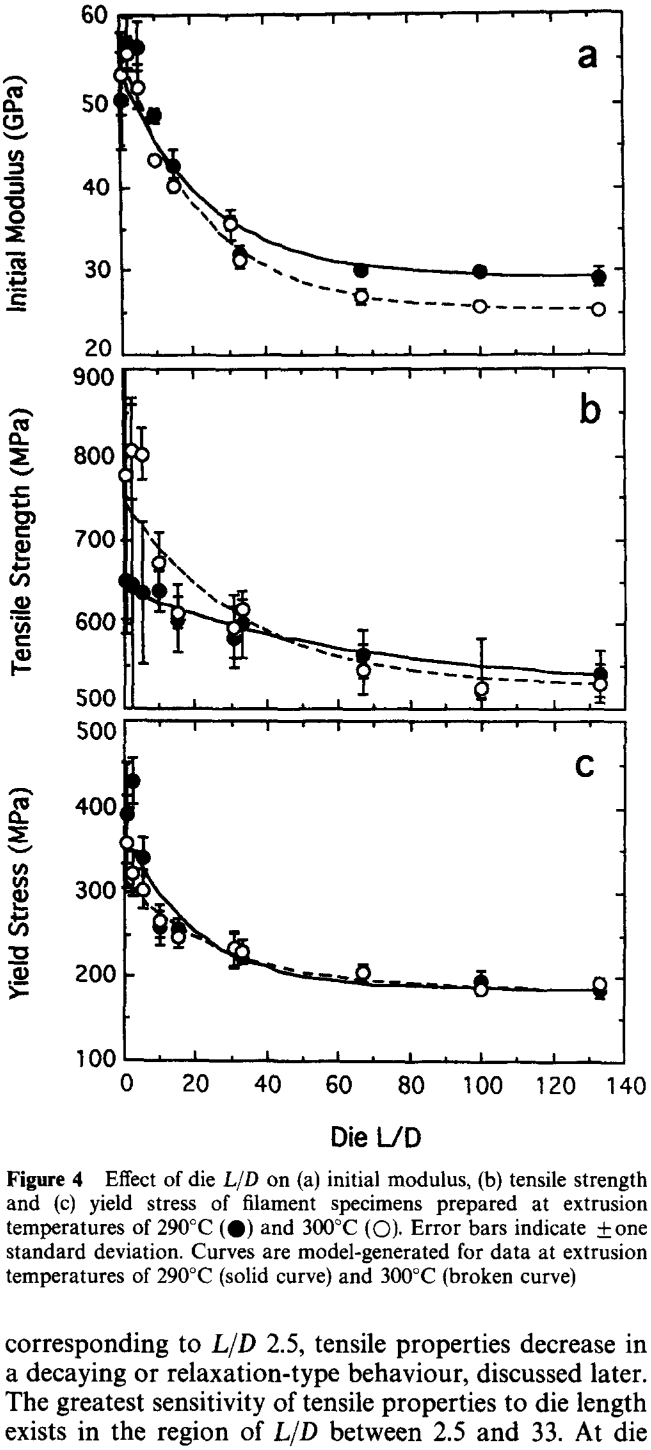

Figure 4 Effect of die *L/D* on (a) initial modulus, (b) tensile strength and (c) yield stress of filament specimens prepared at extrusion temperatures of 290°C (●) and 300°C (○). Error bars indicate ±one standard deviation. Curves are model-generated for data at extrusion temperatures of 290°C (solid curve) and 300°C (broken curve)

corresponding to *L/D* 2.5, tensile properties decrease in a decaying or relaxation-type behaviour, discussed later. The greatest sensitivity of tensile properties to die length exists in the region of *L/D* between 2.5 and 33. At die *L/D* 67 and greater, properties are predominantly insensitive to die length. It appears that reduced tensile properties are associated with extrusion from the die of *L/D* 0.5 compared to that from the slightly longer die of *L/D* 2.5.

Extruding the material at the lower temperature of 290°C produced extrudates that have increased stiffness and yield stress values. However, the temperature dependence of tensile strength differs. Maximum tenacity occurs in the extrudate produced at the higher temperature of 300°C. Not unexpectedly, it is noted that greater variability is observed for the determination of tensile strength relative to the other parameters.

Comparing the tensile properties of materials prepared using the tool-steel fabricated die (*L/D* 31) with those from the tungsten carbide Instron die (*L/D* 33), reasonable agreement is apparent. Similar extrusion pressures[2] and morphologies were observed. This confirms that use of the custom-made extrusion dies alongside the existing manufacturer's die is appropriate. Ramamurthy[39] has shown that the effect of changes in the material in the capillary is a weak one where smooth flow exists.

Effect of die L/D *on microstructure*

The microstructures of the specimens prepared using dies of different *L/D* have been investigated in detail. The structure of the extrudate is revealed by: (i) peeling back the outer skin to produce a half section that can be viewed by SEM; (ii) viewing the fracture surface by SEM; and (iii) X-ray diffraction patterns. *Figure 5* depicts these three structures for samples produced using dies of *L/D* 0.5, 2.5, 10 and 33. The results from these dies summarize the range of observed variation in morphological structure and illustrate a subtle difference between the two samples produced using the two shortest dies. Measurements of an orientation parameter derived from the X-ray diffraction patterns and the results of a comparative study of the first-heating d.s.c. traces are discussed later.

The peeled back exposed surfaces (*Figures 5a–d*) of the materials extruded using the above variety of dies exhibit a correlation with the previously reported tensile properties. The textures of the extrudates produced in the shorter dies, *L/D* 0.5 and 2.5 (*Figures 5a* and *b*), indicate the presence of a highly fibrillar structure. Each filament is composed of fine fibrils of approximate diameter 2–5 μm. The fineness and degree of fibrillarity appear greater for the sample produced using the die of *L/D* 2.5 than that from the die of *L/D* 0.5. With increasing die length beyond *L/D* 2.5 reduced numbers of increasingly coarser, distinct fibrils, or macrofibrils, are observed for die *L/D* 5, 10 (*Figure 5c*) and 15. Their respective diameters or widths are estimated to be of the order of 5, 10 and 15 μm. These later combine to produce a non-fibrillar structure apparent in the materials produced using dies of *L/D* 33 (*Figure 5d*) and longer. For this range, the surface is more pleated with a hair-like texture only. Fibrillar textures have been commonly reported for drawn TLCP extrudates[31]. In these studies their fineness and number increase with increasing draw ratio. The fibrillar texture is associated with a high degree of orientation[31]. Our results demonstrate that orientation decreases with increasing *L/D* and that this is reflected in the observed changes in tensile properties (*Figure 4*).

The tensile fracture surfaces of extrudates produced from the different dies are shown in *Figures 5e–h*. A remarkable dependence of fracture behaviour on die length was observed. Samples produced using the short dies of *L/D* 0.5, 2.5 and 5 demonstrated no distinct localized fracturing. The material failed by splintering or delaminating into continuous fibrils existing along the entire gauge length, as viewed perpendicularly to the fibre axis in *Figures 5e* and *f*. This mode of failure could be detected audibly, and stress–strain behaviour indicated that the tearing process of these individual fibrils occurred at around a constant maximum force over a time period of approximately 1 s. Extrudates from the longer dies failed at random locations between the grips and showed a decreasing degree of fibril structure with increasing die *L/D* (*Figures 5g* and *h*). This confirms that the strengths of TLCP and LLCP fibres correlate with the known fibrillarity of the fracture surface[31]. These results complement the tensile data that indicate materials

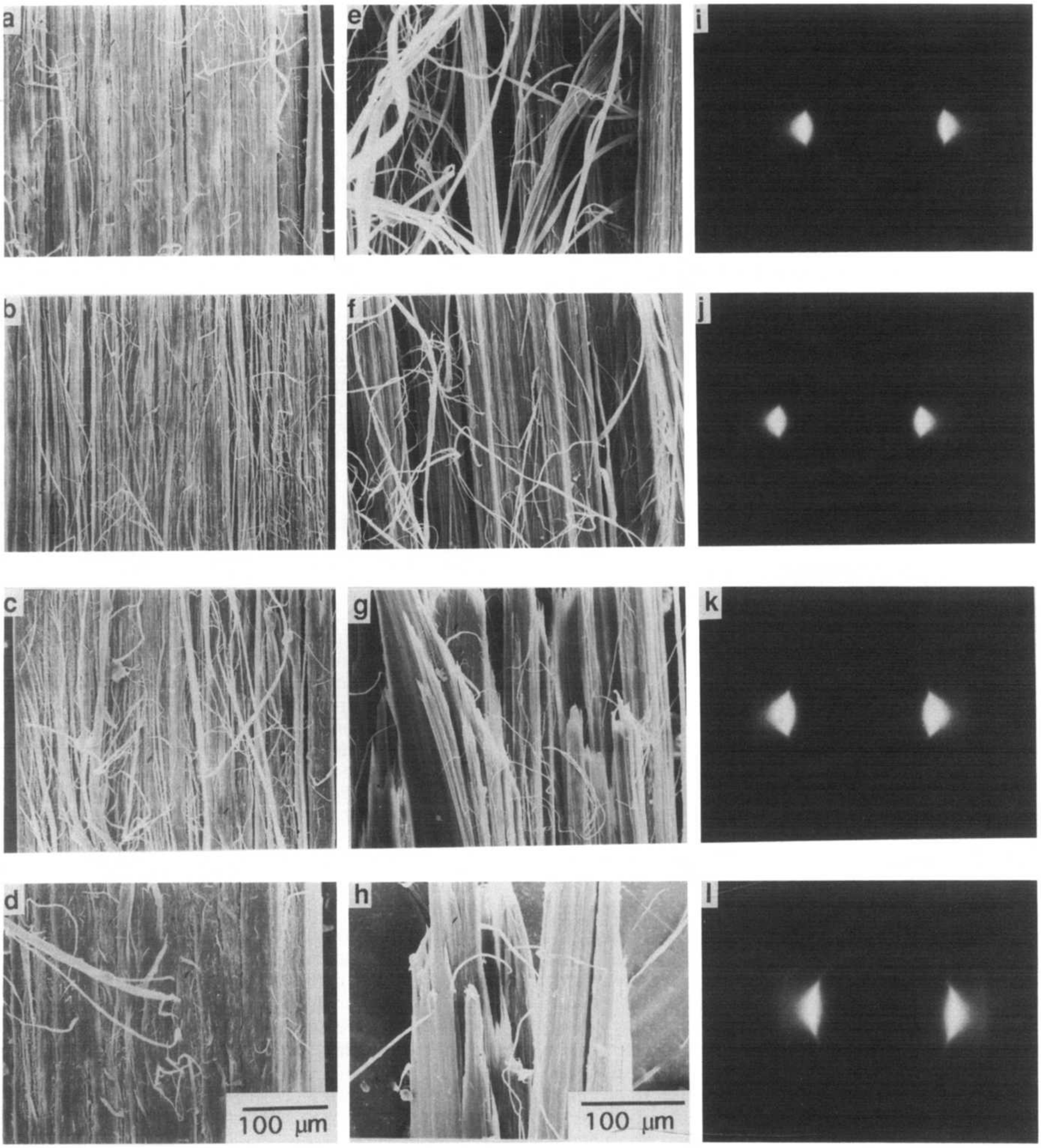

Figure 5 Microstructures of samples produced using dies of *L/D* 0.5 (a, e and i), 2.5 (b, f and j), 10 (c, g and k) and 33 (d, h and l) at an extrusion temperature of 290°C and a draw ratio of 4. Micrographs illustrate peel back texture (a–d), fracture surface (e–h) and wide-angle X-ray diffraction pattern (i–l)

produced using the shorter dies are highly oriented, and less orientation is developed in dies of larger *L/D*. The lack of difference in microstructure between the sample produced from the longest die of *L/D* 133 (not shown) and that from the die of *L/D* 33 indicates the ineffectiveness of shear in producing further orientation.

To examine the orientation in further detail, WAXD patterns were obtained from the samples produced at varied die *L/D*, summarized in *Figures 5i–l*. Of particular interest here is the azimuthal breadth of the predominant ⟨110⟩ equatorial crescent (4.53 Å) which can be used to quantify the orientation distribution. The narrow arc associated with the filament produced using the dies of *L/D* 0.5 and 2.5 increases in breadth with increasing *L/D* to that seen for the samples produced using the die of *L/D* 33. Based on radial microdensitometer intensity traces of these arcs, the relationship between the orientation parameter $\langle P_2 \rangle$ and die *L/D* is shown in *Figure 6* for materials produced at 290 and 300°C. The orientation is maximized using short dies and is diminished with increasing die length. This confirms that the observed fibrillar texture and the corresponding

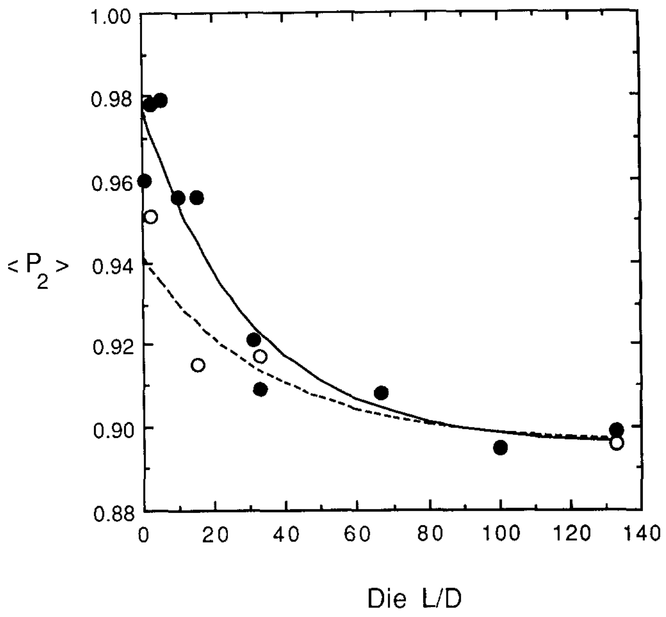

Figure 6 Effect of die *L/D* on orientation parameter $\langle P_2 \rangle$ for samples prepared at extrusion temperatures of 290°C (●) and 300°C (○) and a draw ratio of 4. Curves are model-generated for data at extrusion temperatures of 290°C (solid curve) and 300°C (broken curve)

increased stiffness and strength of samples produced using the shorter dies results from increased orientation. The slight reduction in orientation observed with the die of *L/D* 0.5 relative to the die of *L/D* 2.5 (at 290°C) is in agreement with the corresponding slight reduction in tensile properties and the slight difference in peeled back microstructure observed by SEM.

D.s.c. traces of the specimens prepared using different die *L/D* were investigated to determine: (i) any gross changes in the melting peak endotherm indicative of differences in crystalline structure; and (ii) any differences in the overall melting behaviour that correlated with the observed differences in morphology. Sarlin and Tormala[40] have shown that the first-heating traces of TLCP pellets and fibres differ from those obtained in the second heating, where the material was previously heated to a temperature above melting. In addition to the phenomenon of crystalline melting, it is believed that the observed broad softening and, hence, gradual melting behaviour, along with the potential occurrence of double melting peaks and exotherms, is related to the thermal history and stress history of the specimen. In a study of drawn nylon 6 fibres[41], the melting peak temperature and the presence of multiple melting peaks were shown to be influenced by the draw ratio applied in processing.

The first-heating d.s.c. trace of a typical sample reveals a broad endothermic shoulder that precedes a small melting peak at about 285°C. The effect of increasing the heating rate is to emphasize the broad or shoulder-like melting behaviour. In the work of Sarlin and Tormala[40], high heating rates of 40 and 80°C min^{-1} were used as they produced splitting of the melt endotherm and occasional exotherms. *Figure 7* shows thermal traces produced from specimens prepared using dies of different *L/D* ratios representative of morphologies that vary in orientation from relatively high (*L/D* 0.5 and 2.5) to medium (*L/D* 10) to low (*L/D* 33 and 67) at a heating rate of 40°C min^{-1}. These curves can be characterized as having in common a broad initial melting endotherm followed by the more distinct endotherm. Variable, temperature-located exotherms superimposed on this behaviour (*Figure 7*, trace A) were not consistently observed in repeated runs. This suggests that their occurrence is related to the measurement technique and cannot be reliably correlated with morphology differences. The onset temperature of the broad and distinct endotherm, the peak endotherm temperature and the overall enthalpy of the transition changed little with sample morphology.

The materials evaluated here exhibit large relative differences in tensile properties and morphology which are not discernible by their thermal properties. This result implies that there are no gross changes in the crystalline nature of the material, and that property differences relate to the orientation developed in flow only. Although it would appear that no effect exists, this result does not necessarily exclude the possibility that the first-heating traces reflect the stress history in the specimens. Since all samples produced share similar deformational and thermal histories in the spinline (i.e. only changes in the die flow history exist), the lack of difference in the first-heating traces may reflect the existence of similar frozen-in stresses.

Relationships between processing history and properties of samples prepared using dies of various L/D

The effect of processing history associated with the use of extrusion dies of various aspect ratios on tensile properties and microstructure is significant. The effects of deformation rate within the die and varied post-extrusion, spinline-applied extension are additional processing parameters that require investigation.

The effect of employing dies of reduced *L/D* in extrusion is to shift the balance of extensional and shear deformational history in favour of increased extension. For the dies of approximately zero length, the tensile properties developed relate mainly to the flow associated with the converging section. This flow involves a complex combination of both extensional and shear flow. Increasing die length increases the proportion of shear flow through flow in the constant diameter die region. In all cases, the material leaves the die at the same average velocity and experiences a similar post-extrusion deformational and thermal history. This post-extrusion behaviour includes velocity rearrangement, drawdown within the spinline and solidification. Given

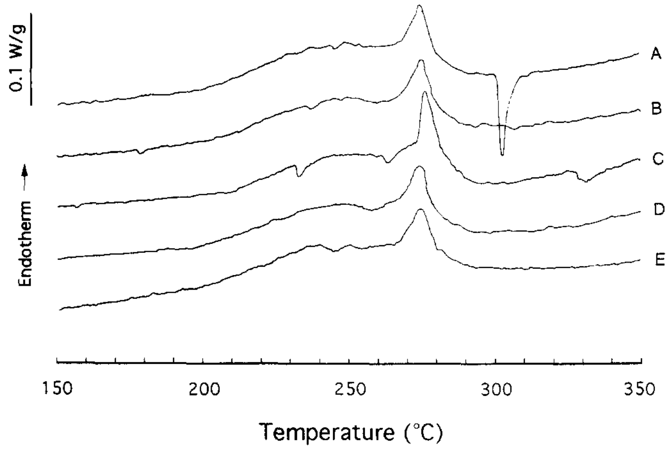

Figure 7 First-heating d.s.c. traces of extrudates prepared using dies of *L/D* 0.5 (trace A), 2.5 (trace B), 10 (trace C), 33 (trace D) and 67 (trace E) at an extrusion temperature of 290°C and a draw ratio of 4

that this study aims to observe changes in the properties of extrudate due to alterations in die geometry, referring to the previous figures (*Figures 2–6*) it is clear that the extensional flow regime in the die entrance region is responsible for improved orientation and, hence, tensile properties. Relationships between the degree of orientation and tensile properties are presented in the accompanying paper[1]. The ability of elongational flow to cause orientation in the converging section of the die is in agreement with previous studies that have dealt mainly with the effects of changes imposed in the spinline outside the die.

The mechanical properties and orientation appear not to be fully developed in the die of *L/D* 0.5, as slightly greater strength and stiffness values are observed with the die of *L/D* 2.5. The marginal property improvement associated with the slightly longer die must result from the advantageous presence of the longer capillary section. Thus, maximum tensile properties appear to be developed in very short, converging flow dies that have a critical minimum length, constant diameter section.

Potential explanations for the reduced properties of the extrudate produced from the shortest die of *L/D* 0.5 relate to the influence of the short, constant diameter section on the flow history. It is not possible to determine accurately the critical length at which a shear velocity profile is developed in the capillary section without undertaking additional experimentation. It is reasonable to suggest that in the shortest die of *L/D* 0.5 the flow field may not adapt to the presence of the very short capillary section. In the die of *L/D* 2.5, however, the approximately 2 mm long capillary section may be sufficient to allow the flow to arrange itself into a shear velocity profile following convergence.

Firstly, the material in the region of the die wall exiting the die of *L/D* 0.5 may be travelling at a higher velocity than if a modified parabolic velocity profile were present. Therefore, the stretching flow in the skin region (due to flow rearrangement on exiting the die, as discussed previously) that leads to increased orientation may not occur to the same extent.

Secondly, the lack of a shear velocity profile in the constant diameter section may cause the entrance flow pattern to be different from the case where this profile is present. That is, the flow history in convergence may be different (presumably less strong), resulting in a reduced level of orientation if an effective length, constant diameter section does not follow.

A third explanation may lie in the inability of post-extrusion extension to restrain the stronger disorienting forces associated with extrudate swell from the die of *L/D* 0.5. Die swell involves the elastic recovery (and hence disruption) of orientation produced in the converging section and is maximized in the shorter dies. The greater die swell from the die of *L/D* 0.5 may not be sufficiently restrained, as it is in the longer die of *L/D* 2.5, by the small level of take-up tension and therefore a lower degree of orientation results.

Table 1 Equation (2) coefficients B, C and τ that represent changes in various parameters with die L/D

Parameter	Temperature (°C)	B^a	C^b	τ^b
Initial modulus (GPa)	290	29	25	24
	300	25	31	23
Tensile strength (MPa)	290	520	120	71
	300	520	220	34
Yield stress (MPa)	290	190	130	35
	300	190	100	48
$\langle P_2\rangle$	290	0.895	0.0823	31
	300	0.896	0.0456	34

[a] Parameter value at L/D 133
[b] Derived from a least-squares fit of equation (3)

Where the length of the die employed is much larger than the critical length required to develop maximum properties (*L/D* 2.5), extrudates with relatively poor tensile properties are produced. The reduction in properties with increasing die length is accounted for by the relaxation of a morphology developed in the die entrance region which decays with increasing residence time in the die land. It is apparent from the data that beyond a critical die length, in the region of *L/D* 33 to 67, relaxation of this orientation is effectively complete.

The change in tensile properties and orientation with *L/D* beyond 2.5 can be approximated by a simple relaxation model given the following assumptions.

1. The effect of the die entrance section is to develop an orientation which relaxes within the constant diameter die section as a function of the flow residence time and equivalent die length (due to constant flow velocity).
2. Further relaxation of the die-developed morphology outside the die, in the spinline, is restrained due to the presence of spinline tension.
3. The property development in the die section is additive to that in the post-extrusion spinline process, thus producing the overall tensile or orientation parameter value.
4. Where the die length is significantly large (such as *L/D* 133) and where negligible sensitivity to die *L/D* exists, the convergent flow developed morphology can be said to be fully relaxed. The value of this minimum tensile property reflects the influence of the spinline-applied extension only.
5. The effect of shear strain (predominant in long dies) on tensile properties and orientation is neglected.

Given these assumptions, the relationship

$$A = B + Ce^{(-1/\tau)(L/D)} \qquad (2)$$

can be proposed. This can be written as

$$\ln(A - B) = \ln C + (-1/\tau)(L/D) \qquad (3)$$

A is the magnitude of the parameter being fitted (e.g. modulus, tensile strength, yield stress, $\langle P_2\rangle$). B is the magnitude of the contribution of the parameter (e.g. modulus) that results only from spinline extension and corresponds to the minimum, die *L/D* insensitive value experimentally observed (e.g. modulus at die *L/D* 133). C represents the magnitude of the maximum contribution to the parameter (e.g. modulus) due to flow in the die. C is determined from the intercept of a least-squares plot of the natural log of the difference between the experimentally observed parameter values A (e.g. modulus at *L/D*) and B (e.g. fully relaxed modulus) against die *L/D* (equation (3)). The data from die *L/D* 0.5 are excluded from these plots. τ represents the characteristic relaxation *L/D* associated with the decay of the parameter (e.g. modulus) with die *L/D*. It is calculated from the slope of the best-fit line of equation (3).

The values of B and regression-fit coefficients C and τ that characterize the relationships between initial modulus, tensile strength, yield stress and orientation using the above model are recorded in *Table 1*. Reasonable agreement between the experimentally determined data points and the model-generated curves is shown in *Figures 4* and *6*. However, the large initial reduction in properties is consistently under-represented. The nature of the model is such that determination of the coefficients C and τ is sensitive to the small differences between property values of L/D 33 to 100 and L/D 133, resulting in a poor fit at lower L/D. The comparatively poor agreement between the experimentally determined yield stress and the model (*Figure 4c*) exists due to curvature in the plot of the natural log of the difference between the yield stress at a particular L/D and the fully relaxed yield stress against L/D. The regression-fit line in this case was determined using the points from die L/D 2.5 to 33 inclusive. The value of τ associated with the tensile strength of the extrudate prepared at the rheometer barrel temperature of 290°C (71 in *Table 1*) differs markedly from the other values. This is reflected in the observed weak sensitivity of tensile strength to die L/D at 290°C (*Figure 4b*), and suggests the involvement of an additional influencing factor. Changes in tensile strength with processing are addressed in the following section and in the accompanying paper[1].

Clearly, the model used here is a simple representation of a more complex process. Nevertheless, the ability of equation (2), which involves an exponential decay term, to describe changes in tensile properties (*Figure 4*) and orientation (*Figure 6*) with die L/D supports the explanation of orientation–relaxation as the mechanism for the reduction in properties with increasing die L/D. The average of the relaxation L/D calculated for the three tensile parameters and orientation (*Table 1*) is approximately 37 die L/D units. This relaxation parameter can be expressed in the timebase knowing the average flow velocity in the die. This can be calculated from the capillary plunger speed and flow geometries based on the constant flow rate condition. From the average flow velocity in the die of $3.3 \times 10^{-4}\,\mathrm{m\,s^{-1}}$ and a die length of 0.029 m, equivalent to 37 die L/D units, an average convergent flow induced orientation relaxation time of approximately 0.5 s was calculated. This suggests that the values of the tensile and orientation parameters associated with the convergent flow developed morphology decrease to 1/e or 37% of their initial magnitudes within a time of 0.5 s or a flow length of 37 die L/D units.

The effect of temperature (although not thoroughly investigated due to the narrow temperature-processing window of this material) on orientation development can be explained by relaxation effects. At the higher extrusion temperature of 300°C the equivalent stiffness, yield stress and orientation levels for a given die L/D are less than those for samples extruded at 290°C. Increased temperature favours increased orientation relaxation through (i) an increase in mobility afforded by a reduction in viscosity and (ii) a longer time prior to solidification outside the die. This result is in agreement with earlier work which showed that tensile properties of lightly drawn TLCPs (produced using a die of L/D 33 at temperatures ranging from 270 to 350°C) decay with increasing temperature[16].

Where a shear velocity profile exists, the amount of shear deformation is directly related to die length or L/D. In long dies, the bulk of the relaxation of the orientation developed in the converging section is complete and thus the effect of shear on the development of mechanical properties would be expected to be visible. However, the tensile properties of materials produced using dies of L/D 67, 100 and 133 (*Figure 4*) show no clear relationship, and increasing amounts of shear in the die appear to have no significant effect on tensile properties.

To investigate this further, the initial moduli of extrudates prepared from four dies at three different levels of applied drawdown ratio are plotted in *Figure 8*. At similar draw ratios, only a small reduction in tensile modulus is apparent with increasing die length. Although not shown, tensile strength exhibits a similar trend. This slight decrease in the value of tensile properties with increasing shear in the die is explained by the relaxation phenomenon discussed previously. In these experiments, the effect of increasing shear, resulting from flow in longer dies, can be discounted. These results agree with another study[15] which found that no effect occurred with increased die length, but differ from yet another study[25] where it was shown that a slight improvement was observed when using the die of L/D 133 compared to that of L/D 33.

Effect of deformation rate

The effect of deformation or shear rate in the die has been studied using the shortest and longest dies. TLCP samples were prepared at five different flow/shear rates at 290°C. The take-up speed was adjusted in each case to produce an extrudate having a constant applied total amount of extension in the spinline and thus give an approximately constant diameter. Although a constant level of total extensional strain was applied, it was not possible to maintain a constant extensional strain rate in the spinline due to the velocity difference between the material exiting the die and the take-up spool. However, orientation development is reportedly insensitive to extensional strain rate[15]. In *Figure 9*, initial modulus and tensile strength are plotted against shear rate at the

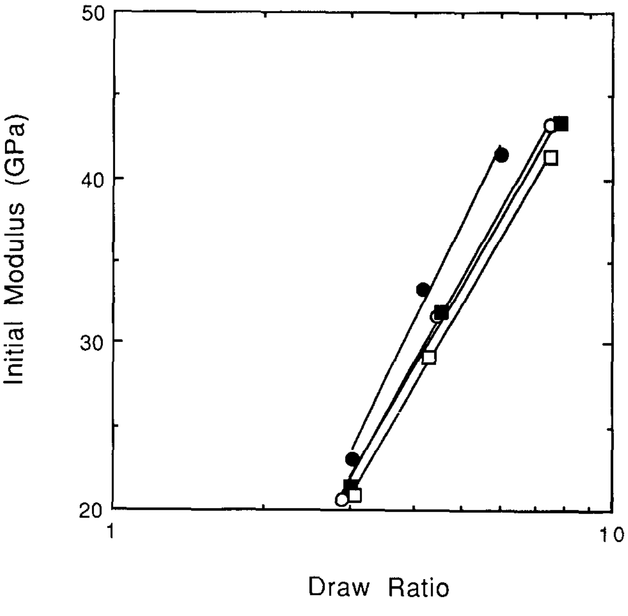

Figure 8 Plots of initial modulus *versus* applied draw ratio using dies of L/D 33 (●), 67 (○), 100 (■) and 133 (□) at an extrusion temperature of 290°C

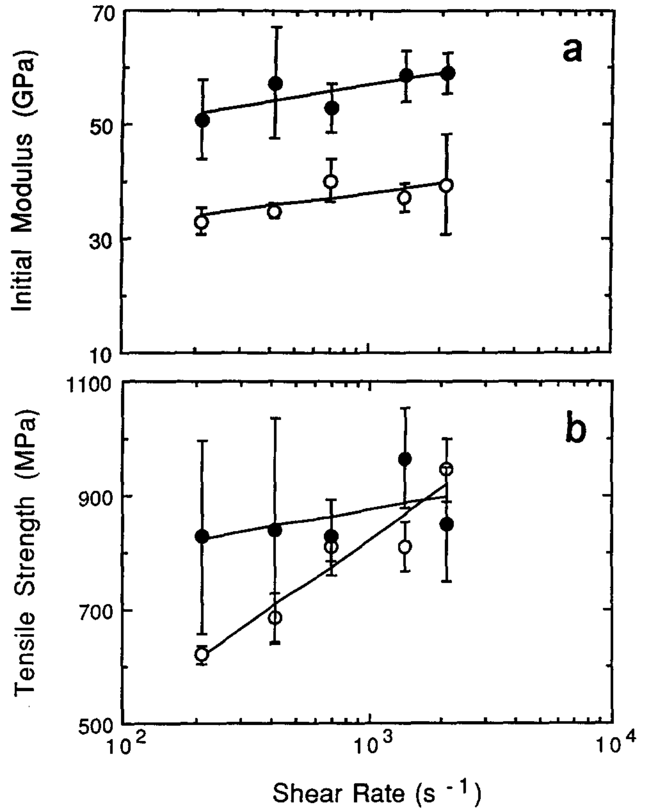

Figure 9 Plots of (a) initial modulus and (b) tensile strength against shear rate at the die wall (Rabinowitsch–Mooney corrected) for dies of *L*/*D* 0.5 (●) and 133 (○). Samples prepared at an equivalent draw ratio of 8 and an extrusion temperature of 290°C

die wall. Over the decade range studied, a slight improvement in initial modulus with increasing shear rate is apparent. This increase, which is independent of die *L*/*D*, can be explained by reduced residence time in the die allowing for less relaxation.

With regards to tenacity, material produced from the die of *L*/*D* 133 is strongly sensitive to deformation rate. This is not the case for material produced using the die of *L*/*D* 0.5. This difference indicates that the effect results from extrusion in the die and not from within the spinline, as they both share similar thermal and deformational histories after exiting the die. The slight increase in modulus compared to the appreciable change in strength suggests that a factor other than orientation is involved in this relationship. To consider that shear rate affects breaking strength in long dies would seem inappropriate as the total amount of applied shear (shear strain) has been previously discounted as having any significant influence on this property for this material.

Extrusion pressure (or shear stress) may offer an explanation for this phenomenon. To maintain the equivalent increasing flow rates in the longer dies, much greater pressure or shear stress differences are developed than in the shorter dies. The differences in extrusion pressures between the lowest and highest shear rates employed for the two dies of *L*/*D* 0.5 and 133 are 0.7 and 27 MPa, respectively. The breaking strength is affected through changes in the microstructure[42], such as free volume effects, which may be influenced by the level of extrusion pressure. At 290°C, near the crystalline to nematic transition temperature, the greater extrusion pressure may refine the microstructure. The greater sensitivity of tenacity to shear rate, associated with the die of *L*/*D* 133, results from the greater difference in extrusion pressure. Implicit in this explanation is the suggestion that the tensile strength of the material produced from a short die is not fully developed at 290°C. This is supported by the different effects that temperature has on tenacity with die *L*/*D* compared to those observed for stiffness and yield stress (*Figure 4*). The tenacities of samples produced at 290°C are less than expected relative to those produced at 300°C, where the orientation is less (as indicated by tensile properties and WAXD). This may be related to the rheological yield stress and the extrudate quality critical stress phenomena[12,16].

Effect of spinline extension

The effect of extension applied in the spinline was studied using three dies representative of the range of *L*/*D* evaluated. The tensile modulus, tensile strength and orientation of extrudate produced from dies of *L*/*D* 0.5, 10 and 133 at different draw ratios are shown in *Figure 10*. An initial increase in stiffness and tensile strength with increasing draw ratio is apparent. In the

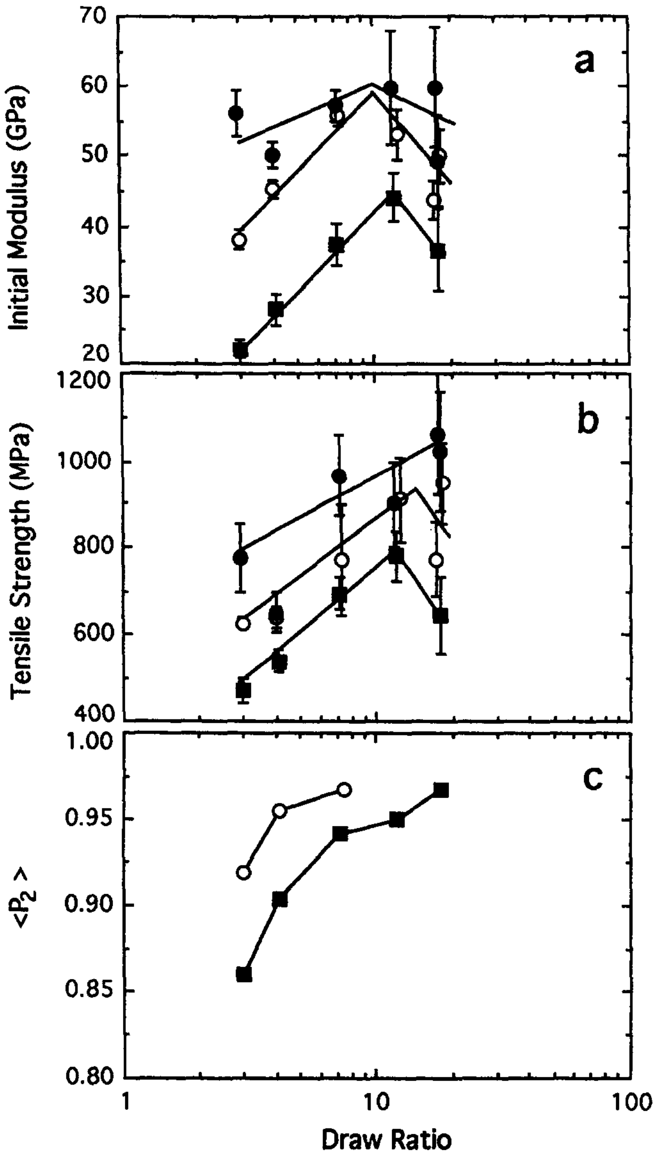

Figure 10 Plots of (a) initial modulus, (b) tensile strength and (c) macromolecular orientation against spinline draw ratio for extrudates prepared using dies of *L*/*D* 0.5 (●), 10 (○) and 133 (■) at an extrusion temperature of 290°C

region of draw ratio 10, maxima in stiffness and strength are observed. However, the degree of orientation continues to increase monotonically with draw ratio with no maxima observed (shown for the sample prepared from the die of *L/D* 133 only). The presence of the maximum in tensile modulus and the fact that orientation continues to increase beyond the critical draw ratio have also been reported by Krigbaum *et al.*[12]. In that study, it was proposed that the reduction in properties results from defects introduced at a higher draw ratio. These defects are associated with the deleterious presence of blocky HBA crystalline groups in the melt.

Several additional observations can be made from *Figure 10*. Firstly, the three dies impart different prior morphologies which are further developed in the non-isothermal, uniaxial–extensional flow field in the spinline. In agreement with earlier observations, extrudate from the die of *L/D* 0.5 is associated with the highest stiffness, and that from the die of *L/D* 10 is superior to that produced using the die of *L/D* 133 at an equivalent draw ratio. Secondly, the maxima in tensile properties with draw ratio increase with the use of the shorter dies. Extrudate from the die of *L/D* 0.5 exhibited a maximum average initial modulus of 60 GPa and a tensile strength 1.1 GPa, while that from the die of *L/D* 133 exhibited values of 45 GPa and 0.8 GPa, respectively. One important implication here is that where a mechanism exists in processing to limit the development of tensile properties in the spinline (such as draw resonance instability[42]), significant attention should be directed to die geometry in order to maximize properties. Thirdly, it appears that the draw ratio at which property maxima occur is largely independent of the die used. This observation is in agreement with the proposed defect mechanism[12], which limits tensile properties irrespective of the degree of orientation, since spinline thermal histories are identical and levels of orientation differ.

CONCLUSIONS

The influence of die geometry on the development of mechanical properties and structure of a thermotropic copolyester is an important processing parameter. A comprehensive study involving several extrusion dies of various aspect ratios has shown that the orientation preserved in lightly drawn solidified material strongly reflects the deformational history in the die. This is attributable to the long orientation–relaxation times associated with these materials. Large differences in extrudate microstructure as measured by SEM and WAXD methods exist, which correlate with the tensile properties measured. Thermal analysis indicates that changes in tensile properties result primarily from differences in flow-induced orientation and relaxation, since no changes in crystalline melting behaviour are detectable.

Extensional flow in the converging section of the die produces a high degree of macromolecular orientation. Maximum tensile properties and orientation are observed to occur in extrudates from the short die of *L/D* 2.5. The use of longer dies and higher extrusion temperatures allows for enhanced relaxation of the morphology developed in the converging flow, resulting in reduced tensile properties. This decay of tensile properties and the WAXD orientation parameter with increasing flow residence time outside the converging section can be accounted for by a model incorporating an exponential decay term. An average relaxation time of the order of 0.5 s indicates that the bulk of the molecular orientation is relaxed in the region of *L/D* 33 to 67. The effect of additional shear strain resulting from flow through longer dies appears insignificant. A critical minimum die aspect ratio in the region of *L/D* 2.5 exists for maximum development of die flow induced orientation as slightly reduced properties were observed with the die of *L/D* 0.5.

In processes where spinline extension is applied to maximize the tensile properties, this work has shown that attention to die design is necessary to optimize properties. The deformation rate appears to have less effect, which agrees with previous studies showing that the resulting filament stiffness is only related to the total amount of extension. The deformation rate is significant to the development of maximum tensile strength where extrusion is undertaken at 290°C, suggesting that the material at this lower temperature is not fully molten. Higher extrusion pressures accompanying the higher deformation rate conceivably act to break up the weak, higher temperature crystalline order that may disrupt and weaken the microstructure.

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