Tensile deformation and failure of poly(*p*-phenylene terephthalamide) fibres

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The tensile deformation and failure of a wide range of poly(*p*-phenylene terephthalamide) fibres is investigated. Fibre tensile modulus and tensile strength can be varied widely through simple processing variations, yet the fibres are found to exhibit similar non-linear elastic deformation responses as elucidated in stress perturbation experiments. An asymptotic modulus characteristic of the local orientation in the fibres is determined and is found to correlate well with the tensile strength of the fibres in accordance with straightforward shear failure criteria. The tensile failure of these fibres is thus dominated by the inherent strength anisotropy of linear chain polymers and the imperfect orientation in the fibres.

(Keywords: poly(*p*-phenylene terephthalamide); aramid; deformation; failure; fibre; tensile properties; shear)

INTRODUCTION

The discovery, development and commercialization of high-strength/high-modulus aramid fibres in the late 1960s and early 1970s by duPont (Kevlar®) revolutionized the polymer community in terms of the potential of polymers in high-performance applications. Never before had mechanical properties for a synthetic polymer fibre been engineered to such high levels on a commercial scale. The success of these endeavours is fundamentally routed in the simplification of the underlying fibre structure. The synthesis of extended or stiff-chain structures, namely poly(*p*-benzamide) and poly(*p*-phenylene terephthalamide) (PPTA), provided for the potential of lyotropic liquid-crystalline processing and the ability to achieve high degrees of uniaxial orientation of essentially fully extended chains. For the first time, the simplistic 'continuous crystal' model of Staudinger[1] bore some relevance to an achieved fibre structure.

The key to achieving high mechanical properties from polymeric structures is, naturally, the inherent strength and stiffness of primary chemical bonding. The continuous crystal ideal, if achieved, represents a structure from which maximal properties could be derived. This idealized structure incorporates the key features of high molecular weight (few chain-end defects), a fully extended backbone, perfect uniaxial orientation and perfect lateral packing of the chains. Also noteworthy is that such an ideal structure elucidates the inherent anisotropy present in near-perfect polymeric systems. Along the chain direction, properties are high, deriving from primary chemical bonding, whereas transverse to the chain, properties are dominated by the much weaker secondary interactions between chains. These much weaker secondary interactions will obviously play an important role in the material's behaviour, especially where imperfect orientations are concerned.

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The mechanical behaviour of such an idealized structure as the continuous crystal has only recently been analysed[2,3]. This work has shown the critical importance of molecular weight on the development of tensile modulus and strength as well as the importance of intermolecular interactions. Experimentally, achievement of such realistic structures has been accomplished in work with various polydiacetylene single crystals[4,5]. That work has shown that the fundamental properties of the primary chemical bonding along the polymer chain backbone can, in fact, be realized. These materials, however, are far from the realm of continuous fibres, where process limitations inherently lead to imperfect structures. It is the role of these realistic imperfections on fibre deformation and failure that is of interest in the current work.

The deformation and failure of aramid fibres have been investigated in a number of studies covering many deformation responses. The high tensile modulus and high tensile strength exhibited by these fibres along with an appreciation of their inherent anisotropy was noted early on[6–9]. Relationships between the development of both orientation and crystallinity and mechanical properties have been observed in film studies[10], but these relationships did not translate to the properties of fibres. Detailed X-ray diffraction studies have further defined the relationship of orientation to modulus[11], including the response of orientation to deformation[12,13]. Earlier work had also shown the dramatic increase in orientation that can occur during tensile deformation from sonic velocity observations[14,15]. Other studies have addressed the variability of tensile strength[16–18] and further characterization of the mechanical anisotropy[19,20]. Detailed analyses of commercial aramid fibres have led to some speculation concerning tensile strength[21], yet no relationships have been established between fibre structure and tensile strength applicable to a wide range of aramid fibres. In the present work, we extend our previous studies[22,23] on commercial aramid fibres (Kevlar®) to encompass the tensile deformation and failure of a wide

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range of PPTA fibres. It will be shown that the tensile failure of these fibres is dominated by the inherent strength anisotropy of linear chain polymers and the imperfect orientation in the fibres.

EXPERIMENTAL

Poly(*p*-phenylene terephthalamide) polymers with inherent viscosities of 3–7 dl g^{-1} (measured in 96% sulphuric acid) were prepared for this work following generally accepted practice[24]. Fibre spinning was carried out using a specially designed laboratory fibre spinning apparatus employing approximately 50 ml of spinning solution. In order to achieve as wide a range of mechanical properties as possible, dominant spinning variables, such as solution concentration, coagulation environment and spin stretch factor, were varied as widely as possible within operable spinning conditions, again, following generally accepted air-gap spinning practice[25]. Likewise, representative heat treatments were also performed.

Mechanical testing of the PPTA fibres was performed using an Instron 1122 testing machine interfaced with a Hewlett–Packard series 300 computer to provide programmed deformation histories, data collection and analysis. Deformations were generally calculated from the rate of testing and elapsed time, although tests were run using a crosshead motion detector to verify accuracy. Simple tensile properties of the fibres were normally evaluated using a 2.54 cm (1 inch) gauge length and a testing rate of 10% min^{-1}. Reported tensile properties are the average of between seven and ten breaks. We define the initial fibre modulus from linear regression of the stress–strain data over the strain window of 0.001 to 0.004. The data collection rate was chosen to provide incremental strain readings of roughly 0.0001. Local moduli were obtained at any point along the stress–strain curve from a linear regression of the stress–strain data using a total of 11 data pairs, five just prior to and five just after any point. This generally represented a local strain window of approximately 0.0011 over which local moduli were evaluated. Filament size (denier) was determined vibroscopically by resonating a 4 cm length using tensions of 10–15 MPa. A variability of 5–7% is associated with this determination of filament size.

For detailed characterization of the fibre tensile deformation and failure, both cyclic and tensile perturbation tests, as introduced previously[23], were employed. Perturbation tests were performed on samples that were first mechanically conditioned by loading to a stress of approximately 90–95% of their anticipated break stress (as determined from the simple tensile tests). The conditioning load was maintained for 30–60 s followed by an unloading at 10% min^{-1}. Perturbation tests were run using a gauge length of 5.08 cm (2 inch), a testing rate of 10% min^{-1} and a relaxation time of 30 s (ref. 23). Normally, five perturbations of successively increasing load were performed on a sample prior to loading to break. Generally, four or eight filaments were evaluated in these tests depending on the breadth of the stress range being investigated.

RESULTS

The wide range of initial tensile modulus and tensile strength that poly(*p*-phenylene terephthalamide) fibres can achieve through simple processing variations is illustrated in *Figure 1*. General relationships between processing history and the development of fibre mechanical properties have appeared[25,26] and similar results were observed in this work. While a more detailed discussion of processing influences on the development of fibre structure and resulting mechanical properties is warranted, such a discussion would be premature without first having established more fundamental relationships between mechanical properties and fibre structure.

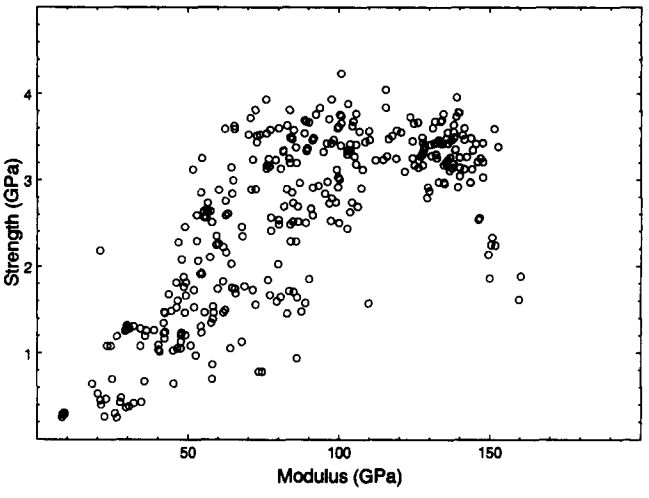

Figure 1 PTTA property map of filament tensile strength and corresponding initial modulus

While the fibres produced exhibit substantial differences in modulus and strength, their tensile deformation behaviour is, in general, very similar and analogous to the behaviour reported previously for commercial fibres[23]. *Figure 2* illustrates typical stress–strain responses for representative fibres. Generally, PPTA fibres exhibit high tensile modulus and high tensile strength. Accompanying these high tensile properties is a correspondingly low elongation to break. Most interestingly, as *Figure 2a* illustrates, the stress–strain curves are not that of a simple linear elastic material. The tensile deformation response is non-linear, generally taking on a sigmoidal shape. The non-linear features of the deformation response are more easily observed by differentiation of the stress–strain curves to yield local modulus information at any point during the deformation. *Figure 2b* compares the non-linearity of the curves as represented by the corresponding modulus response.

Following a high initial modulus, the modulus drops with further deformation and a corresponding shoulder is observed in the stress–strain response. For many of the lower-strength fibres (< 1 GPa), the modulus remains low with further straining to break. However, for the modest- to high-strength fibres (> 1 GPa), the modulus, after initially dropping, is generally observed to increase with further straining, producing a sigmoidal appearance in the stress–strain curves. The initial drop of the modulus at low strains can be quite substantial (*Figure 2b*). Even in the strain window of 0.001 to 0.004 used as a reference for determining an 'initial' modulus, there can be a substantial variation in modulus with strain, especially for the initially lower-modulus fibres.

The shoulders in the stress–strain curves and the apparent softening observed in the moduli data were previously shown to be associated with the onsets of

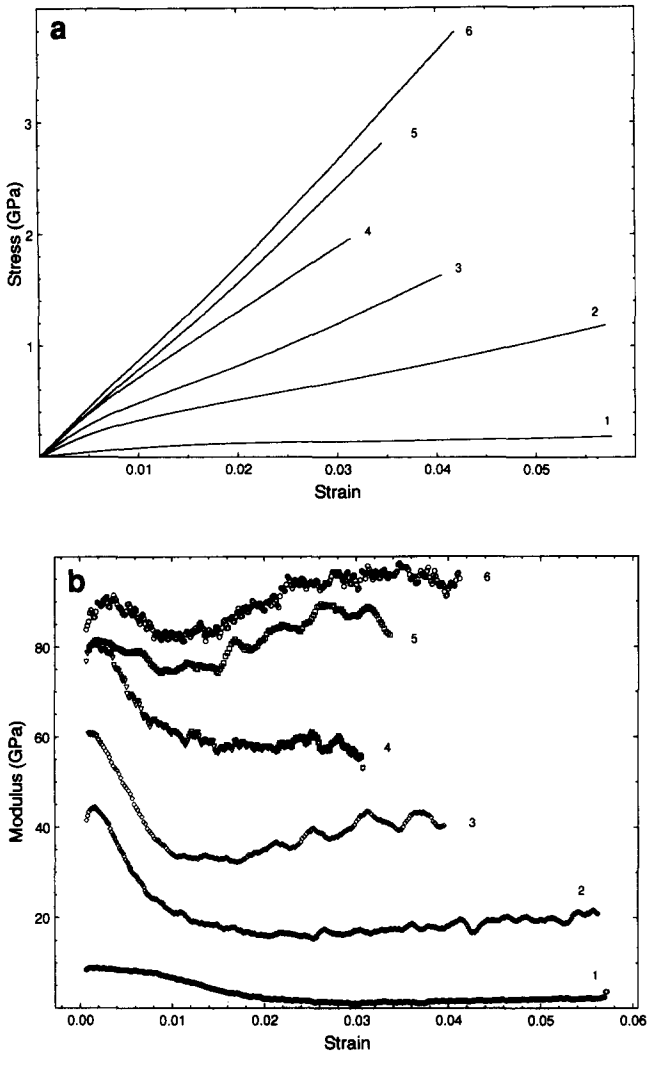

Figure 2 Tensile (a) stress–strain curves and (b) modulus–strain curves representative of the PPTA fibres of *Figure 1*

measurable irreversible deformations and of time-dependent behaviour[23]. *Figure 3* illustrates typical observations of irreversible deformations when fibres are subjected to cyclic loadings to loads approaching the break point. The magnitude of the irreversible deformation is primarily determined by the maximum stress or strain that the fibre has experienced. Repeated loadings to the same stress or strain level generally only produce slight additional amounts of irreversible deformation.

Figure 3 also illustrates the much stronger similarity of the deformation responses subsequent to an initial high stress loading (second loading curves). The response following such a 'mechanical conditioning' reveals the underlying non-linear deformation behaviour of the PPTA fibres. Subsequent to a mechanical conditioning to loads near the break point, the tensile deformation response is less influenced by irreversible effects, which have essentially been removed by the initial conditioning. This subsequent deformation response reveals a modulus behaviour that generally increases with increasing stress or strain. Note also that the initial modulus after mechanical conditioning is generally observed to be greater than the virgin fibre's initial modulus, in contrast with the observations made on commercial fibres[23] but in agreement with other findings[12] also concerned with similar lower-modulus PPTA fibres.

The non-linear deformation response is most clearly revealed in the tensile perturbation tests, where the influences of irreversible deformations and viscoelastic effects could be minimized. *Figure 4* illustrates the non-linear modulus response elucidated by perturbation

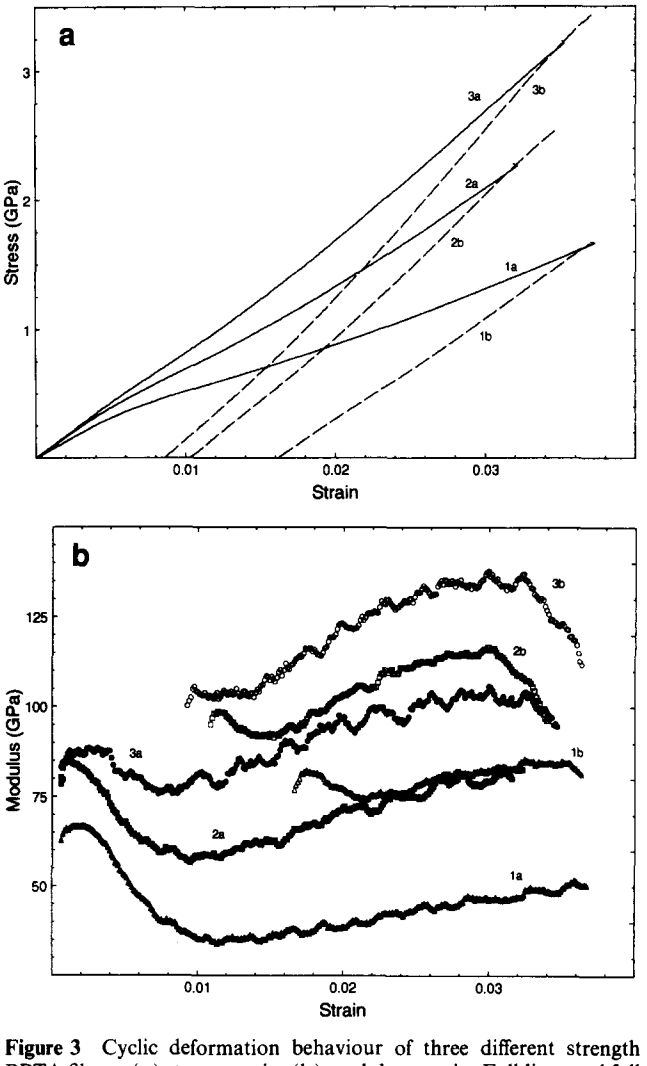

Figure 3 Cyclic deformation behaviour of three different strength PPTA fibres: (a) stress–strain, (b) modulus–strain. Full lines and full symbols correspond to first loadings, and broken lines and open symbols refer to second loadings

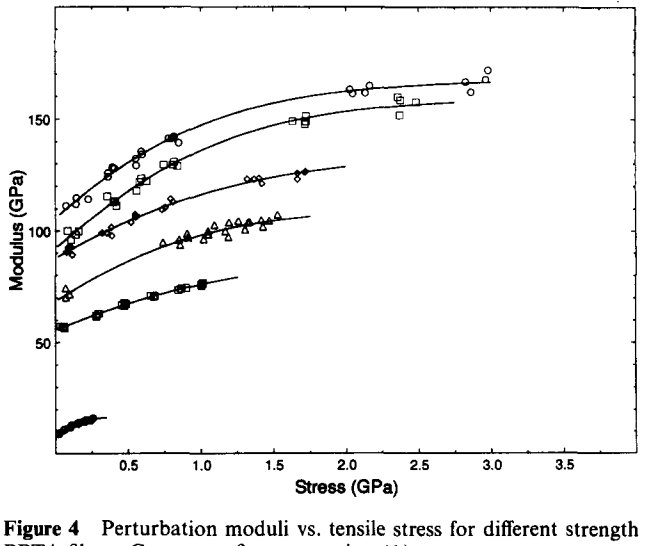

Figure 4 Perturbation moduli vs. tensile stress for different strength PPTA fibres. Curves are fits to equation (1)

tests. The simple extensions to break had suggested only a subtle non-linearity (*Figure 2*) with the underlying non-linear behaviour being suppressed due to time-dependent and irreversible effects dominating the first deformation response[23]. The tensile deformation response revealed from perturbation tests is non-linear, with a substantial increase in modulus being observed during the initial part of the deformation and a levelling off of the modulus at high strains approaching the break point. This observation is in agreement with our previous observations and is comparable to sonic modulus observations made on PPTA yarns[14,15].

DISCUSSION

Our previous findings on commercial PPTA fibres (Kevlar®) have demonstrated a relationship between the non-linear tensile deformation response and the response of the fibre macrostructure[22,23]. The unique macrostructure of PPTA fibres was first briefly described by Ballou[14] in terms of a periodic bending of the molecular chains along the fibre direction with the hydrogen-bonding direction preferentially arranged radially. The supramolecular structure was further investigated by Dobb *et al.*[27,28], who popularized the arrangement as a hydrogen-bonded 'pleated sheet' morphology. From light scattering experiments we have shown a correspondence between the progressive opening-up or alignment of the pleated superstructure and the stress dependence of modulus, which gives rise to the non-linear stress–strain behaviour[22,23]. In accord with these observations, the PTTA fibres investigated in the present work are also well described by this supramolecular organization. Likewise, cursory light scattering observations indicate both a correspondence between the extent of pleating and fibre modulus as well as an analogous supramolecular response to deformation.

Figure 4 compared the non-linear modulus response of various fibres possessing a wide range of tensile strengths. A non-linear response is observed for all the fibres, with the highest-strength fibres most clearly revealing the behaviour. During the early part of the deformation, the modulus increases roughly linearly with deformation or stress, then levels off at high stresses approaching the break point. This non-linear response corresponds well with the opening-up and orienting under load of the fibre's pleated supermolecular structure[22,23]. Historically, this behaviour was first indicated from sonic modulus measurements[14,15] under load, where results comparable to the perturbation results reported here were obtained. Other studies of PPTA fibres have also demonstrated this increase in orientation under tensile load from direct X-ray diffraction experiments[12,13]. These previous works on yarn bundles employing both sonic and diffraction techniques are thus fully supported by the single-filament studies of the present investigation.

An analytical description of the non-linear tensile response was presented previously[23] based on a cooperative local shearing giving rise to the improvement in orientation under load. The behaviour is well described by the form:

$$\frac{1}{E} = \frac{1}{E_a} + \frac{\langle \tan^2 \theta_0 \rangle}{G} \exp\left(\frac{-2\sigma}{G}\right) \qquad (1)$$

where E is the tensile modulus at a stress σ, E_a is the tensile modulus asymptotically approached at high stress, G is the local shear modulus and $\tan^2 \theta_0$ is a measure of the initial cooperative misorientation. The full curves in *Figure 4* illustrate the fit of equation (1) to the observed modulus response for fibres of various strength, showing the wide applicability of equation (1) to the PPTA fibres of this study.

With a general representation of the overall deformation response of the PPTA fibres having been established, it seems appropriate to consider the fibres' ultimate tensile failure. One would expect that, in a uniaxial structure composed of an assenbly of extended polymer chains, both fibre modulus and strength would be critically dependent on orientation. In fact, the relationship between modulus (E) and orientation is well described by standard anisotropic elasticity expressions[11,29,30], e.g.

$$1/E = a_{11} \cos^4 \theta + (2a_{12} + a_{66}) \sin^2 \theta \cos^2 \theta + a_{22} \sin^4 \theta \qquad (2)$$

where the geometric parameters are appropriately averaged over the orientation distribution, and a_{ij} are the local elastic compliances.

It is readily appreciated from equation (2) that modulus thus provides a most sensitive measure of orientation, especially in the regime of low misorientation angles. The lack of a direct correlation of fibre strength with initial modulus (*Figure 1*) is at first suggestive of an orientation-insensitive failure. As illustrated in *Figure 1*, for a given strength, fibres possessing a factor of two times or more variation in modulus can be produced and, likewise for comparable modulus, fibre strengths are observed to vary by easily a factor of two or more. On the other hand, the lack of a correlation in *Figure 1* is not unexpected in light of the variable amounts of irreversible and time-dependent behaviours that can be generated by processing variations. This variability is certainly sufficient to explain the lack of any direct correlation in *Figure 1*.

The virgin PPTA fibres investigated in this work were found to exhibit a wide range of mechanical deformation responses (*Figures 2* and *3*). Depending on processing histories, various levels of orientation and hence modulus are achieved. Additionally, the extent of irreversible deformation and time-dependent character vary considerably among the fibres. However, the mechanical behaviour is in fact quite similar when the behaviour is compared following mechanical conditioning to reduce the influences of the irreversible and time-dependent processes. This underlying non-linear elastic response of the fibres elucidated from perturbation testing is primarily accounted for by the response of the pleated supramolecular structure of the fibres and is well described by equation (1). We have previously noted[23] that the asymptotic modulus E_a observed in the high-stress region need not correspond to the modulus of a perfectly oriented structure. Indeed, as *Figure 4* illustrates, the observed value of E_a is substantially different for fibres of different strengths. From a macrostructureal viewpoint of fibre deformation, E_a may be considered to be a modulus characteristic of the local order[23]. This local order is thus on a scale below which a cooperative alignment in response to the axial stress is observed, and the asymptotic modulus E_a is thus taken as a representative measure of local orientation and local structure in the fibre. Additionally, because E_a is determined in the high-stress region approaching falure,

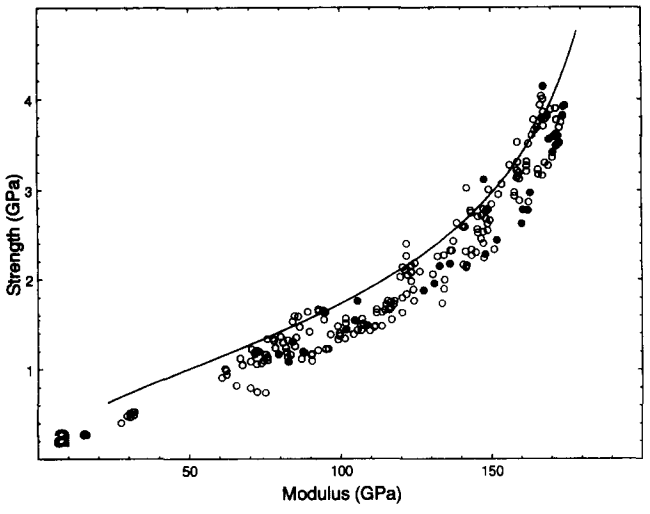

Figure 5 Filament tensile strength and corresponding asymptotic modulus obtained from perturbation testing (for details, see text)

it is also more naturally representative of the fibre structure prior to the failure.

Taking the perturbation moduli as being most representative of the fibres' elastic response under load, and, more particularly, representative of the orientation, it seems reasonable to pursue a correlation between tensile strength and perturbation modulus near break (asymptotic modulus). Schaefgen[31] has previously suggested a modest correlation of similar high-stress moduli obtained from sonic experiments with tensile strength of aramid yarns over a limited range of strengths. To evaluate this correlation further, the wide range of fibres produced for this work were characterized in single-filament perturbation experiments. To characterize orientation at break, the moduli observed in perturbation tests at loads just prior to break were measured. In light of equation (1), these values will be referred to as asymptotic moduli, although it should be noted that the values reported are taken from the experimental data rather than from a fit to equation (1) in order to be most representative of the fibres' actual local orientation at break.

Figure 5 summarizes the observed asymptotic moduli and corresponding tensile strengths for a wide range of tensile strengths representative of the fibres of *Figure 1*. In this case, a good correlation exists between the asymptotic modulus and the tensile strength. The higher the asymptotic modulus, the higher the corresponding tensile strength. Most striking is the dramatic upward curvature observed in *Figure 5*. As local fibre orientation improves, as evidenced by the achievement of higher asymptotic moduli, the strength of the fibre increases and becomes more sensitive to modulus or equivalently to the orientation.

The curvature in the property map (*Figure 5*) indicates an extreme sensitivity of properties to orientation. In fact, the behaviour is quite reminiscent of the behaviour observed in 'off-axis' testing of unidirectional composites, where properties change significantly with the angle of testing. In the uniaxial composite case, both modulus and strength decrease dramatically with increasing off-axis test angle (misorientation) owing to the inherent anisotropy of the material. The equations representing this sensitivity to orientation are the transformation rules of anisotropic elasticity. Modulus in this case is also well described by the form of equation (2) presented above. The strength may be approximated (for small misorientations) by a relation of the form:

$$\frac{1}{\sigma^2} = \frac{1}{\sigma_0^2}\cos^4\theta + \frac{1}{T^2}\sin^2\theta\cos^2\theta \qquad (3)$$

based on various generalizations of a Von Mises criterion[30,32]. Here σ is the composite break strength when tested at an off-axis angle of θ, σ_0 the strength of the perfectly aligned unidirectional composite ($\theta = 0$) and T a parameter whose value is related to the shear strength of the material. Except for near-perfect orientation, this behaviour is also well described by a simple maximum shear stress criterion[33], which gives the composite strength as:

$$\sigma = \frac{\tau_c}{\sin\theta\cos\theta} \qquad (4)$$

where τ_c is an interfacial shear strength. Equations (2), (3) and (4) are illustrated in *Figure 6a* for a fit to a 60 vol% graphite–epoxy unidirectional composite[30]. The extreme sensitivity of properties to orientation is thus readily appreciated from the small range of

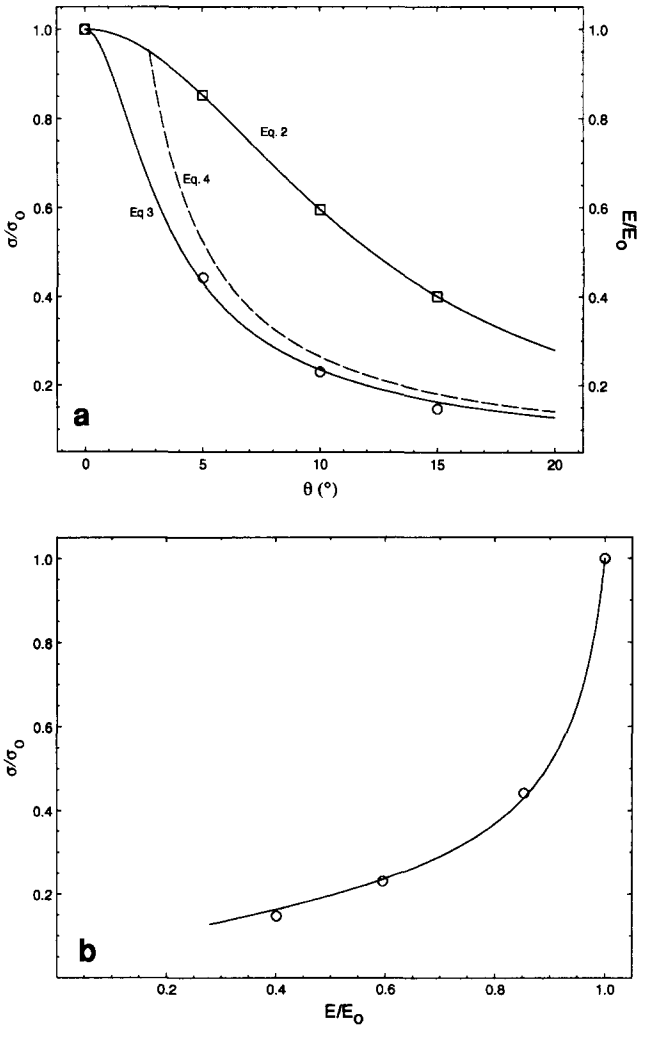

Figure 6 Mechanical property variation of a unidirectonal graphite–epoxy composite tested off-axis. (a) Strength (○) and modulus (□) variation with off-axis test angle. (b) Corresponding modulus–strength property map

misorientations represented in the figure. *Figure 6b* is a cross-plot of the modulus and strength data of *Figure 6a* and illustrates the distinctive upward curvature in this type of a property map for such an orientation-sensitive material. The upward curvature in the PPTA property map (*Figure 5*) suggests a similar failure dependence on inherent strength anisotropy and orientation.

The full curve in the PPTA fibre property map (*Figure 5*) was generated based on a cross-plotting of equations (2) and (4) (or equation (3)). A value of 200 GPa for $1/a_{11}$ was used as representative of the perfected oriented modulus based on refs 2 and 3. A value of 2 GPa was used for $(2a_{12} + a_{66})$ (ref. 34) and the $\sin^4\theta$ term is neglected for high degrees of orientation. From simple torsional experiments[19,20], an upper value estimate of the shear strength of PPTA fibres of 170 MPa was used. The qualitative agreement of the PPTA failure map with that calculated based on these simple values, which are representative of the fundamental modulus and strength anisotropy of the fibres, is remarkable.

As an independent verification of the orientation sensitivity observed in the PPTA property map, some of the highest-strength fibres were twisted to various extents to induce a helical misorientation. The twisted fibres were then examined in the perturbation tests to evaluate asymptotic moduli and strengths. The results were included in *Figure 5* (full circles) and agree with the results of fibres whose orientations were controlled through processing variations.

The simple shear stress criterion (equation (4) or equivalently a criterion of the form of equation (3)) represents the observed failure response of the wide range of aramid fibres investigated in this study. Initial evaluations of the high-modulus/high-strength fibres produced from the extended-chain polymer poly(*p*-phenylene benzobisthiazole) had also suggested dominant roles of misorientation and lateral interactions in determining tensile failures[35]. Related studies of other extended-chain polymer fibres possessing differing inherent anisotropies would be beneficial to elucidating the general applicability of such an approach and are welcomed.

SUMMARY

The tensile deformation and failure of a wide range of poly(*p*-phenylene terephthalamide) fibres produced by simple processing variations have been investigated. Fibre tensile modulus and tensile strength can be varied widely, yet the fibres are found to exhibit a similar non-linear elastic deformation response as elucidated in stress perturbation experiments. This non-linear behaviour was previously shown to be primarily accounted for by the opening of the pleated supermolecular structure in response to tensile deformation[23]. Modelling of this non-linear response had suggested a simple approach to characterizing the local orientation/structure of the fibre from the perturbation testing. An asymptotic modulus characteristic of the local orientation and representative of the fibre structure at failure is determined. The asymptotic modulus is found to correlate well with the tensile strength of the fibres in accordance with straightforward shear failure criteria. The inherent strength anisotropy of linear chain polymers, deriving from having strong primary chemical bonding along the chain backbone and much weaker secondary interactions between the chains, along with the imperfect orientation in the fibres are thus the dominant factors controlling the tensile failures.

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