Macrostructure and Mechanical Behavior of Fibers of Poly-*p*-Phenylene Benzobisthiazole

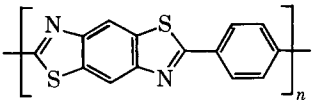
S. R. ALLEN, A. G. FILIPPOV, R. J. FARRIS, and E. L. THOMAS,*
Polymer Science and Engineering, University of Massachusetts, Amherst, Massachusetts 01003

Synopsis

Morphology and tensile behavior of wet-spun fibers of poly-*p*-phenylene benzobisthiazole have been investigated. The as-spun fibers contain a large number of voids, which result in void-localized tensile failure. The stress–strain behavior is elastic–plastic with strain hardening. This behavior is shown to be the result of residual stresses which arise during the wet-spinning process.

INTRODUCTION

Poly-*p*-phenylene benzobisthiazole (PBT), synthesized from 2,5-diamino-1,4 benzedithiol and terephthalic acid via a polycondensation reaction,[1] has been developed for the Air Force Ordered Polymers Research Program.[2]



PBT

The program is concerned with the preparation, processing, and characterization of thermally and environmentally resistant polymers of high strength, intended for use as structural materials. Our effort is centered on the mechanical behavior and morphological features of PBT fibers.

PBT characteristically belongs to the class of extended chain or rodlike polymers. Because of this physical nature, powerful mineral or organic acids are required for solvation of the polymer, which imposes restrictions on equipment and handling. However, processing of the ordered solutions of PBT can result in strong molecular interactions to yield material with very high modulus, strength, and thermal stability.

The fibers of PBT described in this article were produced by dry-jet wet spinning of solutions of approximately 10 wt % polymer in a solvent of 97.5/2.5 methane sulfonic acid/chlorosulfonic acid. We believe that high shrinkage stresses develop during fiber coagulation and have a significant effect on the fiber's mechanical behavior and morphology. This article presents the results of preliminary mechanical and morphological investigations of as-spun PBT fibers in light of this processing concern. Heat treatment and processing directly from the polymerization medium (polyphosphoric acid solution) results in significant property improvement over the as-spun fiber reported here.

* To whom correspondence should be sent.

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EXPERIMENTAL

Dry-jet wet spinning was used to produce fibers from solutions of PBT polymers. Fibers investigated were produced at Carnegie-Mellon University and at Celanese Research Co. Anisotropic polymer solutions of roughly 10 wt % PBT (limited by solubility) were used as the spinning dopes. The coagulation bath was typically a solution of water and methane sulfonic acid (the ratios of which could be varied), although methanol/sulfonane solutions were also used in some cases. After spinning, the fibers were water (or methanol) washed before room temperature drying. Some fibers were neutralized with dilute $NaHCO_3$ during washing. The effects of processing conditions on fiber properties will not be discussed in this work because of the limited variation of these conditions and the observed uniformity of mechanical properties and morphology of the various fibers investigated.

Fiber stress–strain behavior was obtained in accordance with ASTM standards for high-modulus single-filament materials.[3] The tensile tests were performed on a Toyo Tensilon model UTM-11 machine using 20-mm gauge length samples. Typically, a 0.2%/min strain rate was employed; but rates of 0.1, 1.0, and 10.0%/min were also used to observe any strain rate dependence. The mechanical properties reported were based on fiber cross-sectional areas calculated from diameters measured by light scattering and/or microscopy.

The morphological features of the fibers reported here are based on light optical and electron optical microscopy. Scanning electron microscopy (SEM) was done using an ETEC Autoscan operated at 20 kV. Fiber samples for SEM observation were first sputter coated with a 350 Å layer of gold in a Polaron E5100 SEM coating unit to minimize charging problems. The interior fiber morphology was studied in two ways: (1) examination of fibers which were peeled longitudinally using needles and tweezers, and (2) examination of the fracture ends of failed tensile-tested samples.

RESULTS

The morphology of the PBT fibers is of an extremely fibrillar nature. The mechanically peeled fibers clearly illustrate this feature (Fig. 1). Fibrils measured from these fibers had widths ranging from 0.2 to 1.5 μm, with fibril length much greater than width. Further peeling and mild sonication resulted in the observation of microfibrils via TEM down to as small as 70 Å in width with $L \gg W$. These fibrils and microfibrils appear to be lath- or ribbon-shaped rather than cylindrical. Wide-angle x-ray diffraction studies indicate near perfect molecular orientation along the fiber axis.

The PBT fibers studied in this work contained numerous large voids. The outline of the voids is easily seen using optical microscopy (Fig. 2). The large size of the voids is responsible for the void-localized fracture of the fibers (Figs. 3 and 4). The elliptically shaped regions in the SEM end views of Figure 4 indicate such a void. Due to the voids, only 85–90% of the fiber cross section in the void region is load bearing under stress. Relative void dimensions were also obtained from examination of the inner surfaces of the peeled fibers (Fig. 5).

The diameters of the PBT fibers studied ranged from 15 to 50 μm, the majority being in the 20-μm range. The cross sections were approximately circular with slight depressions in the area of a void.

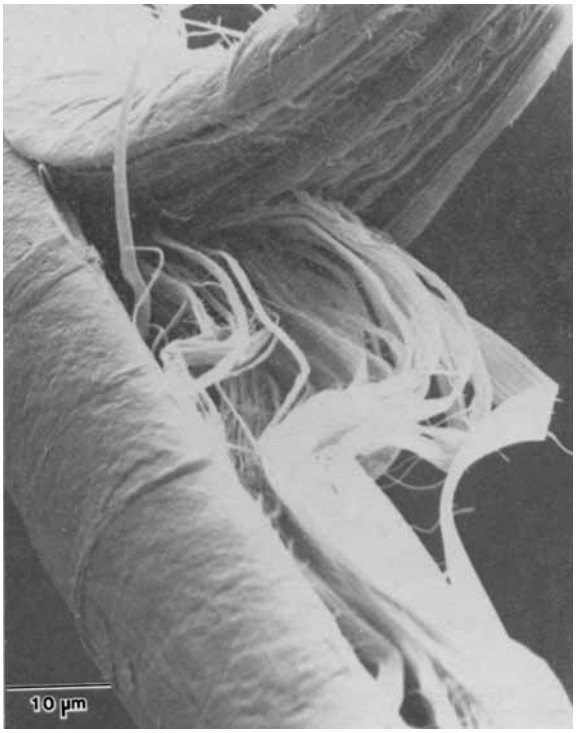


Fig. 1. SEM of PBT fiber peeled to reveal internal fibrillar character.

The outer regions of the cross section of the peeled fibers contained a number of kink bands. Figure 6 shows the presence of such kink or deformation bands which lie perpendicular to the fiber axis. Banding or kinking on a smaller scale in the microfibrils has also been observed in these PBT fibers.[4]

The general mechanical properties of the as-spun fibers are given in Table I. Figure 7 schematically illustrates the nonlinear stress–strain behavior observed for single filaments during tensile tests. The behavior shown is essentially that of an elastic–plastic body with strain hardening. Plastic deformations of roughly 2% were found for the filaments tested. The modulus of elasticity was seen to increase with reextension after initial plastic deformation. Essentially the same stress–strain behavior was obtained for all strain rates used.

DISCUSSION

The microfibril structures observed for PBT fibers indicate a fibrillar morphology similar to that discussed by Peterlin.[5] However, the composition of a microfibril would not consist of noncrystalline regions because of the extended-chain nature of PBT molecules. Also, slack or loose tie molecules in the structure would not be expected by similar reasoning. These differences, owing to the physical nature of the PBT molecules, must then be considered in understanding the fiber's mechanical properties. A similar fibrillar morphology for poly-*p*-phenylene terephthalamide (PPTA) fibers sold under the trade name of Kevlar has also been noted. Because of the similarity of fibrillar structure

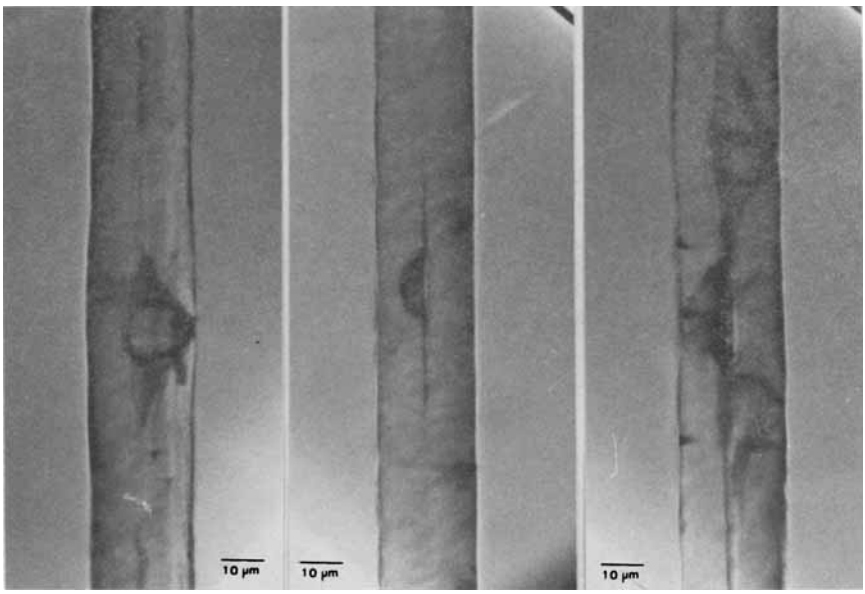


Fig. 2. Optical micrographs of voids in as-spun PBT fibers.

TABLE I
Mechanical Properties of As-Spun PBT Fibers

	Average	Range
Modulus, GPa	80	50–110
Strength, GPa	0.8	0.6–1.1
Strain at break, %	3	1–4

and the extended chain nature of PPTA and PBT, it is useful to compare properties of the two materials in fiber form.

The stress–strain behavior of Kevlar fibers[6–8] is quite different from that of PBT fibers. The Kevlar fibers show linear elastic stress–strain behavior with high modulus and strength. The stress–strain behavior of the PBT fibers (Fig. 7), while exhibiting high modulus, displayed lower strength and a nonlinear elastic–plastic nature. The fibrillar structure (and inherent anisotropic nature) of the PBT fibers does not permit an adequate description of the mechanical properties by conventional models. It will be shown that the essential feature determining both strength and deformation characteristics of PBT fibers is the presence of internal stress.

The existence of a shear or slip mechanism to completely account for the plastic deformation is unlikely for the PBT fibers on account of their structure. Owing to the geometry of the fibrillar elements ($L \gg W$), the activation energy for a shear displacement process would be larger than the activation energy for rupture of the element. Plastic deformations resulting from such shear displacement are normally also much higher than the 2% plastic deformation observed here. Materials that possess such a slip mechanism exhibit a decrease in their elastic limit upon annealing. Our results have shown an increase in the elastic limit and a decrease in the amount of plastic deformation upon annealing. In addition,

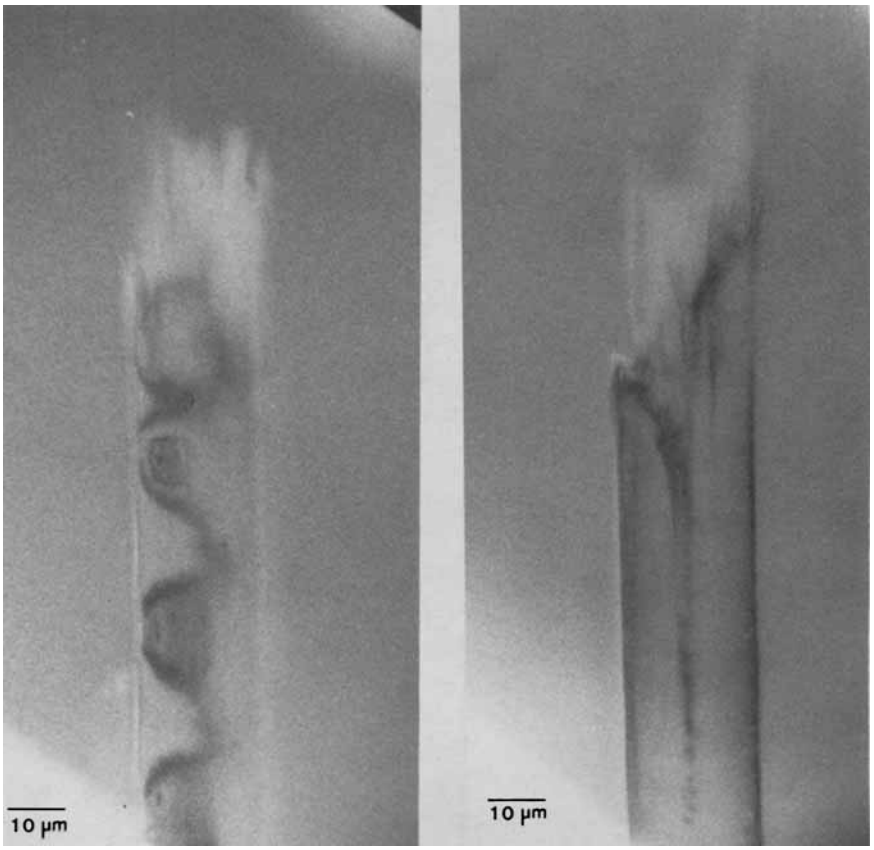
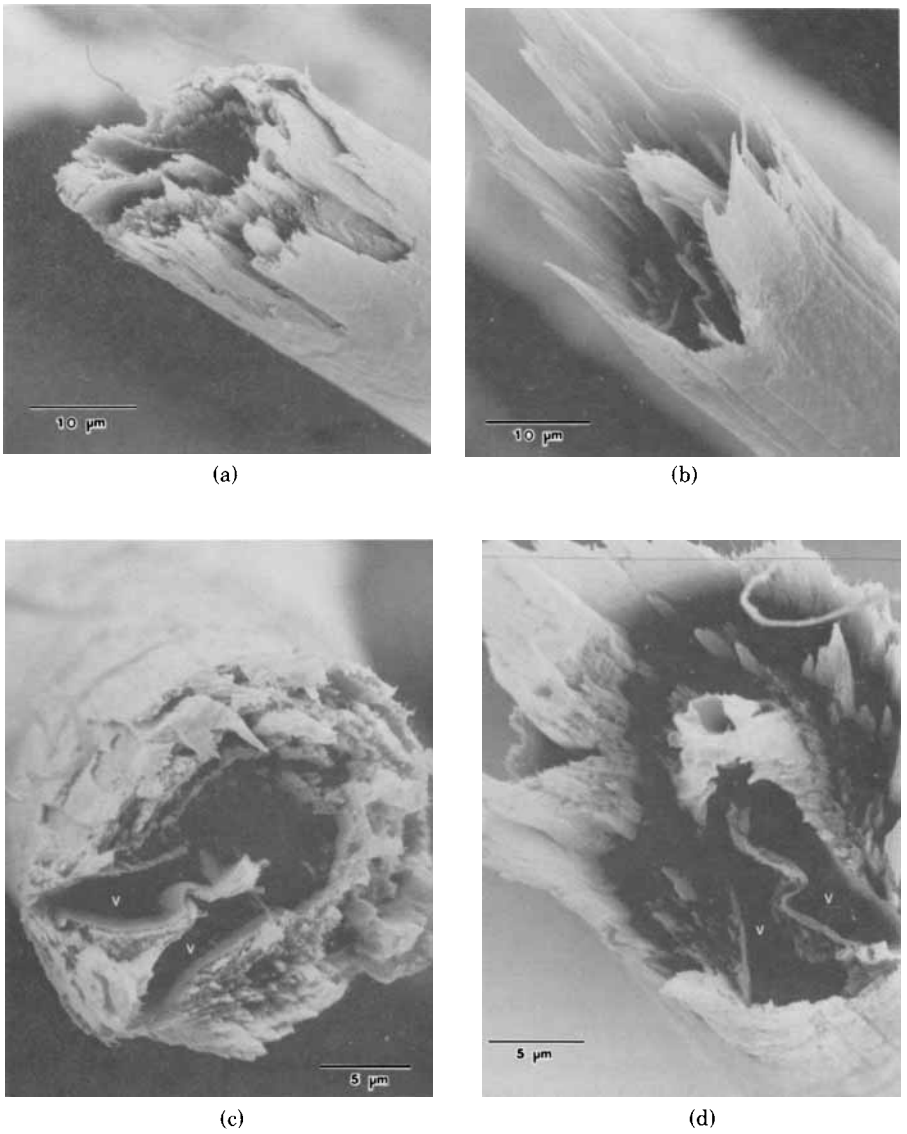


Fig. 3. Optical micrographs revealing void-localized fracture of tensile-tested PBT fibers.

no such plastic nature was observed for Kevlar fibers which possess a similar type of fibrillar structure. From these observations then, it is necessary to examine other possible models which will correctly describe the observed mechanical behavior while being compatible with the observed structure.

A structural model possessing internal stress, such as depicted in Figure 8, can be used to explain an apparent elastic–plastic behavior. Consider three rods all having the same elastic properties but originally of different lengths—the two outer rods having the same length but being longer than the central rod. If the rods are constrained to have the same length (different from the original lengths), internal stress is produced: tensile forces in the center rod and compressive forces in the outer rods. If this elementary model for fibers with internal stress is now deformed, and its stress–strain behavior observed, it is found to exhibit an apparent plastic behavior. This apparent plastic behavior is the result of the redistribution of forces when the center rod reaches its critical breaking load and fails. In other words, because of the initial internal stresses the three rods do not act identically and failure of the central rod precedes complete structure failure giving an apparent plastic behavior. If some distribution of internal stress is assumed across the fiber cross section, a smooth elastic–plastic stress–strain curve can be predicted.



(a) (b)

(c) (d)

Fig. 4. SEM side views (a),(b) and end-on views (c),(d) of matching fracture ends of tensile-fractured PBT fiber. Elliptically shaped regions in (c) and (d) indicate void (v).

This fiber internal-stress model attributes the deviations from linear elastic behavior to the fracture of fibrillar elements which have a higher tensile stress as a result of the applied load plus original internal stress. The plastic part of the stress–strain curve, then, is the result of the continual consecutive fracture of overstressed elements in the fiber. Because the fibrillar elements do not act cooperatively as far as fracture is concerned, the overall fiber strength is less than that of an identical fiber with no internal stress.

This model (based on internal stress), while able to explain a plastic-type behavior, is still inadequate because it is not able to explain an increase in ob-

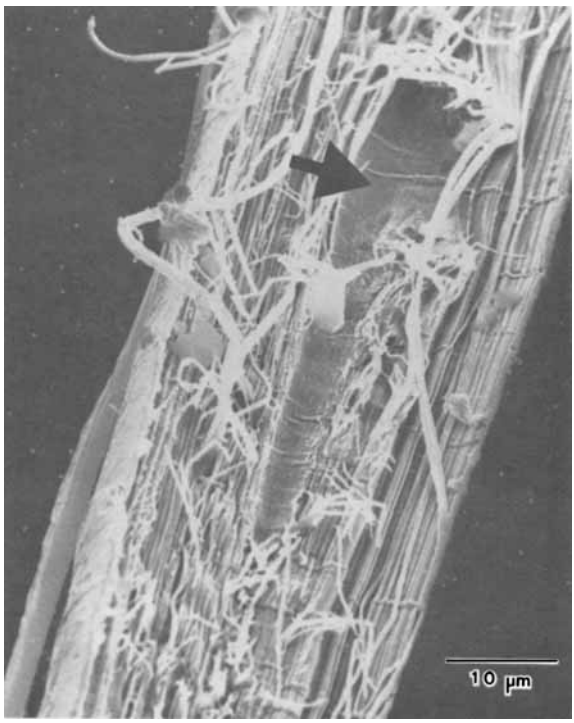


Fig. 5. SEM micrograph peeled PBT fiber revealing presence of void.

served modulus with plastic deformation. A modulus increase due to increased numbers of taut tie molecules is inconsistent with the extended chain nature of the PBT molecules. The small magnitude of the plastic deformation (2%) suggests that orientation and fibril aspect ratio changes would be negligible as far as modulus enhancement is concerned. An elastic–plastic behavior with increasing modulus can be demonstrated, however, by a modified internal stress model (see Fig. 9).

In this model, the compressive internal stresses are high enough to have caused buckling of the outer rods of the model structure. If this structure is now deformed, its stress–strain behavior exhibits an elastic–plastic nature with increasing modulus.

One of the causes of the relatively low strength exhibited by the PBT fibers is the presence of numerous large voids (Fig. 2). The fibrillar morphology and the elongated axial shape of the voids indicate that the voids do not act as strong stress concentrators in the manner normally associated with holes and cracks. The fibrillar structure itself would serve to cause crack deflection provided the interfibrillar forces are less than one-fifth of the axial fibril cohesion[9] and thus provide relief from crack-type stress concentration. The voids do serve as a concentrator of stress via the reduction in effective cross-sectional area caused by their presence. Based on the true load bearing area, the strength values would be between 1.1–1.2 times higher than the strength reported in Table I for PBT.

These adjusted strength values of PBT are still relatively low. The PBT fiber has approximately one-third the strength of the Kevlar fiber tested (σ_b = 3 GPa).

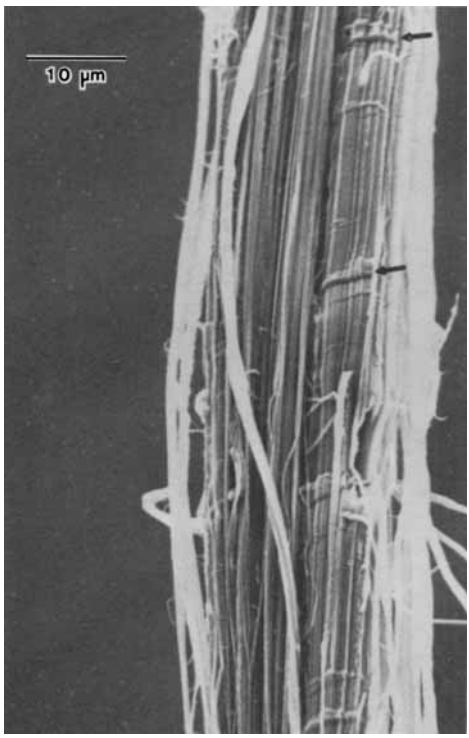


Fig. 6. SEM micrograph of deformation or kink bands (see arrows) in peeled PBT fibers.

It is well known[10–12] that the theoretical strength relative to modulus (σ_b/E) is in the range of 0.05–0.1. Values of σ_b/E of 0.025 for Kevlar and 0.014 for PBT (void corrected) have been measured. The observed strength of these PBT fibers, then, is in the range of 0.14–0.28 of their theoretical values. This relatively low strength could be attributed to the consecutive failure of overstressed fibrillar elements which is believed to dominate the fiber failure process. A more uniform and cooperative fibrillar fracture is assumed for Kevlar or for a fiber with no internal stress giving rise to higher strength values.

The presence of the internal stress discussed previously was seen to be able to explain, in a qualitative way, the stress–strain behavior of the fibers of PBT examined. Formation of such internal stress could arise during the coagulation step of the dry-jet wet-spinning process. The polymer dope filaments are roughly 10% PBT by volume. A substantial (~90%) volume change is required in going from the dope to the solid PBT fiber. As a dope filament enters the coagulation bath, the outer area or skin area is exposed to the coagulant immediately and the process of coagulation (and volume change) proceeds from the outside in. The interior or core of the fiber will, as a result, coagulate slightly later in time than the skin area. If the skin acquires enough mechanical integrity as it coagulates, it will tend to resist further shape changes, which the core region requires as the core now begins to change in volume due to coagulation. The result of the fiber interior wanting to decrease dramatically in volume while the skin areas want to remain unchanged in dimension is the development of a high component of axial tensile stress in the core region and, for equilibrium, the development

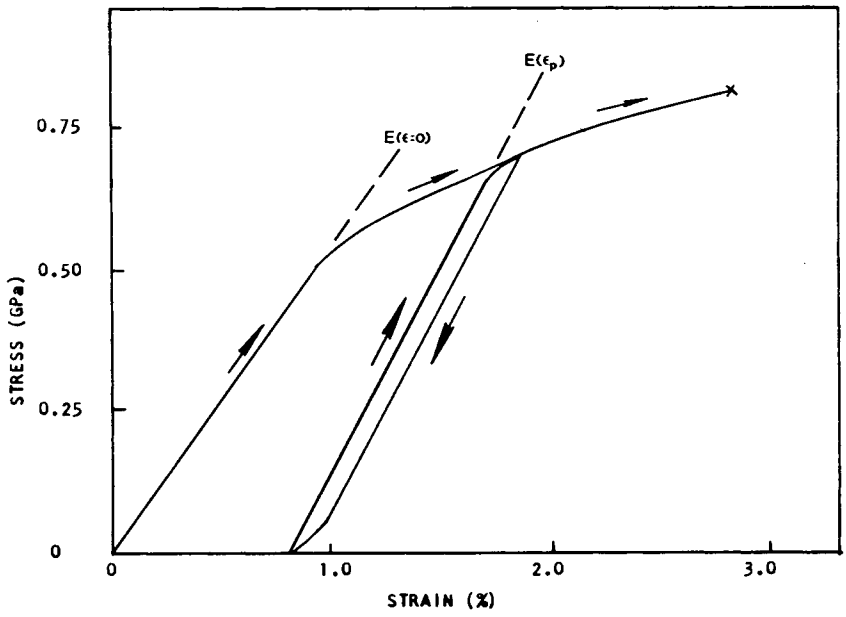


Fig. 7. Stress–strain behavior of as-spun PBT fiber.

of compressive stresses in the skin region. Strong radial and hoop stresses are also produced during the shrinkage.

The presence of the voids and deformation bands are most likely caused by these high shrinkage stresses which develop during the fiber coagulation process. Cavitation (voids) could be caused by the tensile failure of the partially coagulated core. As mentioned, the skin areas would be under the influence of axial

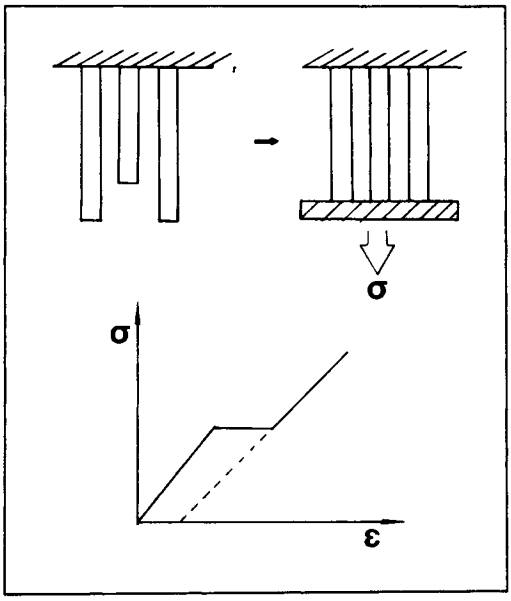


Fig. 8. Simple model for describing apparent plastic deformation arising from residual stress.

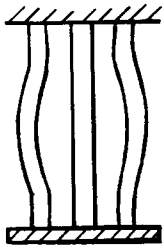


Fig. 9. Residual stress model which incorporates modulus variation with plastic strain.

compressive stresses, and, because of the anisotropy of this material, compressive buckling could result in the banding observed in the fibers.

Residual or internal stresses in materials can be measured by observing changes in shape or strain in an object as a result of removal of part of the material. Residual stresses can also be measured by assessing the elastic strain in the crystal lattice by x-ray diffraction. The small size and limited crystallinity of these PBT fibers make such experiments difficult to perform. Instead of trying to cut away a piece of the fiber, we attempted to selectively destroy a section of the fiber using a laser. The change in fiber shape resulting from this damage could then be easily observed by optical microscopy.

PBT fibers were placed in a laser beam so as to permit damage to occur in a region near the fiber surface. This, according to our model, is equivalent to the release of compressive internal stress in one of the outer rods of Figures 8 or 9. Such a relief of a portion of the internal stress would result in bending of the remainder of the structure with the damage region on the concave side. Figure 10 illustrates a damaged PBT fiber showing the damaged region on the concave side. Kevlar fibers and heat-treated PBT fibers which display linear elastic stress–strain curves (and are therefore assumed to be free of residual stress) showed no warpage from this burning technique. Thus, the laser burning technique has provided a second qualitative measure of internal stress in as-spun PBT fibers.

The severity of the internal stresses and their distribution in the fiber will be

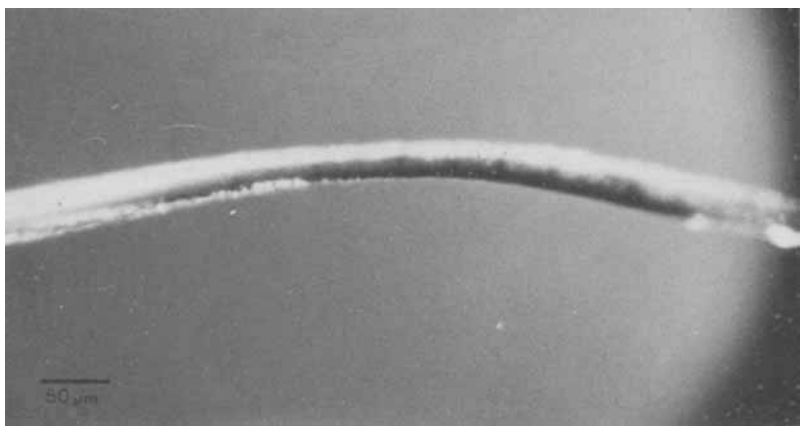


Fig. 10. Optical micrograph of initially straight PBT fiber which was laser burnt. Burnt region is on concave side, suggesting residual compressive surface and tensile core stresses.

dependent on the exact processing conditions employed during spinning. Coagulation rates can be optimized to reduce the severity of the shrinkage stresses by attempting to spin smaller diameter fibers along with optimization of coagulant and dope compositions. Such internal stresses would be lessened if the mechanical integrity of the outer areas did not develop significantly before the integrity of the core. Removal of the internal stresses could also be achieved using proper postspinning conditioning, namely, the use of annealing to relax such stresses.

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