Microfibrillar Network of a Rigid Rod Polymer. 1. Visualization by Electron Microscopy

Yachin Cohen† and Edwin L. Thomas*

Polymer Science & Engineering Department, University of Massachusetts, Amherst, Massachusetts 01003. *Received February 23, 1987*

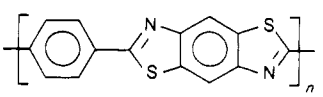
ABSTRACT: In the coagulation stage of the spinning process of fibers and films from solutions of a rigid polymer, poly[*p*-phenylene(benzo[1,2-*d*:4,5-*d'*]bisthiazole-2,6-diyl)] (PBT), a monodomain nematic solution undergoes a transition to the solid state by the action of a nonsolvent. The morphology of coagulated PBT fibers and films is studied by electron microscopy, after impregnation with an epoxy resin. The basic structure formed during coagulation is observed to be an interconnected network of oriented microfibrils, having a typical width of about 100 Å. Visualization of regions which have buckled under compression suggests the relevance of the buckling of the individual microfibrils to the ultimate compressive properties of PBT fibers and films.

Introduction

The utilization of extended-chain rigid polymers in structural elements is abundant in nature, for example, the network of chitin microfibrils in the cuticle of insects,[1] comprising their elaborate bodies and wings. It is therefore not surprising that in the search for stronger and lighter materials synthetic rigid polymers have been developed, from which high performance fibers and films can be fabricated.

The success of both natural and synthetic polymers in fulfilling their structural function lies in a combination of chain rigidity on the molecular level and a suitable morphology on the supramolecular scale, which allows the translation of the intrinsic molecular characteristics to useful macroscopical properties. The nature and origin of the morphological features of such materials on the scale of 10–1000 Å are not well understood. In many cases, involving both natural and synthetic rigid polymers, the microstructure is formed by a phase transition from solution to a solid state having the desired structure and properties.

Poly[*p*-phenylene(benzo[1,2-*d*:4,5-*d'*]bisthiazole-2,6-diyl)] (PBT) is a rigid polymer developed by the Air Force Ordered Polymers Program. It is synthesized by condensation polymerization in poly(phosphoric acid) (PPA)[2] and has the chemical structure given below.



Fibers and films are spun from PBT solutions in PPA by a process which involves a succession of operations. The polymer solution is extruded through a die into an air gap, where it is extended in an elongational flow, and is introduced into a coagulation bath, where a phase transition to the solid state is induced by a nonsolvent (typically water). The coagulated fiber or film is then dried (at which point it is termed "as spun") and subsequently heat treated under tension.[3] The ability to induce elongational flow in PBT/PPA solutions prior to coagulation is essential to maximize the degree of uniaxial orientation of the PBT molecules. This processing results in a highly aligned solution prior to coagulation and hence coagulation takes place in essentially a monodomain nematic state.

PBT fibers are noted for their excellent tensile properties, as well as high thermal stability. Tensile moduli greater than 300 GPa and strength exceeding 3 GPa have been reported;[4,5] yet the transverse and compressive properties are considerably lower. The compressive strength is less than 0.3 GPa, failure invariably occurring by buckling.[6]

Previous studies have focused on the heat treatment[4,5] and drying[7] processes, where under suitable conditions a twofold increase in the tensile modulus and tensile strength has been achieved. This has been attributed to enhancement of the chain orientation along the fiber axis and to better lateral packing of the chains. The lateral dimension of regions of coherently scattering PBT chains has been estimated by dark-field electron microscopy[8] and from the breadth of the equatorial X-ray diffraction maxima.[5] An increase in the dimension of lateral coherence from 10–20 Å in the as-spun state to about 100 Å after tensional heat treatment has been observed. Since the compressive strength in the as-spun and heat-treated states is comparable,[6] it is evident that the degree of coherent lateral packing, which is determined in the drying and heat-treatment processes, does not control the compressive properties.

This study focuses on the coagulation stage of the spinning process. In preliminary observations, the structure formed during coagulation was shown to be composed of oriented microfibrils, about 100 Å in width.[9] The objective of this study is to further characterize the microfibrillar morphology. In particular, the relevance of this morphology to the compressive properties is sought.

Experimental Section

Fibers and films were spun from a 5.6% (w/w) solution of PBT in poly(phosphoric acid) (PPA), its polymerization medium. The intrinsic viscosity of the polymer in methane sulfonic acid (MSA) was 18 dL/g, from which a molecular weight of about 35 000 is estimated.[10] Fibers were spun through a die 0.18 mm in diameter and films through a 1-mm-wide rectangular die. Both were extended 2–3 times in an air gap, coagulated in water at room temperature, and subsequently kept under water. In order to preserve as much as possible the structure in the wet-coagulated state, circumventing the collapse that occurs during drying, a procedure for impregnating the wet fibers and films with an epoxy resin[9] was used. Gradual replacement of water with ethanol was followed by infiltration with increasing concentrations of a low viscosity epoxy resin, as described by Spurr.[11] The specimen was mounted in polyethylene capsules and the resin cured. Longitudinal sections, in which the direction of cutting was either parallel or perpendicular to the fiber axis, were obtained with a Reichert ultramicrotome by using a diamond knife. The sections were observed in a JEOL transmission electron microscope (TEM) operated at 100 KV. Images were recorded about 3.4 μm underfocus to enhance phase contrast.

Results and Discussion

The microstructure formed by the coagulation process in PBT fibers and films, as revealed by electron microscopy, is shown in Figures 1 and 2. The image of a longitudinal section of a wet-coagulated PBT film impregnated

† Present address: Chemical Engineering Department, Technion, Haifa, Israel.

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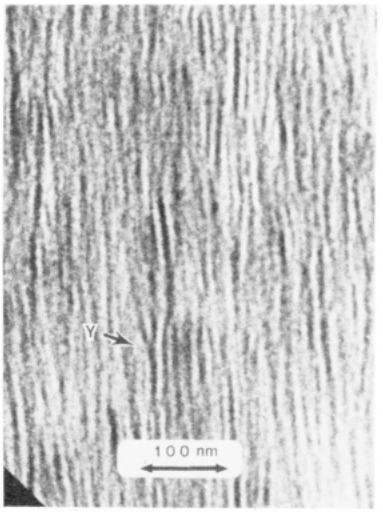

Figure 1. Electron micrograph of an epoxy impregnated PBT film. (Y) "Y"-shaped junction between microfibrils. Both extrusion and cutting directions are vertical.

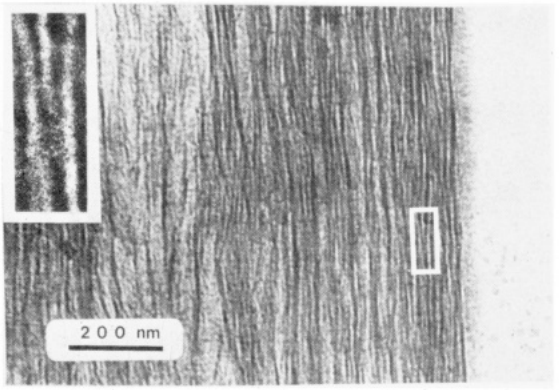

Figure 2. Electron micrograph of a longitudinal section of an epoxy impregnated PBT fiber: Fiber axis vertical; cutting direction horizontal. (Inset) Enlargement of a junction between microfibrils.

with an epoxy resin is shown in Figure 1. The cutting direction was parallel to the extrusion direction. Figure 2 shows an image of a longitudinal section of an epoxy resin impregnated PBT fiber, in which the cutting direction was perpendicular to the extrusion direction.

In both images, dark longitudinal striations appear, parallel to the extrusion direction, with a typical width on the order of 100 Å. These dark striations have been identified as PBT microfibrils embedded in an epoxy matrix.[9] The similarity between the images of the PBT microfibrils shown in Figures 1 and 2 and the chitin microfibrils observed in images of sections of insect cuticle[1] is noteworthy.

The PBT microfibrils appear dark due to several contrast mechanisms reinforcing each other. The density difference between PBT ($\sim$1.5 g/cm^3) and the epoxy resin ($\sim$1.0 g/cm^3), as well as the crystalline nature of PBT, results in stronger scattering of electrons by the microfibrils at angles which are blocked by the objective aperture used in obtaining the bright field images. Furthermore, by underfocusing the objective lense, phase contrast is enhanced,[12] reinforcing mass and diffraction contrast. Appearance of the striations parallel to the extrusion direction irrespective of whether the cutting direction was parallel or perpendicular to it indicates that they are not artifacts induced by the cutting procedure.

An electron diffraction pattern from an area less than 3 μm in diameter within a section of the epoxy impregnated fiber is shown in Figure 3a. It exhibits a superposition of the characteristic PBT fiber diffraction pattern and the amorphous halos of the epoxy matrix. The PBT reflections, although weak and dominated by the amorphous halos of the matrix which is the major component, indicate that the PBT crystallites are less oriented and are less ordered compared to a dried, heat-treated PBT fiber. For comparison the electron diffraction from the epoxy matrix alone and from a heat-treated PBT fiber are given in parts b and c of Figure 3, respectively. A schematic representation of the PBT fiber diffraction pattern is shown in Figure 3d.

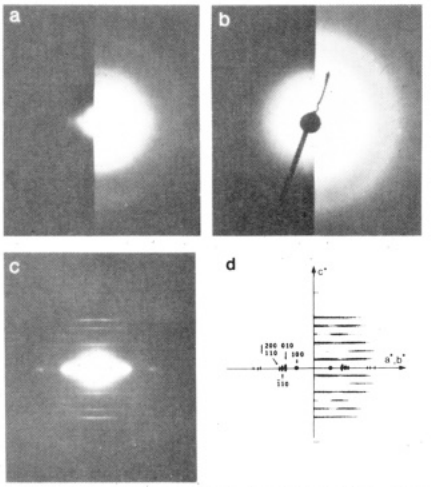

Figure 3. Electron diffraction patterns from: (a) epoxy impregnated PBT fiber; (b) epoxy matrix; (c) heat-treated PBT fiber; (d) schematic representation of the PBT fiber diffraction pattern. All patterns printed to the same scale, details of the PBT diffraction pattern are described in ref 13.

Closer inspection of the micrographs reveals "Y"-shaped junctions between microfibrils as indicated by an arrow in Figure 1 and in the inset in Figure 2. It is problematical to estimate the length of the microfibrils, i.e., the distance between the junction points. The micrographs shown are two-dimensional projections of the three-dimensional structure. Overlap of microfibrils may appear in a projection as junctions. Nevertheless, the micrographs shown in Figures 1 and 2 indicate a wide distribution of microfibrillar lengths, from several hundred to several thousand angstroms.

These structural elements, the microfibrils and their junctions, which are formed in the coagulation process, constitute the fundamental structure of oriented PBT fibers and films, namely, an interconnected network of oriented microfibrils. The network formation is reversible in the sense that replacement of the coagulant with a solvent (i.e., a strong acid) results in dissolution of the microfibrillar network, so that the system reverts to its original state (i.e., a PBT solution). That this network is formed during coagulation explains the ability of the wet-coagulated fibers to sustain a large tensile force[7] and indicates that the microfibrillar network is the basis for the structure and properties of the final material.

Evidence for the relevance of the microfibrillar elements to the compressive properties of PBT is indicated by the electron micrograph shown in Figure 4. It is an image of a kinked region in an epoxy impregnated PBT film, which has buckled under compression during its handling. Compressive failure of PBT fibers has been shown to be due to a buckling instability which is manifested in the formation of kink bands.[6] The technique developed in this study allows the visualization of the microstructure within a kind band. As shown in Figure 4, buckling appears to

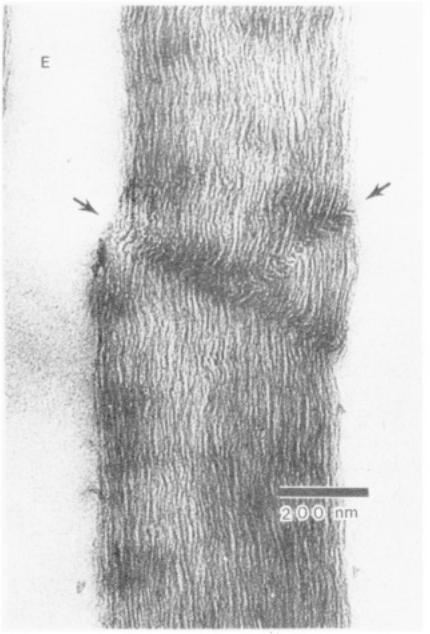

Figure 4. Electron micrograph of a longitudinal section of an epoxy impregnated PBT film exhibiting a buckled region ("kink band"); (E) epoxy matrix. Arrows indicate the kink bands.

result from sharp (close to 90°) bends of the individual microfibrils. This indicates that the microfibrils are the structural elements responsible for the compressive properties, as it is the buckling of the individual microfibrils which results in the compressive failure.

The propensity of the microfibrils for bending at sharp angles, as seen, for example, at the buckled region in Figure 4, is also manifested in the image of a transversal section of the epoxy impregnated fiber. Figure 5 shows a transversal section, "looking down" the fiber axis, in a region close to the circumference of the fiber. The thick diagonal lines appearing within the fiber are knife marks. Their orientation indicates the cutting direction. Closer inspection reveals smaller dark striations oriented along the cutting direction. These are fragments of the microfibrils which have been bent at 90° to the fiber axis by the shear action of the advancing knife edge. The electron diffraction pattern verifies that the predominant chain orientation is along the cutting direction, perpendicular to the fiber axis.

It can now be postulated why heat treatment has not been observed to enhance the compressive strength of PBT and why a dimension on the order of 100 Å appears to be the upper limit to the width of regions of coherently packed PBT chains. It is the dimensions of the microfibrils, in particular the length:width ratio, that control the compressive strength of PBT. These dimensions are set in the coagulation process. All subsequent post-treatments influence the packing of chains within the microfibrils but do not alter the microfibrillar morphology. Any possible enhancement of the compressive properties must therefore address the coagulation process in which the microfibrils are formed. The effect of changing the coagulation environment on the microfibrillar dimensions and thus on the compressive strength of PBT fibers is currently under study.

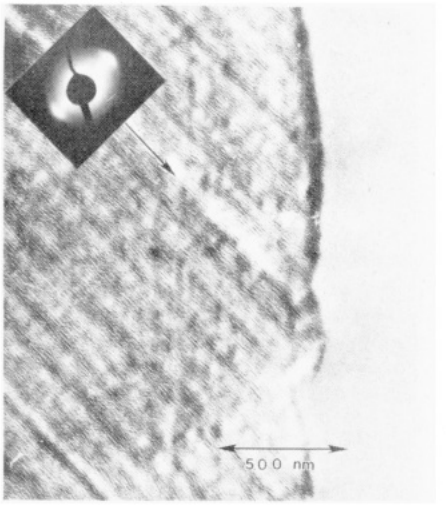

Figure 5. Electron micrograph of a transversal section of an epoxy impregnated PBT fiber, near its periphery. Arrow indicates the cutting direction. (Inset) A correctly aligned diffraction pattern.

Conclusions

(1) An interconnected network of oriented microfibrils, having a typical width on the order of 100 Å, is observed by electron microscopy. This network is identified as the basic structural feature of PBT fibers and films, which is formed in the coagulation process.

(2) Visualization of a region within a film which has buckled under compression indicates that the dimensions of the microfibrils, in particular their length:width ratio, may be controlling the compressive strength of PBT fibers and films.

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Registry No. PBT, 69794-31-6.

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