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DIRECT CARBONIZATION OF PBO FIBER

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Abstract—Poly p-phenylene benzobisoxazole (PBO) fiber appears to display unusual characteristics during its conversion to carbon fiber. This introductory study focused on specific aspects of the carbonization behavior that differentiate PBO from other materials. Results showed that oxidative stabilization did not affect the tensile properties of carbonized fiber produced from PBO precursor fiber. Unlike other polymeric precursors, unstabilized PBO fibers could be directly converted to carbon fibers with promising mechanical and thermal properties. The carbonization characteristics of unstabilized PBO were found to be similar to those of stabilized PAN-based fibers. However, the PBO-based carbon fibers exhibited a radial texture similar to pitch-based fibers. Surprisingly, the PBO-based carbon fibers exhibited electrical resistivities in the range of commercial pitch-based fibers, implying that their thermal conductivities also will be similar. Low-temperature carbonization studies showed that PBO fiber can be carbonized at rapid rates without adversely affecting the tensile properties of the carbonized material. Its ability to be directly carbonized, combined with the unusual thermal properties of the final carbon fiber, may make PBO an attractive precursor for some carbon fiber applications.

Key Words—Carbon fiber, PBO, poly p-phenylene benzobisoxazole.

1. INTRODUCTION

Although both polymeric and carbon fibers are used to reinforce high-performance composite materials, each fiber has significant deficiencies. High-performance polymeric fibers display exceptional tensile properties but are limited by their poor compressive properties. Carbon fibers possess excellent tensile properties and substantially better compressive strengths, but currently are too expensive for most high-volume applications [1]. Their high cost is the direct result of the lengthy, multistep process needed to convert existing precursor fibers into high-performance carbon fibers. Today, polyacrylonitrile (PAN) serves as the precursor fiber for over 90% of all carbon fibers. PAN, like other known precursors, requires oxidative stabilization prior to final heat treatment. This oxidative stabilization step is slow and difficult to control. In fact, stabilization represents the limiting step in current carbon fiber processes. Thus, the objective of the current work is to improve the economics of carbon fiber production by utilizing a precursor that does not require stabilization to produce a high-quality carbon fiber.

Its rigid-rod structure, high melting point, and high carbon content make poly p-phenylene benzobisoxazole (PBO) (see Fig. 1) a likely candidate. PBO can develop tensile properties that are superior to other high-performance polymers, including PBZT (poly p-phenylene benzobisthiazole), and Kevlar (poly p-phenylene terephthalamide)[2,3].

PBO forms a liquid crystalline solution when dissolved in polyphosphoric acid[4]. Commercially,

this liquid-crystalline solution is dry-jet wet spun, yielding a PBO fiber with high degrees of molecular orientation and crystallinity. In a preliminary study, Rogers *et al.*[5] demonstrated that its chemical structure and crystallinity give PBO remarkable thermal stability, allowing PBO fibers to be directly converted to carbon fibers without oxidative stabilization. While the tensile properties of the final carbon properties were far from optimum, the study demonstrated the potential advantage of employing a PBO precursor in the production of carbon fibers.

The purpose of this study is to examine some of the unusual aspects of the carbonization behavior of this intriguing material. Although not a comprehensive study of carbonization, the following results should illustrate the potential benefits of using PBO fiber as a carbon fiber precursor.

2. EXPERIMENTAL PROCEDURE

The PBO fibers used in this study were supplied by the Dow Chemical Company. The as-received

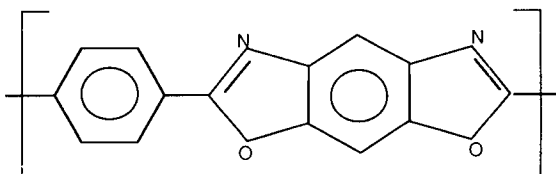


Fig. 1. The repeat unit of cis-PBO.

fibers were divided into 31 different samples and subjected to a matrix of heat treatment conditions. The objective was to determine the effects of stabilization, the overall carbonization behavior, and the role of processing variables during low-temperature carbonization (<1400°C). After thermal processing, each sample was characterized by X-ray diffraction, electrical resistivity, scanning electron microscopy (SEM), and single-filament tensile testing.

2.1 Stabilization

The preliminary study[5] had indicated that oxidative stabilization was unnecessary for the carbonization of PBO. In the current study, a series of three stabilization trials were performed to verify this surprising result. During stabilization, each fiber sample was hung in a forced convection oven under approximately 0.1 g/d tension. Then, three samples were heated at a rate of 5°C/min to 310°C and held at that temperature for 30, 60, and 120 min, respectively. Finally, all three stabilized fiber samples were heated at 20°C/min to a temperature of 2000°C in a graphite resistance furnace. As a control, a length of as-received PBO fiber also was carbonized at the same conditions.

2.2 Overall carbonization

To determine the overall carbonization and graphitization behavior of the fiber, a series of batch carbonization trials were performed. In these trials, six unstabilized fiber samples were heated in a graphite resistance furnace at a rate of 20°C/min to temperatures of 700, 1000, 1400, 1600, 1800, and 2000°C, respectively. All samples were maintained at the carbonization temperature for 15 min, then allowed to cool to room temperature.

2.3 Low-temperature carbonization

Once the general carbonization behavior of PBO was characterized, a second series of studies was initiated. The overall carbonization trials showed that the behavior of PBO at low carbonization temperatures was distinctly different from its behavior at high carbonization temperatures. Obviously, if a high-quality carbon fiber is to be produced, this carbonization process must be understood. Thus, the overall objective of this second series of tests is to examine more closely the behavior of PBO in each temperature region.

The effects of five major processing variables were examined: treatment temperature, heating

rate, cooling rate, soak duration, and applied tension in the early carbonization range (<1400°C). Tension was applied by hanging the 648 filament fiber tow from a tungsten hook and attaching a graphite weight to the bottom of the tow. To minimize the required number of trials, a Greco-Latin square experimental design was employed[6]. This required the establishment of four levels for each of the processing variables. Table 1 details the levels used in this study.

2.4 Evaluation of carbonized fibers

Tensile strengths and moduli of carbonized PBO fibers were determined by single filament testing, by using an Instron model TM universal testing machine that had been modified and upgraded by Measurement Technology, Inc. All single-filament tests employed 25-mm tabs and followed the procedure outlined in ASTM Standard D-3379-75[7]. Fiber diameters were measured with a laser diffraction technique that is accurate to $\pm 0.1 \mu\text{m}$. Fifty single filaments were tested from each fiber set to determine average tensile values.

A four-point probe technique, analogous to that described by Coleman[8], was used to determine the electrical resistivities of the carbonized PBO fibers. Fifteen single filaments were tested from each fiber sample to determine its average resistivity.

X-ray diffraction was used to analyze the microstructure of the carbonized PBO fibers. A 1-in. length of fiber was cemented to a circular aluminum ring. Then, this ring was placed in a Scintag XDS 2000 diffractometer, and Bragg scans were performed to determine the average interplanar d_{002} spacing and the average stack height (L_c) of the graphene layer planes.

To make qualitative observations concerning the microstructure of the carbonized PBO fibers, representative samples were cut and attached to aluminum stubs with copper tape. The fiber samples were coated with an approximately 35-nm layer of gold to prevent charging. Once coated, the sample was placed into the stage chamber of a JEOL 848 scanning electron microscope and scanned at an accelerating voltage of 20 kV.

3. RESULTS AND DISCUSSION

3.1 Stabilization of PBO

Figures 2 and 3 show that stabilization did not enhance the tensile properties of the final carbon fiber. Neither tensile strength nor modulus im-

Table 1. Levels of variables applied in low temperature carbonization study

Level	1	2	3	4
Temperature (°C)	800	1000	1200	1400
Heating Rate (°C/min)	1	1	13	20
Cooling Rate (°C/min)	1	7	13	20
Soak Duration (min)	0	10	20	30
Applied Tension (g/d)	0	0.13	0.25	0.38

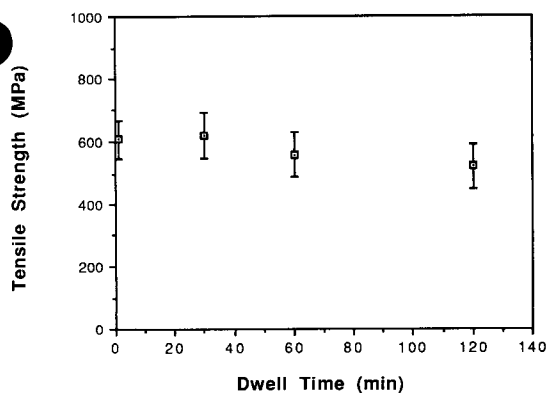


Fig. 2. Tensile strength versus stabilization dwell time for PBO stabilized at 310°C and then carbonized at 2000°C.

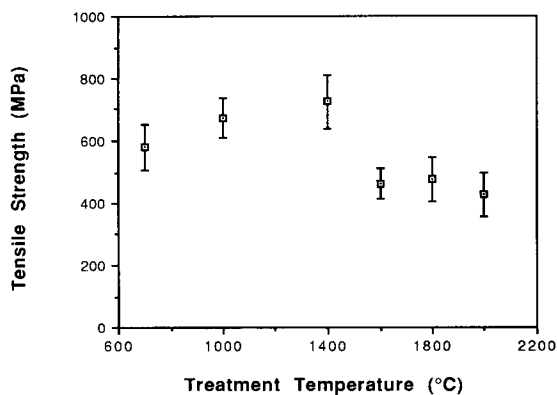


Fig. 4. Tensile strength versus carbonization temperature for unstabilized PBO fiber.

proved with stabilization, regardless of the stabilization dwell time.

Although PAN and pitch fibers typically gain weight during oxidative stabilization[9], PBO fibers experienced no detectable weight gain. Thermogravimetric analysis of PBO heated in air shows that no detectable mass gain occurs between 20° and 580°C. At approximately 580°C, the PBO begins to oxidize, and less than 10% of the mass remains by 800°C. This is consistent with the work reported by Nielsen[10]. The only effect of the stabilization on PBO was a slight disordering of the structure that was observed by X-ray diffraction. These results indicate that PBO may be converted directly to carbon fiber without the need for lengthy and expensive oxidative stabilization. This behavior appears to be unique even among other rigid-rod polymers. Jiang *et al.*[11] studied the oxidative behavior of PBZT fibers, a close relative of PBO. They found that, unlike PBO, oxidative stabilization improved the tensile properties of PBZT fibers.

3.2 Overall carbonization of PBO

The overall carbonization behavior of PBO is illustrated in Figs. 4 and 5. At low carbonization

temperatures (less than 1400°C), the final tensile strength of the unstabilized fiber improved continuously as the carbonization temperature was increased. However, at temperatures greater than 1400°C, the final fiber strength decreased dramatically with further increases in carbonization temperature. This event appears to coincide with the release of nitrogen, an event that causes structural damage in PAN-based carbon fibers. As Fig. 5 shows, final tensile modulus increased continuously with carbonization temperature.

The effect of carbonization temperature on the properties of unstabilized PBO fibers is depicted in Figs. 6 and 7. In past studies, Fitzer[12] and Reynolds[13] have studied the influence of this same variable on the development of tensile properties for PAN-based fibers, and their results are plotted for comparison. Clearly, the strength and modulus relationships for PBO are directly analogous to those of stabilized PAN, implying that the carbonization behavior of the two materials is similar. It should be noted that the maximum tensile strength obtained by Fitzer[12] is nearly double that reported by Reynolds[13]. The three factors that account for this increase in strength are improvements in the precursor

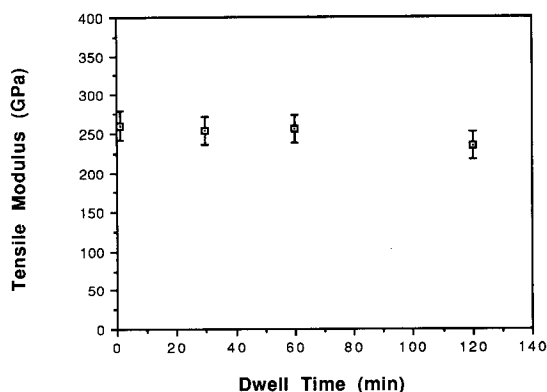


Fig. 3. Tensile modulus versus stabilization dwell time for PBO stabilized at 310°C and then carbonized at 2000°C.

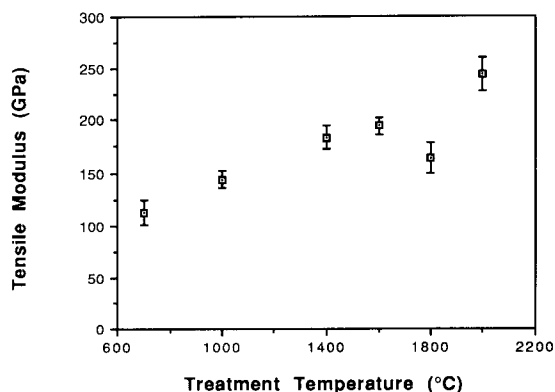


Fig. 5. Tensile modulus versus carbonization temperature for unstabilized PBO fiber.

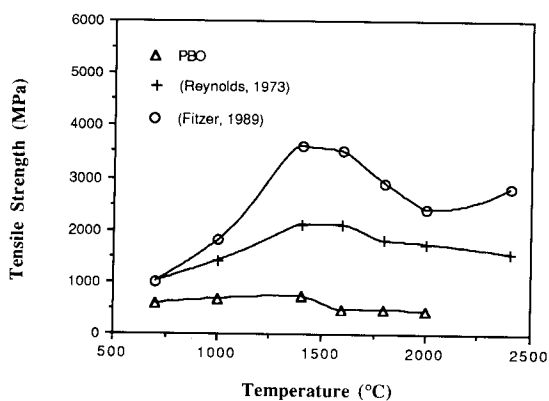


Fig. 6. Effect of carbonization temperature on the tensile strength of stabilized PAN and unstabilized PBO fiber.

quality, optimization of heat treatment schedules, and the application of stress graphitization.

The TGA and X-ray analyses showed that major structural changes occur during the carbonization of unstabilized PBO fibers. Figure 8 depicts a TGA profile for the heat treatment of PBO fiber up to 800°C in an argon atmosphere. Except for the apparent loss of water vapor, little activity is observed at less than 550°C. However, over 38% of the total fiber mass is lost between 550° and 800°C. Because oxygen and hydrogen combined account for less than 20% of the total fiber mass, the mass loss must involve disruption of the polymer chain. One might expect this to create an amorphous phase in which the order is largely a relic of the original structure of the liquid-crystalline precursor fiber[14]. X-ray diffraction profiles of the as-received and carbonized PBO fibers confirm that, at approximately 600°C, the fibers begin to pass from this ordered initial state to an amorphous state. Ultimately, the carbonized fiber begins to form a turbostratic carbon structure at approximately 1600°C, and this structure continues to develop throughout the graphitization process.

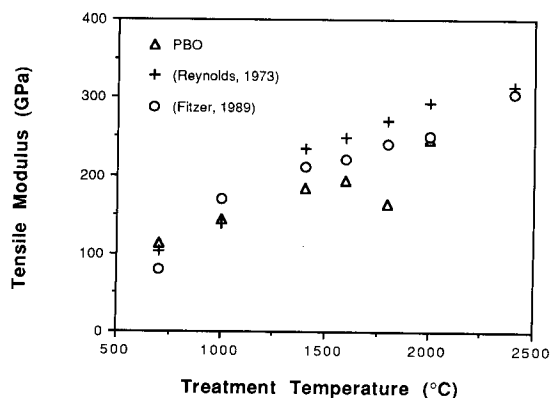


Fig. 7. Effect of carbonization temperature on the tensile modulus of stabilized PAN and unstabilized PBO fiber.

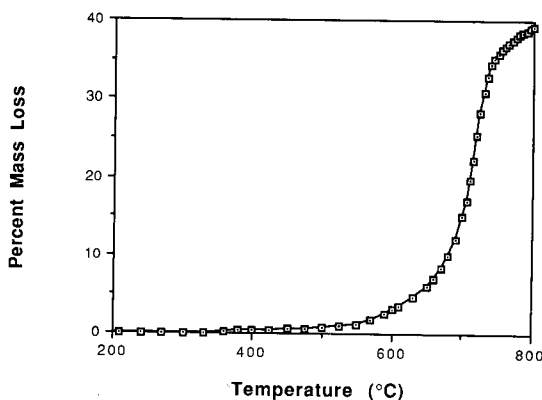


Fig. 8. TGA profile for PBO fiber sample.

Electrical resistivity tests also were performed on the carbonized fibers. Ideally, the electrical resistivity should decrease with the increased molecular ordering within the fiber at elevated temperatures. However, Fig. 9 shows that the electrical resistivity of PBO fibers decreases with temperature only to 1400°C; at greater than this temperature, an increase in resistivity is observed. This is a further indication that the PBO fiber begins to experience "puffing" damage at 1400°C. Surprisingly, the electrical resistivity of PBO fiber at 1400°C was found to be 11 $\mu\Omega\cdot\text{m}$, superior to most commercial PAN-based fibers and in the range of many pitch-based fibers, as shown in Table 2. In contrast, Kevlar fibers develop an electrical resistivity of 23 $\mu\Omega\cdot\text{m}$ when subjected to identical treatment conditions. Additionally, the tensile modulus of the PBO-based carbon fiber was found to be 180 GPa compared with 120 GPa for the Kevlar-based fiber. Both differences indicate an improved molecular order present in the PBO fiber.

The role of nitrogen puffing may be understood by considering the carbonization process through the amorphous region. At approximately 600°C, the

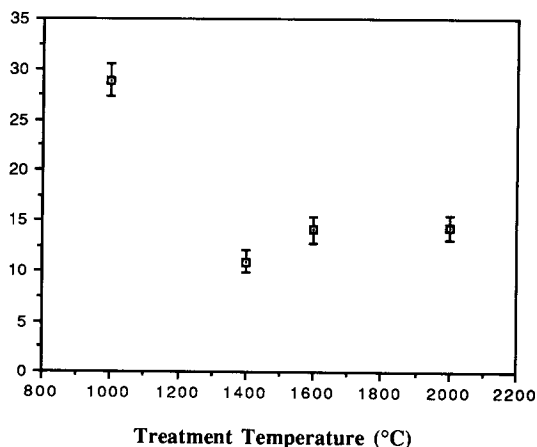


Fig. 9. Electrical resistivity as a function of treatment temperature for unstabilized PBO fiber.

Table 2. Electrical resistivities of various carbon fibers[15]

Classification	Precursor	Electrical resistivity ($\mu\Omega\cdot\text{m}$)
Amoco T-300	PAN	18.0
Amoco T-650	PAN	14.9
Amoco T-40	PAN	14.5
Amoco P-25	Pitch	13.0
Dow PBO (1400°C)	PBO	11.0
Amoco P-55	Pitch	8.5

PBO fiber begins to depolymerize[10]. Nonaromatic species are eliminated and, as the bonding between the repeat units decays, the structure develops much greater conformational freedom. If no puffing occurred, the remaining carbon atoms would condense gradually into aromatic rings. This would lead to crystal growth and the formation of turbostratic order in the carbon fiber. However, if a rapid release of nitrogen occurs during this process, the crystallite formation and growth is disrupted. This leads to a decline in both tensile strength and electrical resistivity. The effects of puffing in other carbon fiber precursors have been controlled by regulation of heating rates and application of tension[16]. It is likely that further decreases in electrical resistivity will occur as the effect of puffing on carbonized PBO is minimized.

Scanning electron microscopy analysis was performed on fracture surfaces of carbonized PBO. Two significant observations were made. First, Fig. 10 shows that carbonized fiber possesses a radial structure similar to pitch-based fibers rather than the fibrillar structure derived from PAN fibers. This radial structure may be responsible for the excep-

tional thermal conductivities of the carbonized PBO fibers. The SEM studies also revealed voids in the carbonized fiber. A typical defect is shown in Fig. 11.

3.3 Low-temperature carbonization of PBO

The work discussed thus far focused on the effects of temperature on the final fiber properties, but other controllable variables may influence the carbonization kinetics. Specifically, the soak duration[17], the heating rate[18], the cooling rate[18], and the application of tension[19] also may influence fiber properties. This series of low-temperature carbonization experiments were performed to determine the effects of these variables, as well as temperature, in the carbonization region prior to the apparent puffing.

Figures 12 and 13 show that both tensile strength and modulus were found to increase monotonically with temperature within this region. By contrast, soak duration did not significantly effect either property, as shown in Figs. 14 and 15. This implies that the kinetics of PBO carbonization are rapid, making lengthy exposure at the highest treatment temperature unnecessary.

Heating and cooling rates had no significant effect on the final fiber properties, as shown in Figs. 16–19. In commercial process, this characteristic is critical because rapid heating and cooling can reduce production costs. In fact, for a carbonization process to be commercially viable, it must be continuous rather than batch, making rapid heating and cooling essential for efficient operation.

Finally, tension also had little effect on tensile properties as shown in Figs. 20 and 21. This indi-

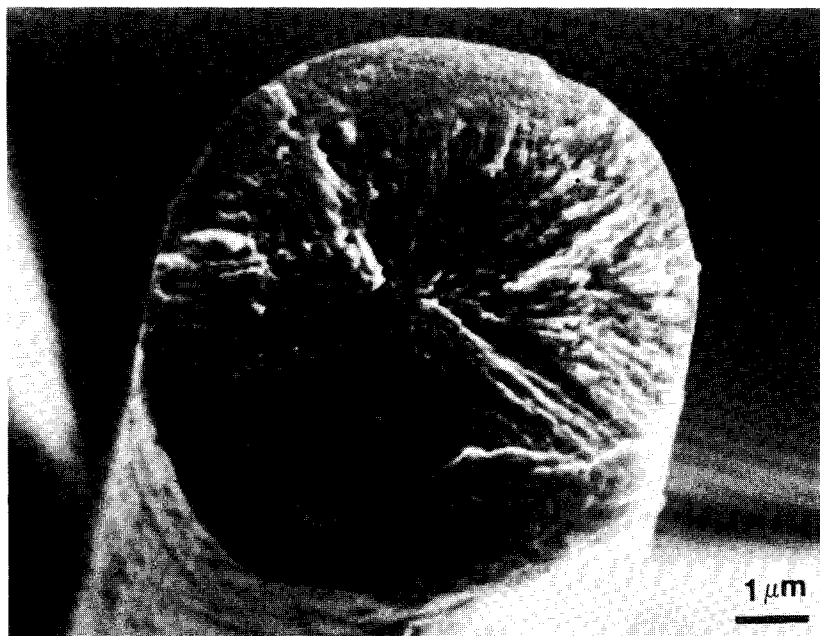


Fig. 10. SEM photo of unstabilized PBO fiber carbonized at 2000°C.

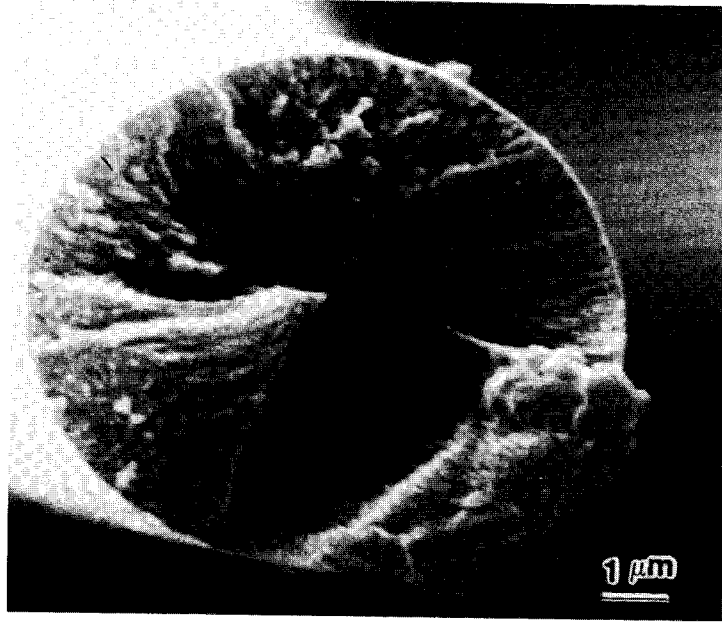


Fig. 11. SEM photo of a typical flaw detected in PBO fiber after carbonization at 2000°C.

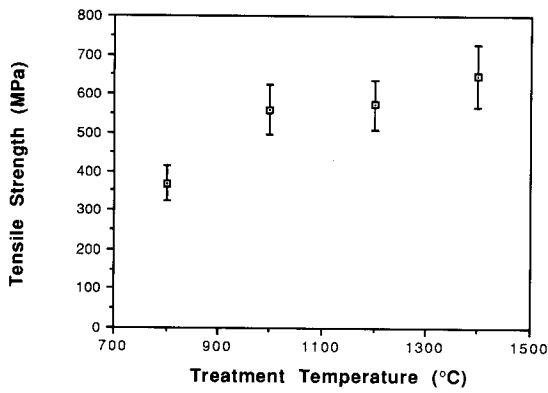


Fig. 12. Effect of treatment temperature on tensile strength of unstabilized PBO fiber.

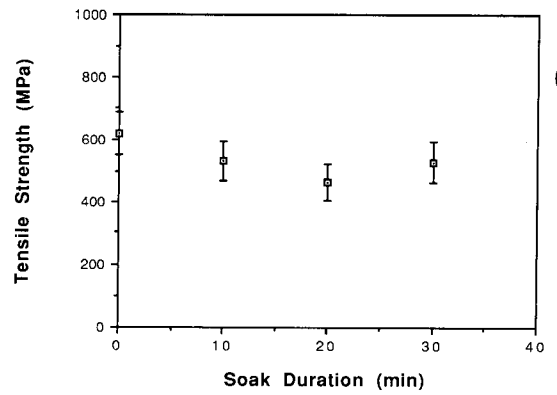


Fig. 14. Effect of soak duration on tensile strength of unstabilized PBO fiber.

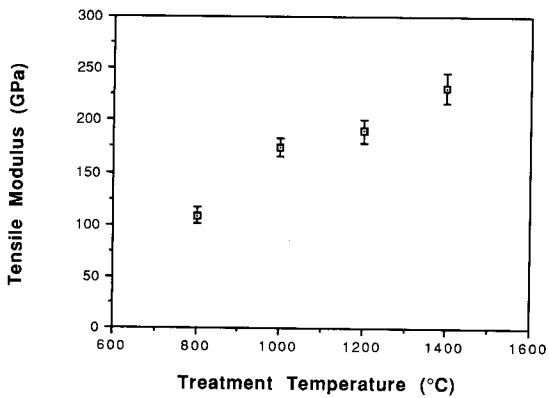


Fig. 13. Effect of treatment temperature on tensile modulus of unstabilized PBO fiber.

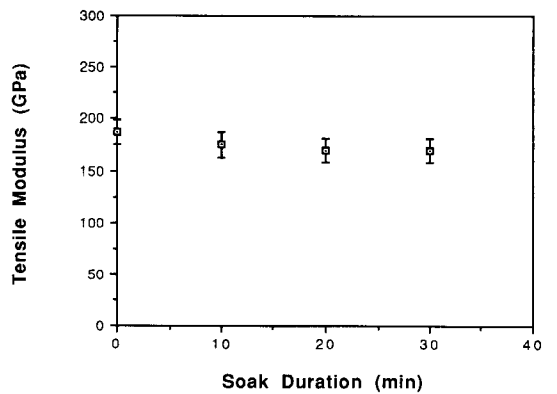


Fig. 15. Effect of soak duration on tensile modulus of unstabilized PBO fiber.

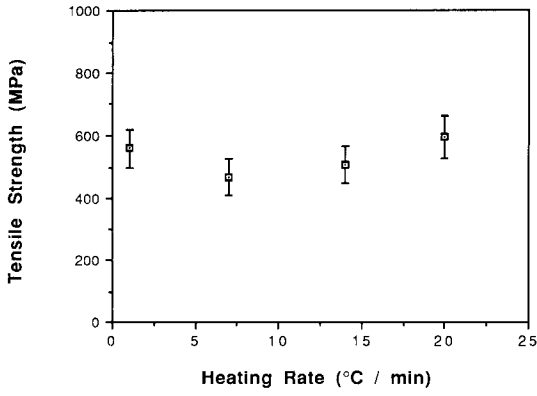


Fig. 16. Effect of heating rate on tensile strength of unstabilized PBO fiber.

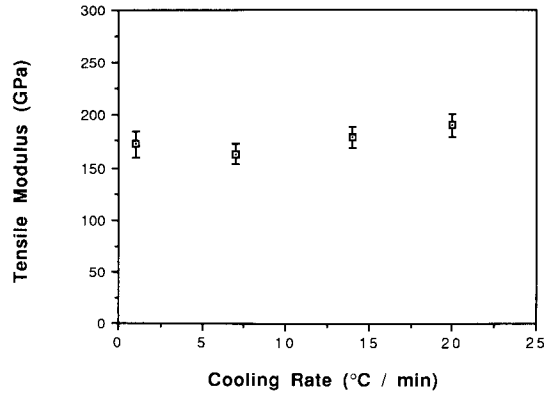


Fig. 19. Effect of cooling rate on tensile modulus of unstabilized PBO fiber.

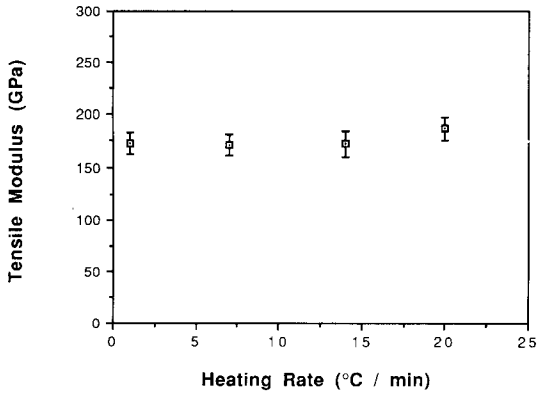


Fig. 17. Effect of heating rate on tensile modulus of unstabilized PBO fiber.

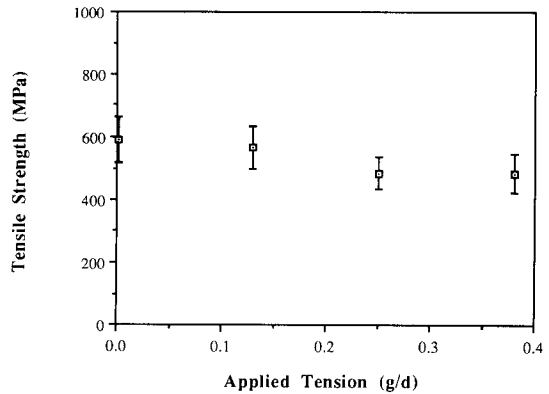


Fig. 20. Effect of applied tension on tensile strength of unstabilized PBO fiber.

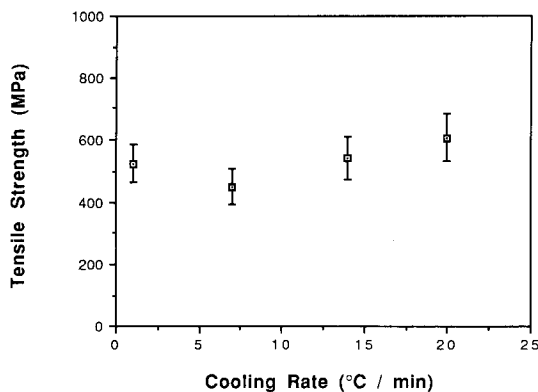


Fig. 18. Effect of cooling rate on tensile strength of unstabilized PBO fiber.

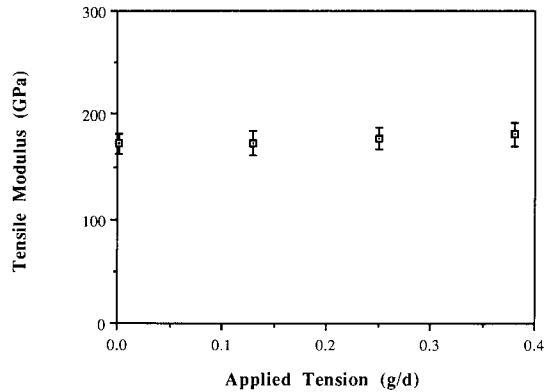


Fig. 21. Effect of applied tension on tensile modulus of unstabilized PBO fiber.

cates that the carbonization of PBO consists primarily of depolymerization at temperatures below 1400°C. Otherwise, one would expect tension to improve molecular ordering and increase order-dependent properties such as modulus.

The low-temperature carbonization experiments demonstrated that treatment temperature alone has a significant effect on the properties of the carbonized fiber at temperatures of 1400°C or lower. This observation has several ramifications. The low-temperature carbonization of PBO may be carried out at rapid heating and cooling rates and with very little high-temperature soak time. This minimizes production energy costs and indicates that the material is well suited for industrial-scale continuous processing. Also, because no processing variable other than treatment temperature affected the fiber properties, the processing conditions best suited to high-temperature graphitization also may be applied throughout the low-temperature carbonization region, without adversely affecting the fiber properties. This eliminates the need for a multiple-stage process.

The carbonization behavior of PBO is unique even when compared with other rigid-rod polymers. Jiang *et al.*[11] found that carbonized PBZT fibers exhibited a fibrillar rather than radial structure. Additionally, the PBZT fibers developed improved tensile properties when they are oxidized prior to carbonization.

The primary structural differences between PBO and PBZT are that the oxygen in PBO is replaced by sulfur in PBZT, and that the cis-form of PBO is generally utilized while the trans-form of PBZT is more common. The oxygen content of PBO is approximately 12%, similar to the amount absorbed in most stabilization processes[9]. The fact that PBO does not require stabilization, whereas PBZT does, may indicate that oxygen present in the PBO chain is able to cross-link the structure during stabilization.

4. CONCLUSIONS

The unique carbonization behavior of PBO fiber makes it an intriguing carbon fiber precursor. PBO has been shown to carbonize without the need for preliminary oxidative stabilization. The carbonized fiber developed a radial texture and to display thermal conductivities in the range of some pitch-based

fibers. PBO may be carbonized at rapid heating and cooling rates without impairing the final fiber properties, an ideal characteristic for a continuous carbonization process. Currently, the strength of carbonized PBO is limited by nitrogen puffing and flaws in the precursor material. However, as the spinning technology improves and the role of puffing is minimized, PBO may become an attractive precursor for high-performance carbon fibers. These results indicate that a more detailed analysis of the specific carbonization mechanism is warranted. Such a study is currently in progress.

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