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13. ABSTRACT (Maximum 200 words)

Research studies have been performed on various fibers using supercritical carbon dioxide treatments. In these studies, Nylon6,6, PBO (Zylon) and other polyester fibers are treated under various conditions and post-treated fiber properties are measured and reported. In this research, supercritical CO2 is used as a plasticizing medium, a transport medium, and as a pressurizing medium to enhance the mechanical performance of selected high performance fibers. In a variety of cases, moderate enhancements in mechanical behavior are observed.

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Section I. Problem Statement and Summary of Major Findings

Commercial polymer fiber moduli and strengths are far below their theoretical strengths. This is due in large part to the inability of commercial drawing and annealing processes to produce highly oriented perfect crystal structures. In addition, the inability to extract residual plasticizers, or solvents can further reduce performance and detrimentally affect their environmental resistance.

This report summarizes results from post-treatment process studies conducted on commercial fibers using supercritical carbon dioxide. In this research, supercritical carbon dioxide (scCO_2) is used as a reversible plasticizer, a transport and extraction medium, and a pressurizing medium for crystal annealing studies. Initial studies focus on nylon6,6 fibers and both one and two-stage drawing studies in the presence of scCO_2 are investigated. For the case of nylon6,6 fibers, results show that a nearly 30% increase in modulus and tenacity can be achieved and nearly an 80% increase in both modulus and tenacity can be achieved. In the two-stage process, the first stage primarily induces orientation, while the second stage promotes crystallization in the oriented stage. The fibers that showed the best increases in properties using this post-treatment process were those with the lowest crystallization (i.e., carpet fiber as opposed to tire chord). Fibers produced with higher levels of crystallinity prohibited further orientation in scCO_2 regardless of process conditions. Finally, the amount of plasticization using scCO_2 is well predicted using the Chow model and equivalent thermal/plasticizing effects are evaluated. Concomitant crystallization studies using scCO_2 on other semi-crystalline fibers are also investigated and the ability for scCO_2 to act as a nucleating agent is characterized.

Additional studies were conducted on poly-p-phenylenebenzobisoxazole (PBO) currently manufactured by Toyobo under the commercial name Zylon. These fibers were selected because of they are among the strongest and stiffest commercial fibers produced today, yet recent data published by Toyobo suggest that they are subject to significant environmental degradation. Studies were conducted to elucidate mechanisms of degradation and to identify if scCO_2 could be used to improve their environmental resistance.

Process studies show that under certain process conditions, scCO_2 can provide moderate enhancements in fiber modulus and tenacity. Additionally, the mechanisms of degradation due to moisture appear to be mechanically or physically dominated while exposure to visible/UV light appear to be chemically dominated. Various strategies for stabilization using scCO_2 as a transport/extraction medium as well as a reaction medium are proposed.

Section II. Scientific Personnel

Alan J. Lesser

EDUCATION

- 1988 Ph.D., Civil Engineering, Case Western Reserve University, Cleveland, Ohio.
- 1985 M.S., Civil Engineering, Case Western Reserve University, Cleveland, Ohio.
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PROFESSIONAL EXPERIENCE

- 2003- Pres. University of Massachusetts, Amherst, MA
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Associate Professor, Polymer Science and Engineering Department
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- 1991-1994 Shell Development Company, Polymeric Materials Department, Houston, Texas
Research Engineer
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Associate Research Engineer
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RESEARCH INTERESTS

Deformation, Fracture, and Adhesion of Polymers and Composites in multi-axial stress states. Fracture mechanics and micro-mechanics of multi-phase alloys and blends. Damage mechanics of polymers subjected to mechanically and chemically aggressive environments. Processing films and fibers in SCCO₂ mediated environments.

HONORS AND DISTINCTIONS

- Fellow – Society of Plastics Engineers
Editor – Polymer Composites Journal, Society of Plastics Engineers
Assoc. Editor – Polymer Engineering and Science Journal, Society of Plastics Engineers
Advisory Board- Journal of Applied Polymer Science, Society of Plastics Engineers
Society of Plastics Engineers – Member of the Board of Directors, New England Chapter
Society of Plastics Engineers – Advances and Polymer Composites Processing – 1999 Technical Program Organizer
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- 1995-1998 Ph.D., Polymer Physics and Chemistry, State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, The Chinese Academy of Sciences, Beijing, China
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- 6/2001-present University of Massachusetts at Amherst
Postdoctor, Polymer Science and Engineering Department
- 8/2000-present: Institute of Chemistry, The Chinese Academy of Sciences, Beijing, China
Associate Professor, Head of Polymer Processing & Morphology Group, State Key Laboratory of Polymer Physics and Chemistry
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RESEARCH INTERESTS

Focus on polymer physics, polymer composites, high performance and functional polymeric materials, especially fibers and pipes. Products and technologies derived from them for the technical applications such as geo-synthetics, optical fiber communication, water saving in agriculture irrigation and environmental protection. More than 20 papers and presentations have been published and 26 patents have been applied.

HONORS AND DICSTINCTIONS

- 2001- 1st Advanced Prize in Science and Technology (Beijing)
- 2000- Head of Polymer Processing & Morphology Group, Institute of Chemistry

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Section III. Scientific Accomplishments Nylon6,6 and Polyester Fibers

Background

The drawing behavior of nylon 6,6 has been studied extensively over the past several decades. Nylon 6,6 contains polar amide linkages which hydrogen bond excessively. This feature along with no known relaxation mechanism in the crystal structure makes deformation in the solid state very difficult. Typical commercial fibers are produced by drawing to a ratio of 5 resulting in fibers with 40% crystallinity and ultimate strength values near 0.85 GPa.

Various techniques have been proposed to improve the properties of drawn polymers. These include solid-state extrusion, solid-state co-extrusion, solution and gel spinning, and zone drawing and annealing techniques (1-6). Most of these techniques use multiple drawing stages in order to achieve high levels of orientation. A mechanism or means of relaxation must be present to allow for drawing to occur in the later stages. These techniques have been quite effective for different polymers as the processing conditions are studied systematically in relation to structure. However, a great deal of insight is still lacking. Often processing variables such as pressure cannot be controlled or measured in a process such as solid-state extrusion. In addition, elusive concepts such as entanglement density cannot be directly measured or quantified.

During the past few years, we have been investigating a new technique; tensile drawing in high pressure CO₂. In this technique, pressure and temperature are systematically controlled to alter the properties of the polymer in the CO₂ -mediated environment. This process is unique in that concomitant effects of pressure (on non permeated regions of the polymer such as crystal structure) and plasticization (through CO₂ penetrating the amorphous phase) are realized under typical drawing conditions.

Little is known about the effect of pressure on polymer crystallization and behavior. Past research has largely focused on extremely high pressures well above common polymer processing operations such as extrusion or injection molding. Limited results with PET have shown that pressure treatment at elevated temperatures can double crystallinity values (7).

Hydrostatic pressure imposed on a polymer during drawing can have several additional effects. These include suppression of brittle failure in the yield envelope, consolidation of the substrate, and promotion of crystal-crystal transitions in the drawing process (8). Many of these effects have documented in the drawing of poly(oxymethylene) (POM) under mild hydrostatic conditions using silicon oil (9). At relatively moderate pressures (200 atm), the drawn fibers had significantly higher orientation, modulus, strength, and crystallinity values (10).

Our technique is unique in that CO₂ can permeate the amorphous region of the polymer and directly apply pressure to the crystalline phase in most polymer systems. Temperature, pressure, orientation, and the molecular composition of the polymer complexly affect the diffusion of CO₂. Despite these complexities, we hypothesize many potential advantages to this new technique based on our own and other's research. CO₂ behaves as a reversible plasticizer and is easily removed by depressurization. Generally, diluents or non-solvents such as CO₂ improve the segmental mobility of the polymer chains. This improved segmental mobility can aid polymer chain relaxation and crystallization.

Experimental

Materials

The as-spun nylon 6,6 fibers were supplied by Solutia, Inc. The tire cord grade fibers had a weight percent crystallinity of 31% and a birefringence of 0.005.

Drawing Conditions

The nylon fibers were cold-drawn using a specially designed drawing facility see Figure 1. The apparatus is capable of making in-situ force and displacement measurements. Heating is controlled using an internal thermocouple and standard PID controller. Fibers were drawn in the apparatus at a strain rate of 0.1 min^{-1} until individual filaments began failing.

The drawing conditions were determined based on previous research published in the literature. The pressure for most of the drawing studies was 240 atm. This pressure is well above the critical pressure for CO_2 and has been shown to effectively improve polymer properties and prevent void formation (12). The two main thermodynamic variables for the experiments are temperature and pressure, which significantly affect the CO_2 density along with the drawing and crystallization behavior of polymers (13,14). For nylon 6,6, the temperature range studied was $95\text{--}145^\circ\text{C}$. This region is near a structural relaxation where hydrogen bonding is thermally interrupted.

Measurements

The draw ratios for the nylon 6,6 fibers were determined by measuring the displacement of ink marks. The second stage draw ratios for the nylon 6,6 were based on strain measurements which were in agreement with ink mark results. Single filament tests were performed on an Instron 5564 or 1123 at a strain rate of 0.1 min^{-1} and a gauge length of 25 mm. Specimens were tabbed onto a cardboard template using an epoxy adhesive. The fiber diameter was measured using a high magnification microscope calibrated with a micrometer scale.

Both single and two-stage drawing studies were performed. In all cases, comparable drawing studies were conducted in air to isolate the effects of the CO_2 on the nylon6,6 drawing behavior.

Results and Discussion

Initial studies of the in-situ measurements of the drawing behavior of the nylon6,6 fibers were conducted over a broad temperature and pressure range to identify regimes where the drawing behavior was most affected. The pressures investigated ranged between 102 and 340 Atm (1500 and 5000 psi) and the temperatures ranged between 23 and 150 C. The in-situ drawing curves indicate that the most dramatic difference in the yield point and post yield draw behavior occurs at the lower pressures and temperatures and becomes less pronounced at the higher temperatures and pressures. Consequently, other studies have been directed to estimate the degree of plasticization occurring as a consequence of the relative solubility of CO_2 in the nylon6,6, its effect in reducing hydrogen bonding in the amorphous phase, or crystal and pressure effects. Careful study of the in-situ behavior together with subsequent analytical characterization of the morphological structures of fibers drawn under these conditions

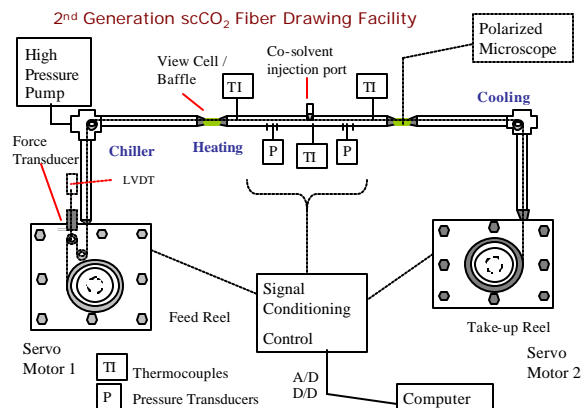


Fig. 1 Schematic of scCO_2 fiber drawing facility.

suggest that the lower temperatures and pressure regimes allowed for better orientation through plasticization effects, while the higher pressures and temperatures promoted crystallization to occur. Thus, current experiments have emphasized two-stage drawing studies with the first stage conducted at room temperature in liquid CO₂ and the second stage at an elevated temperature in SC CO₂. The results from these studies are described in the following sections.

Physical Characteristics of Fibers in CO₂-mediated Environments

SC CO₂- assisted drawing requires that the CO₂ assist in orientation through plasticization of the amorphous phase as well as promote crystallization. To this point basic comparative assessments of physical characteristics are made between nylon6,6 and other commercially available fibers to assess the scope and limitations of this process. The fibers included in this study are Polypropylene (PP), Polyethylene Terephthalate (PET), and High Density Polyethylene (HDPE). The physical properties of these fibers are presented in Table 1.

Table 1: Physical properties for four organic fibers

Fiber	Crystallinity (%)	T _m (°C)	Fiber Diameter (um)
Nylon 6,6	31	258	28
HDPE	80	147	35
PP	50	164	28
PET	39	255	41

Annealing Effects in SC-CO₂

Separate studies were conducted to assess what effect annealing in a CO₂ mediated environment would do to the basic physical properties of the fibers without drawing. A range of temperatures were studied for all fiber systems and only at elevated temperatures were effects noticed. This is illustrated below for three fibers soaked in SC CO₂ at 10.3MPa (1500psi) and 110°C for 10h. The results of this study are given graphically in Figure 2 and in tabular form in Table 2.

Table 2: Annealing effects of fiber treatment in SC CO₂ at 10.3MPa and 110°C

Fiber	X _c		T _m	
	Before	After	Before	After
HDPE	79	82	147-155	147
PP	50	50	164	166
PET	39	39	255	255

The results of this annealing experiment show a strong dependence on the fibers melting temperature. PET, with a melting temperature of 255°C, shows a small shift in the relative sizes of the two peaks, but this does not manifest itself in a measurable increase in crystallinity. PP, with a melting temperature of 164°C, shows a very small amount of annealing. HDPE, with a melting temperature of 147°C, shows a significant change in crystallinity as well as changes in the very nature of the crystallite distribution. These annealing effects tend to complicate the kind of quantitative analyses undertaken with the model system of Nylon 6,6 which did not exhibit annealing effects in CO₂.

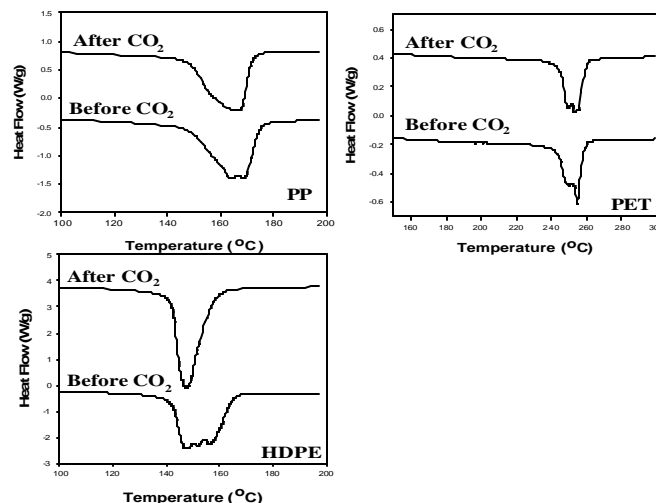


Fig 2: DSC curves for PP, PET, and HDPE fibers before and after treatment in SC CO₂ at 10.3MPa and 110°C.

crystallinity of the fibers must also be taken into account and the HDPE fibers are already at significantly high levels whereas the PP, nylon6,6 and the PET fibers are at much lower levels. The SC CO₂-assisted fiber modification described herein is governed by a very complex interplay of thermodynamic equilibrium and kinetic rate constants. The first crucial step involves the partitioning of CO₂ into the polymer. In order to assess the differences in equilibrium partitioning between the various polymer fibers involved in this study it is necessary to run equilibrium uptake experiments. Fibers themselves, however, are not well suited to these types of experiments.

The experiments involve soaking the polymer in either pure CO₂ or a solution of CO₂. After some period of time sufficient to reach equilibrium, the sample is quickly removed from the CO₂, placed on a balance and the weight is monitored as a function of time. Fibers, by virtue of their small diameters and very large surface area to mass ratios, are ill suited for this experiment because the time for CO₂ to diffuse out is too short. Therefore, the majority of dissolved material will have diffused out before accurate weight measurements can be made. In order to overcome this obstacle, polymer film analogs were used for the uptake experiments. Analogs were tested for the PP, PET, and Nylon6,6 samples. These films possessed percent crystallinities within 5% of that exhibited by the fibers, however the morphology of the crystal structures are very different. This approach therefore assumes that the chemical nature of the material dictates the equilibrium uptake and not the morphological characteristics. To the extent to which this assumption is true this data gives us some idea of how each of the polymers interacts with the different components during the fabrication process.

For CO₂ uptake experiments samples of PP film (0.53mm thick), PET film (0.1mm thick), and Nylon 6,6 film (0.1mm thick,dried) were placed inside of a small high-pressure vessel at 65°C and 1500psi of CO₂ for 4h. The films were then quickly removed and placed on a balance where they were weighed as a function of time. The time from removal to weighing must be monitored exactly and averaged 50 sec for these tests. By assuming a Fickian diffusion for the early stages of CO₂ removal, one can calculate the mass uptake of CO₂ at the point the film was taken out of the vessel (t = 0) by a linear extrapolation to time zero.

The data in Table 3 gives equilibrium uptake data for CO₂ in

Table 3: CO₂ uptake experiments for the three film analogs.

the various films. This data suggests no obvious differences in the equilibrium uptake of CO₂ in the three films. It is important to mention at this point that the equilibrium partitioning of CO₂ and reactants is only the first step of the SC CO₂-assisted polymer modification but it must be considered how the mass uptake of CO₂ can alter the properties of the polymer for drawing.

Film Sample	Original Mass (mg)	Mass at t = 0 (mg)	Equil. CO ₂ Uptake (%)
PP	102.8	107.6	4.7
PET	33.96	35.7	5.1
Nylon 6,6	29.58	30.79	4.1

One-Stage Drawing of Nylon6,6 in SC -CO₂

Initial parametric studies were conducted to isolate optimum drawing conditions in the presence of high pressure carbon dioxide. In these studies, temperatures ranging between 25 C (liquid CO₂) and 150 C were investigated together with pressures ranging between 73 and 323 Atm. The parameters investigated were the in-situ drawability along with final physical and mechanical properties of the fibers. The results were compared with fibers drawn in air at atmospheric pressure and the prescribed temperature.

Results from these studies showed that the best drawability occurs at moderate pressure levels just above the critical point of the CO₂. In our studies the optimum pressure occurred at 102 Atm (1500 psi). Further, the drawability tended to improve as the temperature increased up to the limit of the drawing facility. After testing, the basic physical and mechanical properties were characterized. The results showed that most properties were similar including overall crystallinity and modulus of the fibers. However, both the fiber tenacity (strength), and total orientation showed significant increases in those fibers drawn in CO₂. The overall orientation as measured from the birefringence and the fiber tenacity are shown in Figure3.

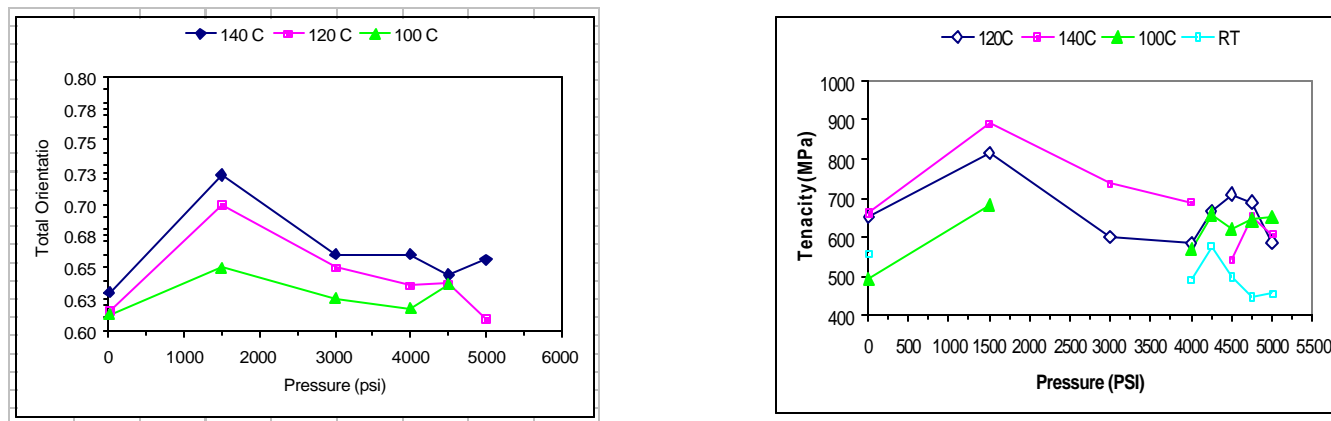


Fig. 3: Plots of overall orientation (left) and fiber tenacity (right) for nylon6,6 fibers subjected to 1-stage drawing in $scCO_2$.

Two-Stage Drawing of Nylon 6,6 in $SC-CO_2$

Previous studies on these fibers have shown that the initial morphology has a significant affect on the overall drawability. This behavior also extends to the two-stage drawn fibers. In order to investigate the effect of the initial fiber morphology on the drawability, both relatively undrawn fiber (carpet fiber) along with commercially drawn fiber (tirechord) were investigated under a range of temperature and pressure conditions. Briefly, it was determined that a first stage draw condition in liquid CO_2 (at 102 Atm, 23 C) followed by a second stage draw at an elevated temperature to promote crystallization produces fibers with the highest stiffness and tenacity.

The two-stage draw ratios achieved ($DR \approx 6$) were observed to be similar for both the air drawn and CO_2 drawn samples. However, there were significant structural differences between the fibers drawn in air and CO_2 . The orientation and crystallinity were also highly temperature dependent for the CO_2 drawn fibers. In both cases, the crystallinity increases significantly over those drawn in air at the same temperatures with the lower pressure having a more pronounced effect. This is very similar to the level achieved in nylon 6 using ammonia as a reversible plasticizer (19). Compared to air drawn fibers at the same temperature, the CO_2 drawn fibers have 25-30 % higher crystallinity values. 50% crystallinity is quite high compared to most experimental techniques.

Similar trends were also observed on the total orientation calculated from the birefringence measurements. The orientation results mimic the crystallinity results (Fig. 2) in that the CO_2 treated fibers all showed a higher overall orientation. This is a direct result of higher birefringence values for CO_2 fibers at this temperature. A large contribution to the birefringence is due to the higher crystallinity of the CO_2 treated fibers. The crystalline phase has a higher intrinsic birefringence compared to the amorphous phase. This is further supported by the high degree of orientation in the crystalline phase as well. It is widely known that the crystalline orientation, f_c is ≥ 0.9 at higher draw ratios. All of the compared CO_2 fibers had higher birefringence values compared to their air drawn counterparts above $100^\circ C$.

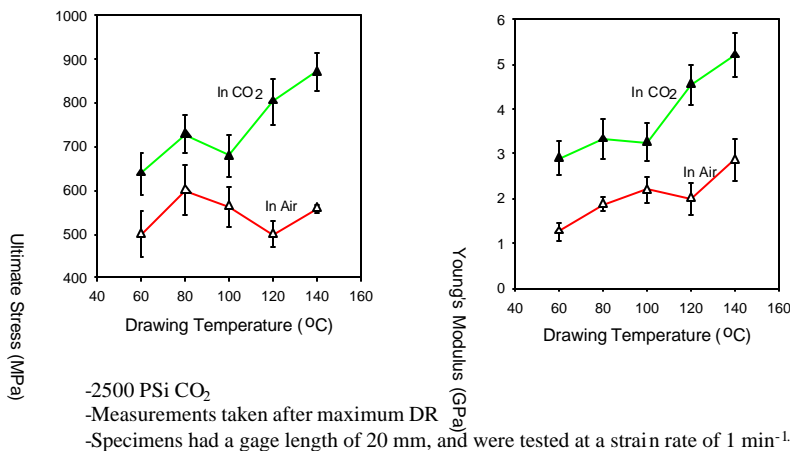
Based on the total draw ratios achieved and birefringence results, CO₂ aids primarily in crystallization partially through the ability to contribute to the thermal breaking of hydrogen bonds. Based on the known density of CO₂ under these conditions, the solubility of CO₂ in the nylon 6,6 is probably low. In addition, CO₂ does not appear to significantly swell, dissolve, or deform the nylon fibers. This can be attributed to the combined effects of orientation and crystallinity. Drawing in SC CO₂ significantly affects the crystallinity and orientation in drawn fibers.

The WAXD patterns for fibers drawn in CO₂ and fibers drawn in air at 130°C were extremely similar. There was only a slight difference in the overlap of the equatorial intensities. Both fibers have a highly oriented α-crystalline phase. CO₂ does not alter the crystal structure and its effects like NH₃ are limited to the non-crystalline domains. The highly oriented nylon 6,6 shows a typical triclinic unit cell with higher order reflections of the crystallographic planes perpendicular to the fiber axis. Based on these patterns, it seems that the moderate pressure imposed by the CO₂ does not have a significant effect on the crystal structure. Previous results on the drawing of nylon 6 at higher pressures in silicone oil resulted in improved crystal perfection, as diffraction scans became sharper (20). However, the pressures where this occurred (1450 atm) were significantly higher than the CO₂ pressure that we are using.

The tensile properties of nylons are significantly affected by degree of orientation and crystallinity. It was shown previously that these structural characteristics are highly temperature dependent so one would expect the engineering properties to be influenced by temperature as well. Figure 4 shows the dependence of ultimate tensile strength and modulus on temperature. The trend is correlates well with the global orientation and crystallinity in these fibers. The CO₂ treated fibers have significantly higher tensile strength values compared to air drawn fibers. Under certain conditions, the tensile strength and stiffness of these fibers are nearly twice that of those drawn in air. Strengths approaching 1 GPa and moduli approaching 5 GPa are realized under certain conditions. It is interesting to note these fibers maintain appreciable ductility with %strain to failure values ~20%. The fibers could probably be drawn further in a third stage. In addition, these fibers show great potential for energy absorption because they have high strength and ductility.

The temperature dependent behavior of the fiber modulus is similar to the strength and orientation as discussed earlier. The tensile moduli of CO₂ drawn fibers are compared to air drawn fibers in Figure 7. The highest modulus of 6.4 GPa is higher compared to commercial fibers but much lower compared high tension annealing (8-12 GPa) or ammonia aided extrusion (13 GPa) (21,22). All of these values are still extremely low compared to the theoretical modulus of nylon 6,6 being 180-250 GPa (23). The structural analysis and tensile results indicate that the CO₂ treated fibers have relatively low amorphous orientation. This is

Temperature Effect on Drawing Nylon6, 6 in SC CO₂
Mechanical Properties



directly reflected by the relatively low birefringence values. Our values are 25-30% lower compared to the five stage drawn fibers discussed earlier. All the results indicate that further drawing stages may be necessary. Despite this, drawing in a CO₂ environment appears to be highly effective in a two-stage draw technique. The CO₂ drawing process is also very efficient for nylon 6,6. Also, no apparent optimum in conditions is observed. It is anticipated that drawing fibers above the current limit of our drawing facility will show additional improvements. This will be investigated further in 2003 once our second generation drawing facility is operational (summer of 2003).

Additional Physical and Mechanical Studies

Additional studies are ongoing to investigate the effect of cosolvents along with CO₂ to further enhance the drawability of the nylon6,6 fibers including water. Typical in-situ stress vs strain curves showing this effect are illustrated in Figure 8. The plasticizers were chosen by their ability to affect the significant hydrogen bonding present in the nylon structure. Note that water as well as a variety of alcohols can effectively plasticize the fibers. The limitation of this technique in of itself is that the plasticizer must be extracted during after the processing is complete. It may be possible to use SC CO₂ for this extraction process.

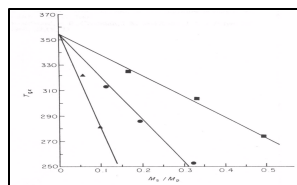
Additional tests have been conducted to systematically study how the yield behavior is associated with the T_g in the nylon6,6. Reports on other materials show that the yield behavior is intimately related to the difference between the test temperature and the glass transition temperature. This occurs since yielding in polymers has been shown to be a stress-induced thermally activated process and scales with the distance away from the glass transition temperature. Once this relationship is known for a the nylon6,6 under these strain rates and stress states, the glass transition temperature can be estimated for a given test condition. We have initiated experiments to elucidate this behavior and the stress-strain curves for a range of temperatures. Similarity in response that both temperature and plasticizer have on the yield behavior of the nylon. From this information, assessments of the reduction in T_g as well as concentration of plasticizer in the fibers are being conducted.

Recent studies have focused on estimating the effect that CO₂ has on reducing the T_g, and thereby yield and draw stress during processing of fibers. This is critically important in the first stage of drawing to enhance orientation during the draw process. Chow²⁴ proposed a molecular interpretation for the effect that diluents have on the T_g of polymer systems. Based on statistical mechanics, Chow uses a Bragg-Williams approximation of an order-disorder transition to determine the configurational partition function. The T_g is then related to nondimensional parameters, which are functions of the intrinsic properties of the pure polymer and diluent. The Chow model predicts the depression in T_g given the molecular weight of the repeat unit, the molecular weight of the diluent, the weight fraction of diluent, and the isobaric specific heat of the polymer. Our group interrelated the T_g to the yield stress of polymer systems to the measured yield stress during drawing. This interrelationship is based on the premise that yield of the polymer is a stress-induced

Effect of Different Plasticizers on Fiber Drawing

Prediction of yield stress of as-spun fibers drawn in air at different temperature

Draw temp. (°C)	Yield stress (MPa)		Fiber used
	calculate	tested	
65	34.53	35.24	Tirecord
70	32.49	31.37	Tirecord
100	22.5	20.33	Carpet
120	17.5	17.6	Carpet
140	13.6	18.21	Carpet



Effect of plasticizer content on T_g
 □, Water; ○, ethanol; △, methanol

Efficiency of plasticizers in depressing yield stress

Drawing condition (at room temperature)		Yield stress (MPa)	Equal to drawing temp. (°C)
Pressure (psi)	plasticizer		
1500	CO ₂	47.17	39.4
3000	CO ₂	37.32	58.6
4500	CO ₂	47.47	38.9
14.5	Water	10.21	164.9
14.5	Water	18.0	117.0
1500	(average) CO ₂ +Water	26.79	85.7
14.5	Methanol	12.62	147.5
1500	CO ₂ +Methanol	33.33	67.9
14.5	Ethanol	34.64	64.8
1500	CO ₂ +Ethanol	41.07	50.9
14.5	2-propanol	38.03	57.1
1500	CO ₂ +2-propanol	43.01	47.0

thermally activated process in which polymer chains transition from solid type conformation to more liquid like conformations.

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Section IV Research Accomplishments on PBO (Zylon) Fibers

Overview

Initially, the Lesser Research Group focused their efforts on one of the strongest and most thermally resistant fibers commercially available today. These fibers are poly-p-phenylenebenzobisoxazole (PBO) currently manufactured by Toyobo. The unique combination of exceptional thermal stability, high stiffness and strength make them ideal materials to incorporate in protective garments for personnel protection and body armors. The initial research focuses on isolating mechanisms of degradation (both physical and mechanical) and methods that involve post-treatment with supercritical carbon dioxide to rectify degradation.

These fibers were selected for the following reasons:

- It has been recently reported that these fibers degrade when exposed to moisture, ultraviolet light, and visible light. In some cases, more than 50% of their strength is lost. Identifying the mechanisms responsible for degradation and strategies to alleviate the problem is critical to able their implementation in protective wear.
- The way these fibers are fabricated and processed produces a nano-porous structure. This morphology makes them ideal for further modification to improve their mechanical, physical, and chemical resistance. Thus, the fibers can be used as scaffold the enable modification for chemical or biological interaction with the environment as well as be used as reinforcement in laminates that provide various forms of protection.

Research to date has shown that PBO fibers are susceptible to environmental degradation when exposed to a variety of conditions including moisture, exposure to UV-visible light, and other environments. We systematically identify mechanisms of degradation and have started research initiatives to eliminate the degradation when exposed to these conditions.

Our research is focused on post-treatment of commercial fibers that would enable rapid scale-up of promising techniques. Moreover, in some instances, the modifications considered are also applied to other commercially available high performance fibers including Kevlar and M5 fiber. Both physical and chemical treatments have been considered. The physical treatments involve annealing fibers and fabrics in the presence of supercritical carbon dioxide to extract residual acids (that may contribute to the degradation of the fibers) as well as to remove defects and densify the fiber structure. The chemical treatments include methods to neutralize any residual acids using supercritical carbon dioxide as a transport media as well as methods to provide UV-visible light stabilization.

Additional efforts have focused on characterizing the deformational response of these fibers during heating to extremely high temperatures. New measurement techniques developed in our group have shown that these fibers actually contract as the temperature is elevated (negative coefficient of thermal expansion) and also dilate under the application of tensile load (negative Poisson's ratio). Further, it is suggested that post-treatments can alter this magnitude of these responses, and the temperature when they activate. This implies that it may be possible to design garments to mechanically dilate (swell) or contract that might aid in controlled adsorption or emission selected reagents.

Finally, we have identified process methods to produce highly oriented nano-fibrils from the commercial PBO feedstock. These fibers could provide reinforcement in composites at length scales that enable other functionality. For example, it may be useful to use these fibers in the fabrication of protective eyewear or other applications that

require optically transparent protection. Moreover, unlike electro-spun fibers, these fibers are highly oriented and thus have excellent physical, thermal, mechanical performance.

Background

High performance (high strength, high modulus, and thermally stable) organic fibers have been increasingly used to make high performance composites. Their very high strength-to-weight ratios as well as the excellent thermal stability make them the ideal candidates for replacement of metals in a broad variety of civil and military applications including space and aviation applications. These materials are currently critical elements in a number of personal protective armors used in both military and domestic applications. Currently the fibers that meet these requirements are spun from rigid-rod or liquid-crystalline polymers.

Polybenzazole (PBZ) fibers, which include poly-p-phenylene benzobisoxazole (PBO), polybenzimidazole (PBI) and Poly-p-phenylene benzobisthiazole (PBT) are known to have excellent physical properties. Typically these fibers have a reported tensile strength of 5.8 GPa, and tensile modulus of 180-270GPa^{1,2}. To date, they are the strongest commercially available organic polymeric fibers. Consequently, they are ideal candidates for many fire fighting applications. Research and development of these materials are being actively pursued for applications in high-performance fiber composites, protective garments, and personnel ballistic armors. Similarly, the tensile strength and modulus of poly{2,6-diimidazo[4,5-b4',5'-e]pyridinylene-1,4(2,5-dihydroxy)phenylene}PIPD or M5 fiber is around 6.0 GPa and 360 GPa respectively, which is comparable with those of PBZ fibers, but their compressive strength is 1.7 GPa, and much higher than that of PBT fiber (0.4GPa).

However, these fibers are far from their theoretical strengths. According to computational predictions^{3,4}, a cis-type polyparaphenylene benzobisoxazole has a crystal modulus of 475 GPa. This has been confirmed by x-ray diffraction⁵. A common rule of thumb is that the theoretical strength should be about 10 percent of the modulus of a single crystal. Based on this rule, strengths achieved to date are only 10-15% of their theoretical limits.

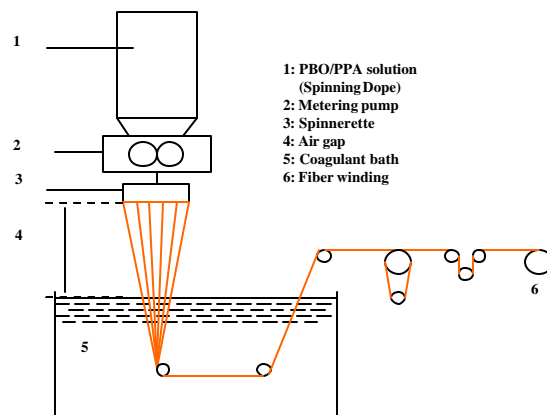
Poly-p-phenylenebenzobisoxazole (PBO) is one of the class of rigid-rod liquid crystal polymers that orients easily into extended chain configurations to produce fibers with excellent strength and modulus. PBO polymer was originally developed by the U.S. Air Force to replace metals in various aerospace applications and is known for its excellent thermal stability and chemical resistance¹⁻⁴. PBO fibers exhibit exceptionally high strength (5.8GPa), stiffness (180-270 GPa), and relatively low density (1.54 g/cm³) which makes them an ideal candidate for ballistic armors in both civil and military applications.

Recently (late 2001), Toyobo published some disconcerting results regarding the susceptibility of PBO fibers to degradation when exposed to relatively mild conditions⁴. In particular, the strength of PBO fibers decreases even at temperature less than 100° C in high humidity. After 100 days at 80% relative humidity and 80° C more than 40% of the strength is lost and the trend in the data suggest that additional losses can be expected with additional exposure. Additional data from Toyobo show that PBO fibers are also susceptible to sunlight. Both as-spun (AS) and high-modulus (HM) fibers loss more than their 50% strength after only 3 months exposure at Ohtsu, Japan. Subsequent to these reports, numerous news reports reiterating these concerns in PBO products have been reported⁵.

Earlier studies have found that PBO in the presence of 1wt % sulfuric acid or polyphosphoric acid and water was at 80 C would render the benzobisoxazole susceptible to bond cleavage to generate carboxylic acid and aminophenol functional groups. Although the conditions reported in the Toyobo technical literature² are not severe hydrolytic conditions, one current hypothesis⁸ is that trace phosphoric residuals present in the fibers from processing combine with humid environments to promote degradation. Given the commercial approach for spinning PBO fibers, it is entirely expected that residual phosphorous containing compounds may be left in the fiber thereby acting as initiation sites for hydrolytic degradation once exposed to humidity.

Fabrication and Processing of PBO Fibers.

PBZ fibers are typically made by employing a dry-jet-wet-spinning process, in which a solution that contains the PBZ polymer and an acid solvent (commonly referred to as a "dope") is spun through orifices of a spinneret to form dope filaments that are combined into one or more dope fibers. These dope fibers are then drawn across an air gap, and subsequently contacted with a fluid that dilutes the solvent and is a non-solvent for the polymer. This contact with fluid causes the polymer to separate from the solvent. The gas in the "air gap" may be air, but it may also be another gas such as nitrogen, carbon dioxide, helium or argon. The extruded dope fibers are drawn across the air gap with preferred spin-draw ratio (see figure at right). When the dope is extruded and drawn in the air gap, PBZ chains are in their ordered configuration, but when water or aqueous phosphoric acid solution is used as a coagulant this order is disturbed. Infiltration of water by diffusion into the dope filaments during coagulation causes disturbance of ordered structure originally formed in the draw zone. As a result, the fiber after coagulation has much lower orientation than found in the draw zone, resulting in lower tensile strength and modulus of the finally dried and heat-treated fibers. Also, the pronounced coagulation further increases the defects of the final PBZ fibers.



A consequence of the spinning of the coagulated polymer is that defects are introduced into the fiber morphology resulting from removal of water and residual acids may be left behind. Although PBZ polymer chains are relatively oriented along the fiber axis, there is still an inherent limitation from the dry-jet-wet spinning process. The structure formed during the coagulation stage in the dry-jet-wet-spinning process of PBZ fiber is an interconnected network of oriented nano-fibrils, the width of which is 8-10 nm. The transmission electron micrograph above showing the nano-fibril morphology is taken from reference 8. Further, it has been shown that a one-dimensional nucleation and growth mechanism is mainly associated with the formation these fibrils.

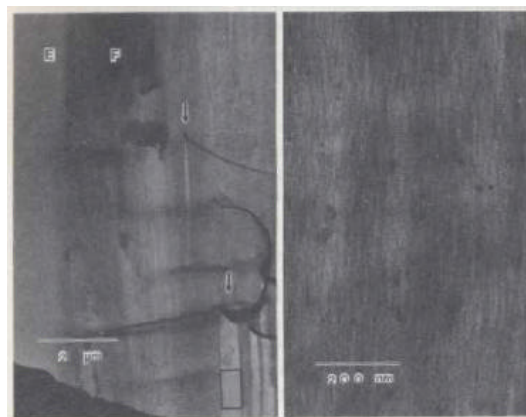


Fig. 1. (a) A longitudinal section of coagulated PBT fiber infiltrated with epoxy resin. E-epoxy matrix; F-fiber. (b) A high magnification image of the outlined area.

The fibril width is controlled by the density of nuclei and deviation in the molecular orientation. During drying, the network is collapsed to yield the “as-spun” fiber. PBZ fibers after the desolvation, however, contain a great amount of the non-solvent in 25% by weight or more, and they exhibit additional volume change on drying producing the nano-fibril morphology. These nano-fibrils are the fundamental structural elements of the final fibers. Consequently, the fibers themselves are inevitably riddled with defects present which can be verified with small angle x-ray scattering. The x-ray studies show that a strong equatorial streak appears when the fiber develops capillary voids which generally arise during the coagulation step and the voids are elongate in the direction of the fiber axis. Tensile strength is mainly related to the concentration of defects, which act as fracture initiation sites and, consequently are responsible for the relatively low strength of the fibers. Therefore, developing methods to remove these defects either during their spinning or with post-treatment processes (as indicated herein) govern the ultimate strength of these materials.

Thus, it has been difficult to further enhance the tenacity of these fibers through traditional post-treatment processes. Heat-treating under tension allows further perfection of the orientation and increases the crystallite size but has only shown to increase the modulus with little or no effect on the tenacity¹³⁻¹⁸. Heat-treating is usually carried out under relatively high tensile loads imposing stresses on the fibers in the range of 1.0 GPa.

Other process methods have tried in an attempt to improve the tenacity of PBZ fibers. These processes mainly focused on optimizing the spinning and the coagulation conditions to make fibers with more a uniform morphology. Coagulating PBZ fibers in cold temperatures is known to slightly enhance tensile properties of the fibers as well as mixtures of acid and water²³, or other nonaqueous solvents have shown mild improvements. It is also known to slightly increase the tensile properties of spun PBO fiber by coagulating the fiber in a mixture of acid and water vs. coagulating the fiber in water alone. High tensile strength and modulus PBZ fibers with high orientation, uniformity and regularity can also be produced by using a nonaqueous solvent instead of water. What is proposed herein is a post-treatment process that does not require the fiber to be under tension thereby enabling fabrics and garments to be treated. Also, indications suggest that the improvements anticipated with this method far exceed any of the improvements reported with these methods. Another disadvantage of these methods is that a huge amount of organic solvents such as ethanol, methanol, propanol, butanol, ethylene glycol, acetone or aldehyde, ketone are used. This increases the energy consumption during fabrication and has a negative environmental impact, or requires recycling these solvents. At the same time, this forms large amounts of wastewater in coagulation and post treatment processes, which is not environmentally preferable. Consequently, there are no specific technologies to further improve the tensile strength of PBZ fibers, especially no processes related to increasing the tensile strength of PBZ fibers by specific post-treatment to date.

It should finally be noted that since both PIPD (M5) fiber and PBZ fiber are formed by a dry-jet-wet spinning process with the same solvent (polyphosphoric acid), coagulated with non-solvents such as water or water/phosphoric acid solution and heat-treated for higher modulus, all of the factors mentioned above, which can influence the mechanical properties of PBZ fiber will have similar effect on the mechanical properties of M5 fiber.

The reported susceptibility of PBO fibers to degrade when exposed to sunlight and/or high humidity is somewhat surprising given the apparent high thermal and chemical stability of this class of polymers. In this paper we discuss potential mechanisms of degradation. PBO fibers are exposed to various controlled environments and subsequently characterized using a broad range of mechanical and physical tests.

Potential Degradation Mechanisms

To date, no mechanism has been confirmed to explain the degradation in mechanical properties of PBO fibers when exposed to relatively mild conditions. However, potential mechanisms can be proposed after considering how commercial fibers are made. Commercial PBO fibers are spun using a dry-jet wet spinning process. In this process, PBO polymer solution containing 10-20% of PBO in polyphosphoric acid (PPA) is drawn through a spinneret into a coagulation bath (water). This is then followed by washing, drying and heat treatment. At the dry jet stage of the process, the fibers consist of highly oriented nanofibrils approximately 10 nm wide making up a relatively defect free filament⁶⁻⁹. However, once coagulation occurs to extract the PPA, some orientation is lost and defects are introduced as a natural consequence extraction process⁶⁻⁹. One hypothesis suggests that trace phosphoric residuals in the fibers combine with humid environments, sunlight and oxygen to promote degradation in the form of hydrolytic attack.

Another hypothesis considers that, although the fibers may be thermally stable, they may be intrinsically susceptible to photodegradation. Recently studies have suggested that these polymers do absorb significant amount of energy in the UV-visible spectrum¹⁰. However, these findings were reported on polymer in solution and not on actual fibers. Also, doesn't necessarily imply degradation. This paper reports results from an ongoing study focused on identifying the degradation mechanisms and alleviating or reducing the potential for degradation under these exposure conditions.

Experimental

Materials. The PBO fiber used in these studies is Zylon AS, which was supplied by US Army Soldier System Command at Natick, MA. The related properties of the fiber can be found in reference⁴. Phosphoric acid (85 wt.% solution in water) was purchased from Aldrich Chemical Company, Inc and was used as received. Phosphoric acid, trimethylphosphate (TMP) pyridine, morpholine, and DMAP were also purchased from Aldrich Chemical Co. and used received. Chemical structure of each of these compounds is given in Table 1.

Artificial light exposure procedure. The artificial weathering was carried out with an Atlas Suntest CPS+ light weather-ometer. A 1500-watt xenon lamp is equipped with an irradiance range from 300nm to 800nm. Both single fiber and fiber bundles were mounted in the specimen tray and exposed at 45^o C and with an irradiance level of 750W/m² for different conditioning times.

Mechanical Testing. Single fibers were mounted on a cardboard template with a gauge length of 20 mm using a 5-minute epoxy adhesive. Tensile tests were performed on an Instron 5500R with a 50N load cell at a strain rate of 0.05/60s. Tensile strength, modulus, and elongation-to failure results were based on 10 specimens and calculated by using the effective gauge length¹¹.

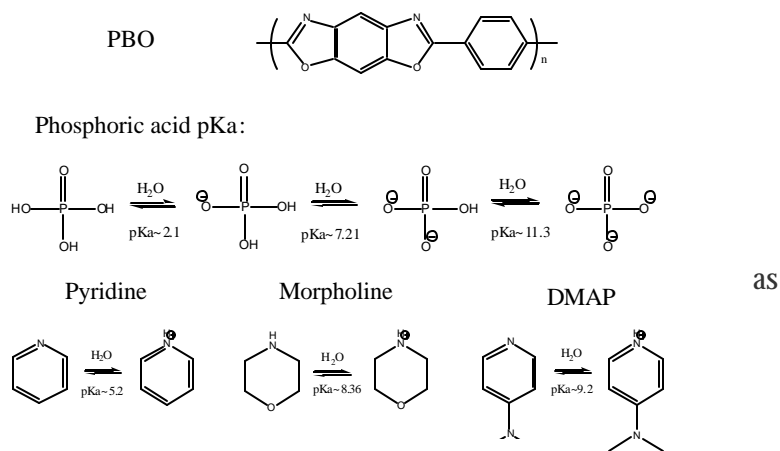


Table 1: Chemical compounds used in study

Characterization. Element analysis: Carbon, Hydrogen and Nitrogen analysis was performed by precisely weighing 2500-3500 μg of sample and combusting it at 1000°C in oxygen over a platinum catalyst, using a standardized Exeter Analytical 240XA Elemental Analyzer based on the modified Pregl-Dumas method. Phosphorus analysis is performed by a standard inductively coupled plasma emission spectroscopy (ICP) technique, after 20-30 mgs of sample is precisely weighed and digested with a combination of sulfuric and nitric acids. A Leeman Labs, Direct Reading Echelle (DRE) ICP was utilized. Thermogravimetric analysis (TGA) was done with a TA Instruments 2050 Thermogravimetric Analyzer (DuPont) at $10^{\circ}\text{C}/\text{min}$ under both nitrogen and air atmospheres, respectively. ATR-FTIR was done with FTIR Spectrometer Spectrum 2000 (Perkin Elmer) in the range of 4000-700 wavenumber at resolution 4cm^{-1} . X-Ray Photoelectron Spectroscopy (XPS) was conducted on a Scanning ESCA microprobe Quantum 2000 (Physical Electronics Inc.) using an Aluminum x-ray.

Results and Discussion

Elemental analysis initially done on the Zylon AS fiber to establish a baseline and to determine if residual phosphoric acid resides in the fiber. The figure at right shows results from these analyses and indicates that a residual amount of phosphorous ranging between 0.3 – 0.4 wt% resides in the fiber. Note that this result supports the first hypothesis in that it illustrates at least residual phosphorous which may be in the form of phosphoric acid is present in the fibers.

In order to assess whether residual PA contributes the reported mechanical degradation, PBO fibers were conditioned in various PA H_2O solutions for 24 hrs, dried and characterized for residual phosphoric acid (Figure 1). Using this approach allowed for adjusting the residual phosphoric acid in a controlled way between 0.3 and 5 wt % as shown in Figure 2.

Subsequent mechanical tests were conducted on filaments after UV-visible light exposure on both conditioned and control samples. The figure below shows how the fiber strength and elongation change with increased exposure time. It should be noted that modulus was measured also, but was not as significantly affected initially. The graph was not included herein simply for brevity. Note in Figure 3 the black squares are results on fibers without any conditioning in PA H_2O solution, the red circles are results from a 10 % solution, and the green triangles represent findings from a 20% solution. These, in turn, translate into residual phosphorous of 0.3, 0.7 and

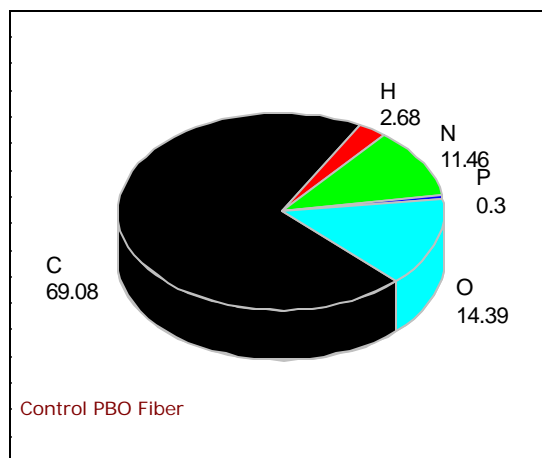


Fig. 1: Elemental Composition of PBO Fibers

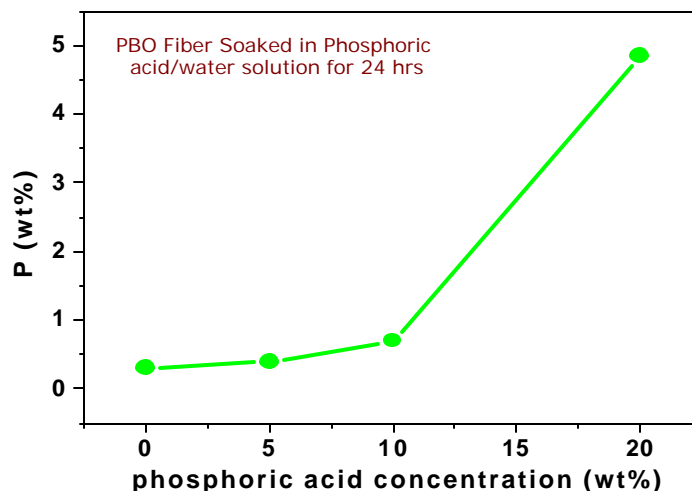


Fig. 2: PA adjustment using water soaking.

4.8 wt % respectively. It can be seen in all cases that exposure to UV-visible light causes a reduction in both the tenacity and elongation to break. The Figure 3 shows that small amounts of additional residual PA dramatically enhance the degradation in mechanical properties. This finding supports the first hypothesis in arguing that residual PA plays a role in the degradation process and underscores the importance of thorough extraction of residual PA. It should be noted that at 4.8% residual PA, the fibers were so degraded that measurements were not possible after more than 50 hours exposure.

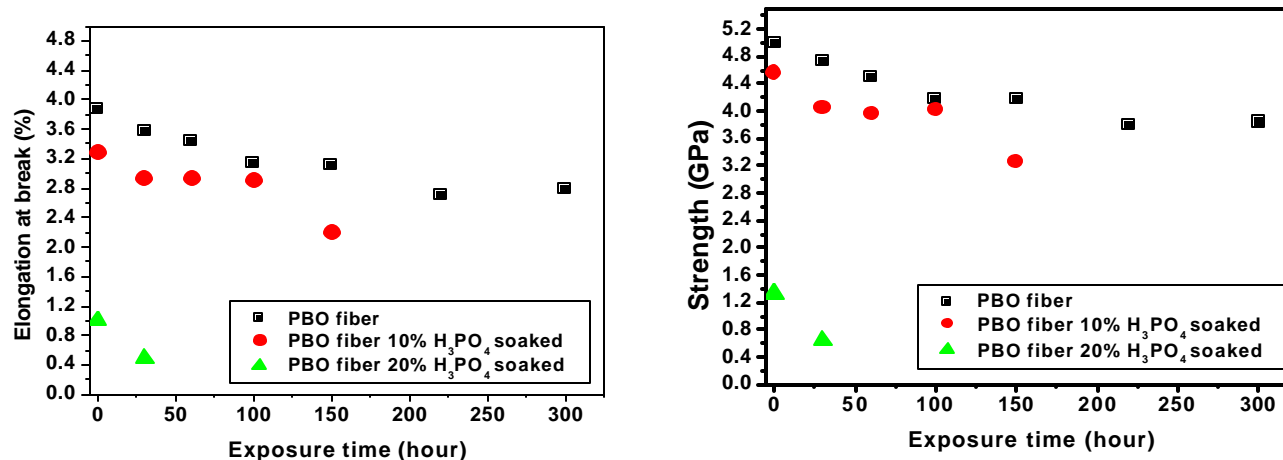


Fig. 3 Strength (right) and elongation-to-break (left) reductions after UV-visible exposure on control (squares) and conditioned (circles and triangles) Zylon AS fibers.

A second set of experiments were conducted to isolate the effects of moisture. Samples of fiber were immersed in water at room temperature and exposed to 90 RH at 50°C. Results from these are plotted in the Figure 4. Note that the data at the right is for exposures for nearly 5 months with systematic testing.

The effects of moisture alone are more gradual than UV-visible light alone. Also, the results tend to vary more with time. Nonetheless, two key facts are evident. First, moisture alone does degrade the mechanical strength of the fibers, and, immersed fibers degrade more quickly than those in humid environments.

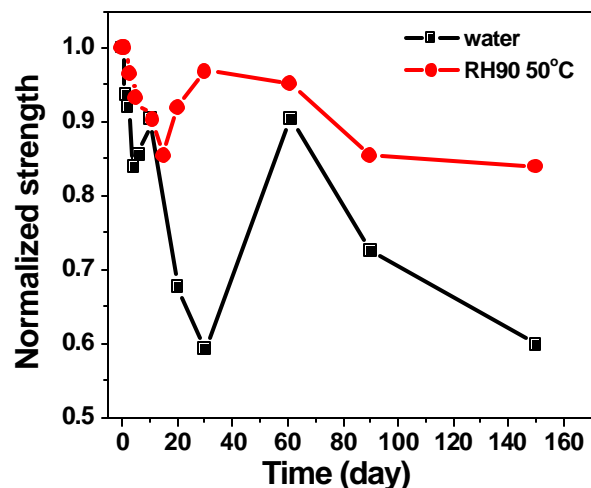


Fig. 5: Strength reduction due to moisture exposure.

Scanning Electron Microscopy (SEM) and Optical Microscopy (OM) were also performed on fibers. The micrographs in Figure 6 are SEMs of a fiber before exposure. The micrograph on the left shows a typical surface morphology prior to any exposure or mechanical testing, while the micrograph on the right shows a fiber tip after failing in tension. Note that the left micrograph shows evidence of a striated surface characteristic of the highly oriented nanofibril morphology reported in these systems⁹. This is also reflected in the splintered fracture surface observed after tensile failure (Figure 6 right). It

should also be noted that this type of fracture pattern is characteristic in anisotropic systems that have high strength. In such morphologies, stress concentrations from defects in one particular region (e.g. one nanofibril) do not easily transfer to adjacent fibrils in the fiber resulting in high strengths and cracks deflecting along the fiber axis.

Optical microscopy on fibers exposed immersed in water showed evidence of nanofibril delamination. This is illustrated in the figures below where delamination is evident after water exposure.

This illustrates the type of delamination observed after fibers are exposed to water. Subsequent studies also indicated that this delamination is exacerbated by associated increases in residual phosphoric acid as well as by mechanical agitation (e.g. sonication). Initial chemical studies on exposed samples also suggest that the degradation mechanism caused by water may be predominantly mechanical in nature. That is, the interfaces between nanofibrils are disrupted causing physical alterations in the fiber, potentially altering load transfer between nanofibrils, and increasing surface area for other potential chemical attack.

Similar morphological studies were conducted on fibers exposed to UV-visible light. Typical results are shown in the Figure 7. After exposure to UV-visible light, the PBO fiber surface morphology changes dramatically. Careful inspection of the exposed fibers indicates a scalloped surface morphology which is more characteristic of polymer surfaces subjected to chemical attack. Similarly, the failure surfaces reflect how the fibrillation is altered by the degradation process. Although, the direct mechanisms of chemical degradation cannot be extracted from such studies, they provide strong evidence that chemical degradation is occurring in these systems when exposed to UV-visible light. Ongoing studies are currently underway to identify degradation products stemming from these exposure conditions. Further, additional efforts are being taken to alleviate these effects¹².

Additional studies are ongoing to ascertain what affects other small amounts of residual acid or bases might have on the mechanical and chemical stability of these fibers. To that end, PBO fibers were initially conditioned in a

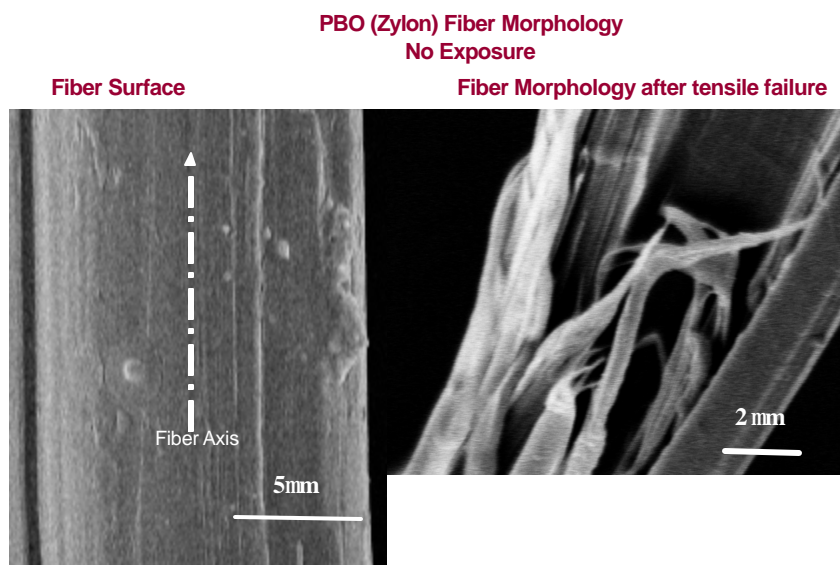


Fig. 6: Scanning electron micrograph illustrating typical fiber morphology (left) and failure surface (right) on Zylon AS fibers.

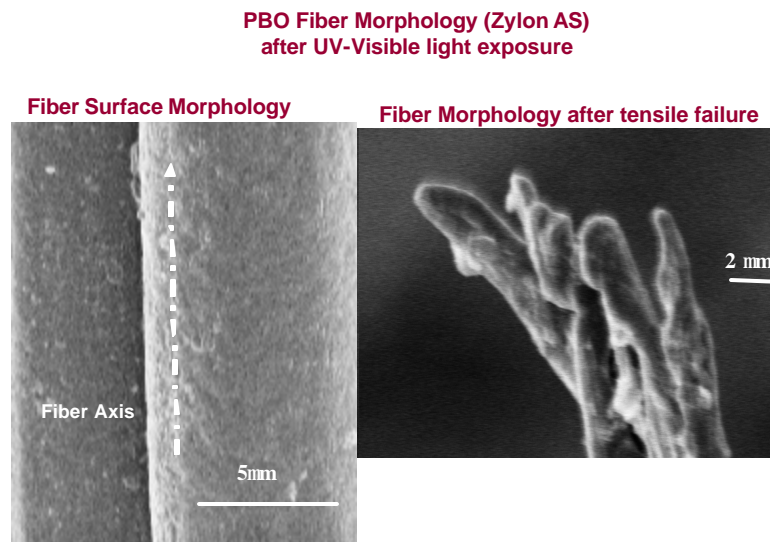


Fig. 7: SEM micrographs illustrating fiber morphology (left) and failure surface (right) after UV/visible light exposure.

range of other low molecular weight compounds (see Table 1). Trimethylphosphate (TMP) was one of the selected compounds since it has a chemical structure very close to phosphoric acid and has shown in other polymers to actually work as a molecular fortifier. The other compounds (pyridine, morpholine, and DMAP) were chosen since they are bases with increasing pKa values and may be used to neutralize any residual acids present in the fibers. For these experiments, PBO fiber was immersed in 100% concentrations of each compound at room temperature for approximately 160 hours. Afterward, one sample set with initially tested and additional samples were exposed to UV-visible light and subsequently tested. Figure 8 shows what effect these compounds and subsequent exposure have on the fiber tenacity. Considering first the effect that TMP has on the PBO tenacity and subsequent stability it is noticed that no improvements are observed. In fact, careful comparison to the results shown in Figure 3 to those in Figure 7 indicates that the TMP affects the tenacity in a fashion similar to that of the PA..

Although no measurement of the pKa of TMP was made, it is anticipated that it may be acidic and have a similar affect to the PA.

With regard to the base compounds (pyridine and morpholine), reductions in the PBO stability were also observed. This result was somewhat surprising since it was initially anticipated that the residual PA played a key role in at least accelerating the degradation of the PBO, and the introduction of a base should neutralize the PA. Nonetheless, the results in Figure 8 show that the stability of PBO fiber in the presence of UV-visible light is highly sensitive to the environment, and any condition either basic or acidic can accelerate the degradation. This observation also supports the second hypothesis in that the fiber may be intrinsically susceptible to photodegradation. Recently studies show that these polymers do absorb significant amount of energy in the UV-visible spectrum¹⁰. It should be emphasized that absorption of energy doesn't necessarily indicate stability. However, energy is absorbed nonetheless and, if these fibers are intrinsically unstable in this spectral range, the presence of either an acid or base is expected to simply catalyze the degradation process.

Final Remarks

Results from long-term exposure studies on PBO fibers indicate that these fibers are susceptible to mechanical degradation over a range of exposure conditions. The results show that exposure to moisture, or water, as well as UV-visible light degrades the mechanical performance of the fibers. The effect of water and moisture are not as detrimental as UV-visible light alone and the mechanisms for water degradation appear to be predominantly mechanical or physical in nature resulting in delamination and creation of surface area. Exposure to UV-visible light, in contrast, appears to cause chemical degradation and can diminish properties rapidly. Further exposure studies show that PBO degradation can be exacerbated when either residual acids or bases are present, thereby showing a pronounced acceleration in mechanical degradation.

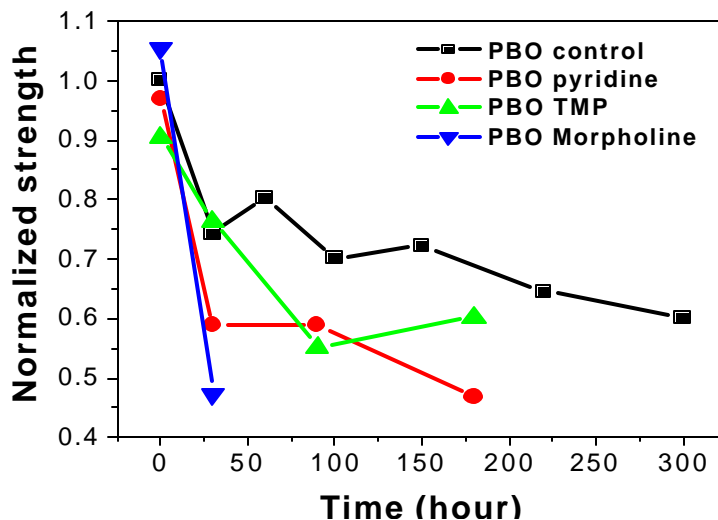


Fig. 8: Strength reduction of PBO fiber due to UV-visible light exposure after conditioning in small compounds

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Treatment Studies in Supercritical Carbon Dioxide

The Lesser Research Group in the Polymer Science and Engineering Department at the University of Massachusetts, Amherst has developed considerable expertise in using supercritical carbon dioxide (scCO₂) as both a process and reaction media. We have demonstrated unique aspects associated with scCO₂-based solvent welding, polymerizing one phase within the amorphous phase of another semi-crystalline polymer to produce interesting immiscible blends, fabricated unique laminated composites in scCO₂ mediated environments where fiber and interface are both modified during the process, produced extremely highly reinforced nanosilicate composites (nano-laminates), in addition to conducting a broad range of fiber drawing studies in scCO₂ - mediated environments.

Using scCO₂ to draw flexible chain polymeric fibers has two concomitant effects. First, it acts as a plasticizer and helps to reduce entanglements during the drawing process. scCO₂ has the distinct advantage over conventional solvents in that it has no surface tension, it diffuses into the fiber at the rate of a gas, the solvent strength is independently tuned by either pressure or temperature, and the plasticizer is reversible. That is, once the pressure and temperature are dropped, the CO₂ evacuates from the sample and low molecular weight residuals are not left in the fiber. The second effect is that the regions that are not permeated by the scCO₂ (e.g. crystalline phase) are subjected to the hydrostatic pressure. This pressure assists in annealing defects from the crystalline phase, can promote additional crystallization, stabilize crystallization during drawing, and suppress failure during drawing.

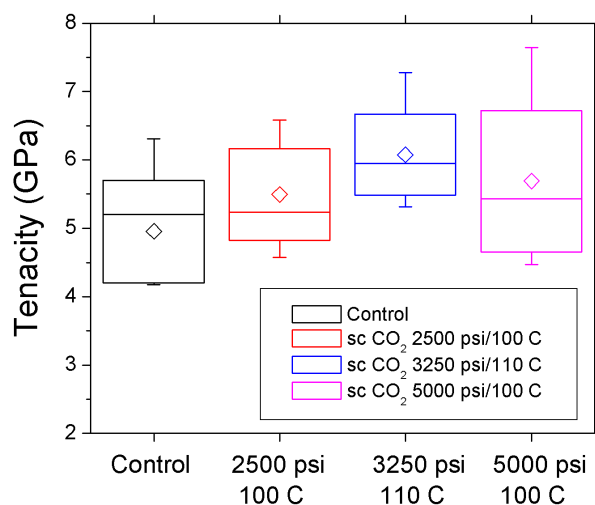
Last year the Lesser research group started specific investigations on poly-p-phenylene benzobisoxazole (PBO, Zylon™ AS) fibers. In these particular studies, we started feasibility studies associated with using scCO₂ as an extraction media. Specifically, we started studies to assess the potential of using scCO₂ to extract residual polyphosphoric acid from the fibers thereby enhancing their environmental resistance.

Additional experiments were conducted to identify if scCO₂ would have any detrimental effects under a range of selected extraction conditions (based on scCO₂ density and temperature for solvent strength). Mechanical tests were conducted on fibers both before and after scCO₂ exposure and a serendipitous result was found. The table below shows results from a series of experiments after conditioning PBO and PIPD fibers in scCO₂. Figure 1 shows that effect of scCO₂ treatment on the tenacity of PBO as spun fibers.

It should also be noted that no tension is applied to the fiber bundles during the treatment process. This implies that fabrics and articles made from these fibers might also be treated with similar results.

Understanding the mechanisms of property enhancement, fiber degradation, and subsequent process optimization are the main objectives of the proposed research.

The aim of these studies is to develop a post-treatment process for rigid-rod and liquid crystalline polymeric fibers that enhances their initial strength and alleviates their susceptibility to environmental degradation. The post-treatment process we propose will use



supercritical carbon dioxide $scCO_2$ to both anneal defects in the fiber and as an extraction media for residual acids as well as a transport media for neutralizing bases. Additional studies are proposed to develop a new process for making nano-scale fibers from the commercial filaments.

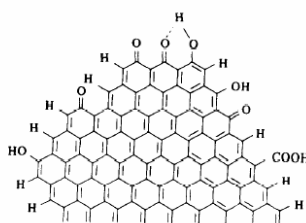
All of the necessary equipment is in place, or is currently being fabricated for this study. In addition to access to the equipment in the central facilities in the Conte Research Center for Polymer Research, specific equipment devoted to this research include a fiber drawing and treatment facility (DURIP – grant DAAD19-02-1-077) as well as a larger reactor for treating ballistic targets and garments (being constructed under contract DAAD19-01-1-0580 2004 supplemental award). Additional instrumentation are in place to conduct controlled environmental exposure studies including a Suntest Weatherometer for UV exposure, a broad range of analytical methods to characterize any degradation, and all necessary equipment to characterize the mechanical performance of treated and exposed fibers. This equipment is covered in detail in the Facilities Section of this proposal.

Further studies are also planned and include x-ray analyses to quantify defect size and distribution both before and after treatment. Additional morphological investigations are also planned to identify if the treatment is throughout the fiber or only occurs to a specific penetration depth.

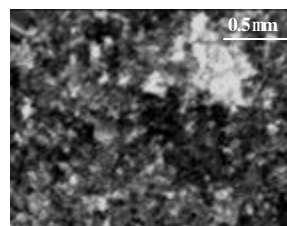
scCO₂ Induced Coating Methods and Treatment for Enhanced Stability

The Lesser Research Group has also started studies focused on using $scCO_2$ as both a reaction and transport media for modifying the PBO fibers. This research has two primary motivations; one being to improve the environmental stability of these fibers, and the other being to impart other functionality. The figure to the right illustrates a sol-gel coating method for treating PBO fibers. This reaction can either be dip-coated using an aqueous solution or can be done in $scCO_2$. The resulting coating is known as a UV-visible light stabilizer and further studies are ongoing into developing tougher coatings.

PBO Fibers for NBC Suits (Nuclear/Chemical/Biological): Coating with High Surface Area or Functional Materials



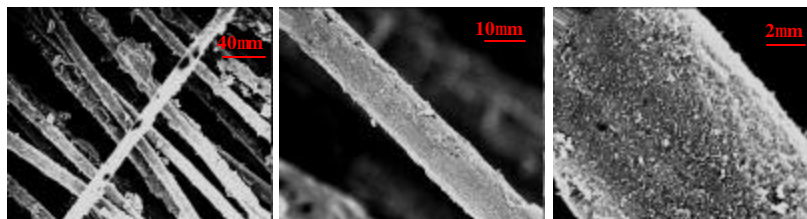
Carbon Black



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SEM Images of PBO Fiber Coated with Carbon Black (without Gold Coating)

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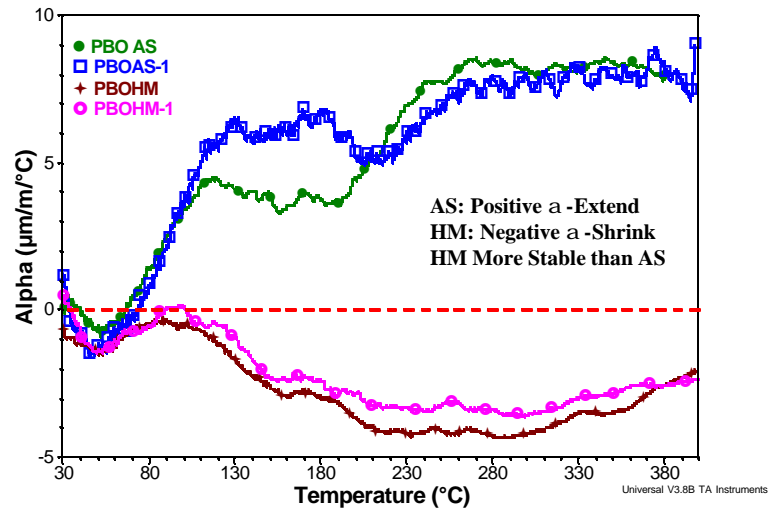
Another method involves coating the fibers with high surface area carbon nanosheets. This can make the fibers electrically conductive as well as enhance their UV-visible light stability (see figure to the right).

Characterization of Thermomechanical Response

The Lesser Group has also started research characterizing unique thermal mechanical interactions with these materials. In these studies, we developed a method to measure the fiber diameter in-situ during tensile testing. The method utilized a laser diffraction technique that has a precision to 0.2 μm . We are currently characterizing the Poisson's ratio for the PBO fibers and comparing them to other rigid-rod fibers. Initial findings suggest that these materials have a negative Poisson's ratio. This implies that they actually dilate (expand) when pulled in tension.

Additional studies are being conducted on the materials to measure their coefficient of thermal expansion. Both the commercial Zylon as spun AS and high modulus HM have been characterized. The results are shown on the right. Note that AS fibers have a positive or near zero coefficient of thermal expansion and the value depends on the actual temperature. In contrast, the HM fibers have a negative coefficient of thermal expansion (shrink during heating).

Coefficient of Thermal Expansion α : 5g Load *Absolutely Different for PBO AS and HM Fibers*



PBO-based nano-fibers

In this effort we investigate the potential to develop a new class of PBO-based high performance nano-fibers. Current methods to fabricate nanofibers (e.g., electrospinning) have shown to have limited properties primarily because of low fiber orientation associated with processing. Herein we propose to utilize the commercially available PBO fibers as a feedstock for the production of nanofibers. And since the commercial fibers are already highly oriented from the dry-jet wet-spinning process, it is expected their nano-fibers will have the same characteristics.

An intrinsic characteristic of the PBO fibers is their highly anisotropic properties that arise from their morphology. Figure 2 (earlier section) shows that the morphological elements of these fibers are nano-fibrils with 8-10nm diameters. As coagulation in the fiber occurs it appears that these interfaces weld to produce a single filament. However, there are also many regions where anisotropic defects remain, both inside the fiber and along the exterior (Figure 4). This morphology, in turn renders the fibers susceptible to damage when transversely loaded excessively.

Recent studies on these fibers suggest that phosphoric acid residuals may reside at the interfaces between nanofibrils. An interesting contrast in damage occurs when PBO fibers are exposed to moisture or an mild acidic aqueous solutions (see figure at right). Note that the fibers tend to splay and delaminate as opposed to the type of degradation when UV light is applied. Thus, the primary effect of hydrolytic degradation appears to be significantly increasing the surface area in addition to weakening the fiber and explains why combining UV and moisture is so detrimental to their mechanical behavior.

However, pre-treating PBO fibers to aqueous solutions of phosphoric acid to weaken the nano-fibril interface followed by mechanical agitation (e.g. sonication) can be used to generate nanofibrils from these fibers. It also should be noted that no effort has yet been made to recover loose fibers that may be suspended in the solution and only those fibers still attached are shown. In this effort we plan to investigate methods like that described herein to produce nano-fibers as well as 'hairy' fibers that might have other potential applications.

It is envisioned that one method to fabricate nano-fibers would be to initially treat PBO fibers to a phosphoric acid aqueous solution and mechanical agitation to achieve the desired delamination followed by a scCO₂ extraction process to halt further degradation.

Nanoscale Carbonized PBO Fibers for NBC Suits: Further increase in Surface Area by Different Methods

