Environmental Effects on Poly-*p*-phenylenebenzobisoxazole Fibers. II. Attempts at Stabilization

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ABSTRACT: Approaches to alleviate the environmental degradation of as-spun poly-*p*-phenylenebenzobisoxazole (PBO AS) fibers by moisture, acidic conditions, and UV–visible radiation were implemented and tested for efficacy. The general approaches tested include: extraction and neutralization of residual phosphoric acid using supercritical carbon dioxide; the use of UV–visible light blocking coatings of exfoliated graphite, carbon black, and glassy titanium dioxide; and improvement of initial fiber properties by the application of forces tending to compact the fiber microstructure. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 3819–3829, 2006

Key words: poly(benzoxazole) fiber; PBO; physical degradation; chemical degradation; supercritical fluid extraction; supercritical carbon dioxide

INTRODUCTION

Poly-*p*-phenylenebenzobisoxazole (PBO) is one of the rigid-rod isotropic liquid crystalline polymers that orient easily into extended chain configurations to produce fibers with excellent strength and modulus. Typically, PBO fibers have exceptionally high tensile strength (5.8 GPa), stiffness (180–270 GPa), and relatively low density (1.54 g/cm^3).[1,2] To date, they are the strongest commercially available organic polymeric fibers. Consequently, they are ideal candidates for many military applications. Research and development of this material is being actively pursued for applications in high-performance fiber composites, protective garments, and personnel ballistic armors.

Recent information released by Toyobo indicates a significant loss of tenacity under relatively mild conditions, including exposure to moisture, sunlight, acidic environments, and basic environments.[1] In Part I of this work, the mechanisms of degradation due to exposure to moisture, acidic environments and UV–visible light (UV–vis) were investigated in detail.[3] The mechanism of degradation for moisture was found to be primarily physical in nature. The loss in properties was accompanied by an increase in the size of voids within the fiber while ATR-FTIR spectroscopy revealed no chemical changes near the fiber surface. Exposure to strong acids in aqueous environments appeared to accelerate the separation of the fibrils within a fiber together with subsequent diminishments in tenacity. This suggests that any residual phosphoric acid present may contribute to degradation by moisture through its affinity with water enhancing moisture adsorption or by a chemical reaction affecting small amounts of material at the surface of individual fibrils. The observation that strength is decreased by swelling of the fibrillar structure of the fiber and the increase in size and/or number of defects actually presents us with an opportunity to increase initial fiber strength through the application of forces that tend to compact the fiber structure and decrease the number and size of defects present.

In contrast to the degradation due to moisture, the effect of UV–vis radiation was found to be chemical in nature. This form of degradation is most likely due to the intrinsic photoreactivity of the PBO polymer due to its highly conjugated chemical structure and π–π stacking within PBO crystals.[4] It should be noted that fibers exposed to concentrated phosphoric acid and subsequently exposed to UV–vis radiation showed an increased loss of strength with higher concentrations indicating that there is a synergistic effect when both a challenging acid species and UV–vis radiation are present.

Having a general concept of the degradation pathways for moisture, acidic environments, and UV–vis radiation, we propose some approaches to alleviate fiber degradation. Given that the presence of acid

accelerates both degradation by moisture and UV–vis radiation, extraction of residual phosphoric acid should improve fiber environmental stability. Super critical carbon dioxide has frequently been employed as an extraction medium due to its unique combination of low viscosity and negligible surface tension.[5] Herein, we investigate the use of super critical carbon dioxide (scCO$_2$) to directly wash the residual phosphoric acid out of the fiber. A related approach involves using scCO$_2$ as a transport medium to introduce a low molecular weight compound that can neutralize the residual acid, and potentially solubilize it in scCO$_2$ for subsequent extraction.

For polymeric materials, a common method for improving weathering resistance or photostability is through the use of additives. During photooxidation, absorption of a photon by the polymer produces an activated species followed by a photophysical and chemical conversion of the activated species. Therefore, various additives such as a UV reflector, a UV absorber, an excited-state quencher, or a free-radical scavenger and/or hydroperoxide decomposer have been long used in industry[6,7] to mediate UV–vis degradation. The approach investigated herein involves coating of PBO fibers with different UV reflectors or absorbers, which are named light blockers here. The materials used are carbon black, exfoliated graphite, and a glassy TiO$_2$ created using sol–gel chemistry.

Carbon black is widely used in the polymer industry due to its thermal and photooxidative stabilization of rubbers and thermoplastics. It is opaque to UV radiation at a thickness of only 0.6 μm. Its activity is claimed to be highly multifunctional. For example, it can act as powerful UV–visible light absorber, chain breaking donor or acceptor, a quencher of excited state species, and a hydroperoxide decomposer. However, good dispersion and coating is necessary for optimum performance.[8]

Exfoliated graphite is also used as a model additive for several reasons. First, graphite has a stacking structure of flat sheets of carbon atoms; adjacent sheets are held together by the weak Van der Waals bonds and separated by a distance 3.35 Å. This stacking structure is very similar to that of π–π stacking with a spacing of 3.5 Å in PBO fibers. Second, graphite and carbon black have similar microstructure. Third, although the typical thickness of exfoliated graphite is very close the primary particle size of commercial graphite, around 10–80 nm the exfoliated structure may assist in a monolayer of nanoparticles depositing on the surface of the fiber.[9] Graphite also has higher aspect ration than carbon black. This may give better shielding of UV–visible light at a fixed concentration.

Titanium dioxide pigments (Titania) are used in many plastics and coatings to increase their durability. Titania exists in two morphological crystalline forms, which exhibit different photoactivities when incorporated into polymers. Anatase pigment is generally more photo-active than the rutile one. In the case of stabilization, the effectiveness increases with increasing coated rutile concentration. Recently, there has been extensive interest in ultrafine or nanoparticle fillers and pigments especially with regard to their properties as UV ''blocker'' in coating applications. The finer the particle the more effective will be the scattering of UV light below 400 nm. Also, for ultrafine titania, physisorption, and chemisorption process are paramount and can significantly effect the performance characteristics of stabilizers in different ways, which can in turn influence the stability of the polymer.[10] In our research, a very thin glassy TiO$_2$ is formed on PBO fiber surface by a sol–gel method [11] and a dip-coating process.

Several approaches to densify the fiber microstructure were undertaken. The first involves applying a twist to single fibers. Twist has long been known to improve the strength of staple fiber materials. It is also used in continuous yarn systems to force the assembly of single fibers to behave as a contiguous unit. It is well-known that PBO fibers have a nanofibrillar structure, which is very similar to that of spun yarns made from staple fiber except that it occurs over a different length scale.[12,13] Generally, for yarns made from staple fibers, the strength shows a maximum while the extension to break continually increases with degree of twist.[14,15]

A second approach is to apply hydrostatic pressure to the fiber in a scCO$_2$ environment with the intent to compact the fiber microstructure and allow the plasticizing ability of scCO$_2$ to aid in the reduction of defects. Finally fibers were exposed to high temperature, tension, and hydrostatic pressure in a scCO$_2$ environment simultaneously. The idea was to use the tension to orient the fiber elements more perfectly and allow the heat and scCO$_2$ to reduce the number and size of defects present.

EXPERIMENTAL

Materials

The as-spun PBO fiber used in our experiment was Zylon AS, which was supplied by US Army Soldier Systems Center at Natick, MA. The related properties of the fiber can be found in Ref.[1]. Morpholine, pyridine, trimethylphosphate, absolute ethanol, and titanium isopropoxide were purchased from Aldrich and used as received. Expanded graphite was supplied by Prof. Lawrence T. Drzal of Michigan State University. Carbon black is Black Pearl 800 provided by Cabot Corp.

Procedures

Elemental 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 was performed by a standard inductively coupled plasma emission spectroscopy (ICP) technique, after 20–30 mg of sample was precisely weighed and digested with a combination of sulfuric and nitric acids. A Leeman Labs, Direct Reading Echelle (DRE) ICP was utilized.

UV–visible light exposure

Controlled exposure to UV–visible light was accomplished using a Suntest CPS + weatherometer. The radiation source is a xenon lamp with a broad spectrum filter that closely simulates the distribution of wavelengths and intensity found in natural sunlight. The fibers were exposed at an irradiance of 750 W/m^2 and held at a constant temperature of 50°C. Fibers used for tensile testing were single fibers fastened to cardboard backing with an epoxy adhesive and placed in the CPS + Suntester sample tray, fibers used for SEM, and ATR-FTIR were tows each comprised of approximately 160 single fibers and placed in the sample tray in parallel arrays.

Tensile testing

Mechanical properties were measured using an Instron 5800 series tensile tester with a 50 N load cell. Tests were conducted on single fiber specimens using a crosshead velocity of 10 mm/min and a gauge length of 20 mm. The single fiber samples were glued at each end to a cardboard backing using Huntsman Araldite 2012 five-minute epoxy. Two holes in the cardboard backing were used to ensure a consistent gauge length. The center section of the backing was removed after the sample was fixed in the Instron grips. The grips were arranged with pin ends between the Instron foundation and the gripping surface so the direction of applied force and fiber axis were coincident. Each reported value of breaking strength is the mean from a population of at least 15 single fiber tests.

Scanning electron microscopy

SEM images were collected using a JEOL 6320FXV high resolution field emission cold cathode scanning electron microscope with semi-in-lens detector configuration, achieving resolution down to 2 nm. Mounted fiber samples were sputter coated with gold in a nitrogen atmosphere.

ATR-FTIR

ATR-FTIR spectra were collected using a Horiba HR800 Lab-Ram microscope with resolution of 4 cm^{-1}.

Fiber samples were prepared by laying a tow of fibers over a clean glass microscope slide. Three spectra were collected at different locations on the sample for each type of fiber to assure that the spectra are truly representative of the fiber surface condition.

UV–vis spectroscopy

UV–vis spectra were collected using an Hitachi U-3010 spectrophotometer in transmission mode

Supercritical carbon dioxide fiber washing procedure

Fiber washing was carried out in a custom-made high-pressure vessel designed to allow the circulation of CO_2. The details of this experimental apparatus are shown in Figure 1. To not damage or disturb the alignment of the fiber tows during washing, bundles of fiber approximately 12 in. in length were supported to an aluminum frame first, followed by insertion into the high-pressure vessel. A regulator was used to control the CO_2 flow rate. Samples were washed in the vessel at fixed temperatures and pressures with different times. After washing, the temperature was allowed to drop and the vessel was depressurized slowly. Washed PBO fibers were used for mechanical testing and weathering experiments.
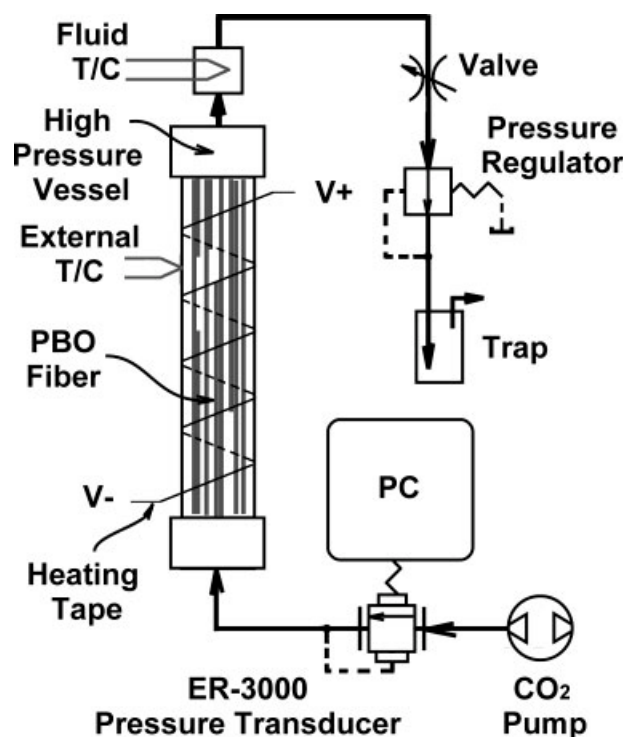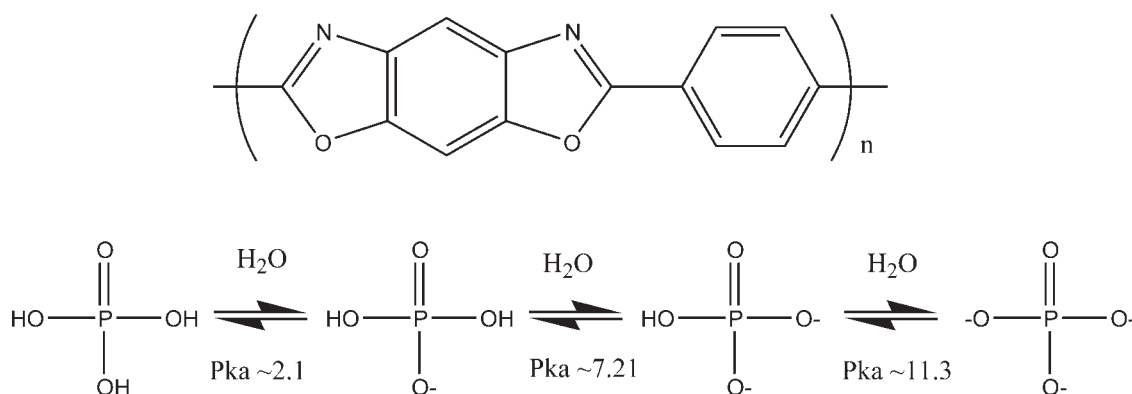

Figure 1 Schematic of supercritical CO_2 washing apparatus.

Scheme 1 pK_a values for phosphoric acid and PBO polymer.

RESULTS AND DISCUSSION

Extraction of residual phosphoric acid in supercritical carbon dioxide

In Part I of this work, elemental analysis determined that an amount of residual phosphorus ranging between 0.3 and 0.4 wt % resides in the PBO AS fiber indicating the presence of residual phosphoric acid (PA). This residual acid may play a role in the fiber degradation with exposure to an aqueous environment. The basic premise is that in aqueous conditions the residual polyphosphoric acid dissociates to form PA. The resulting environment is one in which hydrolytic reactions with the weakly basic oxazole ring may cause disruption of the ring structure or chain scission. The pK_a values for each phosphoric acid proton loss and the backbone structure of PBO are shown in Scheme 1.

In an effort to extract residual PA, PBO AS fiber was washed in supercritical carbon dioxide ($scCO_2$) at various conditions of temperature, pressure, and $scCO_2$ flow rate using the device illustrated in Figure 1. Elemental analysis was subsequently used to measure changes in residual phosphorus. The results presented in Table I show that as flow rate and temperature are increased, $scCO_2$ can remove part of the residual phosphoric acid in the fiber but cannot remove it completely. The concentration of residual phosphorus cannot be decreased below approximately 0.25–0.3 wt %.

TABLE I
Weight Percentage of Residual Phosphorus Remaining in PBO AS Fiber Washed in $scCO_2$ Under Varying Conditions of Temperature and Pressure

T (°C)	P (psi)	Q (LPM)	Residual P (wt %)
Control	Control	Control	0.4
50	2500	5	0.4
100	2500	5	0.3
100	2500	10	0.25
100	5000	10	0.25

This suggests that PBO AS fiber may be only partially permeable to CO_2.

Single fiber tensile testing was used to assess the effect of washing in $scCO_2$ on mechanical properties. Figure 2 compares the tenacity of neat PBO AS fiber to fibers washed at a flow rate of 5 LPM, temperature of ~100°C and pressure ranging from 2500 to 5000 psi. Exposure to $scCO_2$ does not appear to have a detrimental effect on the strength of the fibers. In fact, at pressures of 2500 and 3250 psi, there appears to be a trend toward increase in fiber properties. This will be discussed further in the section on improving fiber mechanical properties via compaction of the fiber morphology. In addition, the SEM images of Figure 3 show that the surfaces of $scCO_2$ washed fibers are relatively unchanged as compared to pristine control fiber. The UV–vis light stability of $scCO_2$ washed fibers was also evaluated. Figure 4 shows the single fiber tensile test-
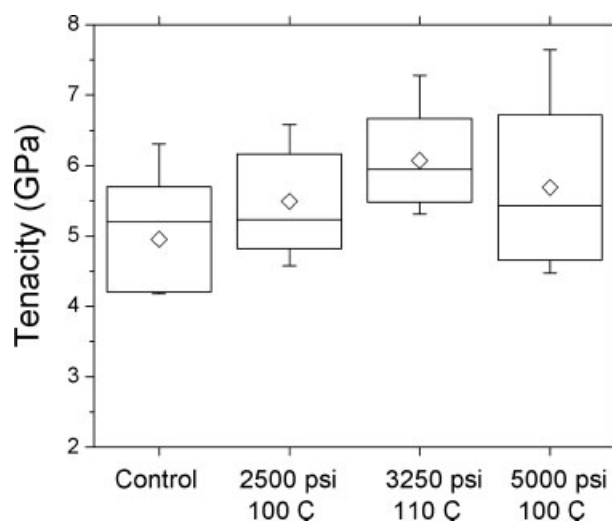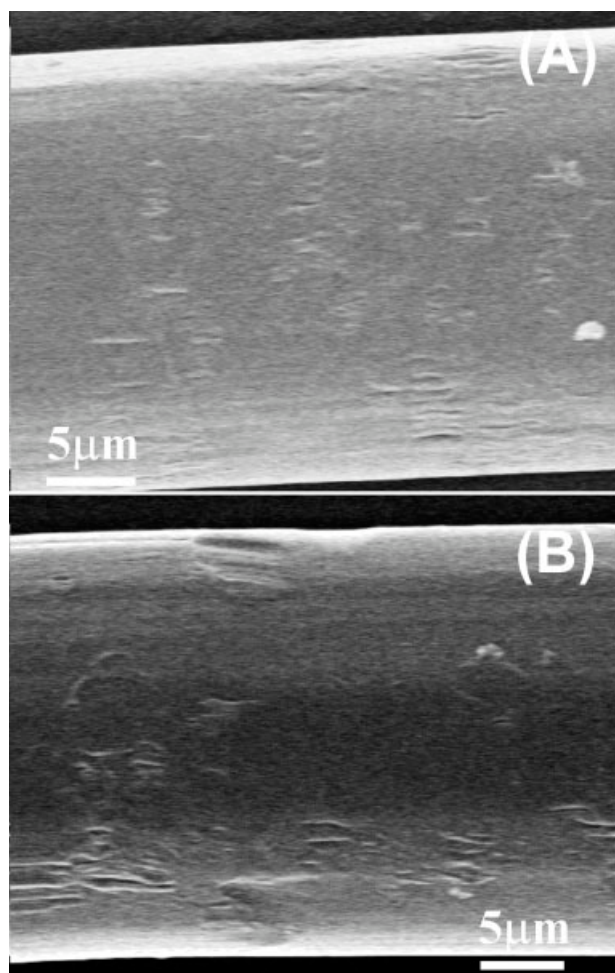

Figure 2 Tenacity of PBO AS fibers washed with $scCO_2$ at 5 LPM flow rate and varying conditions of temperature and pressure compared to pristine control fiber. Whiskers denote minimum and maximum, box denotes median and standard deviation and the open diamond denotes the mean.
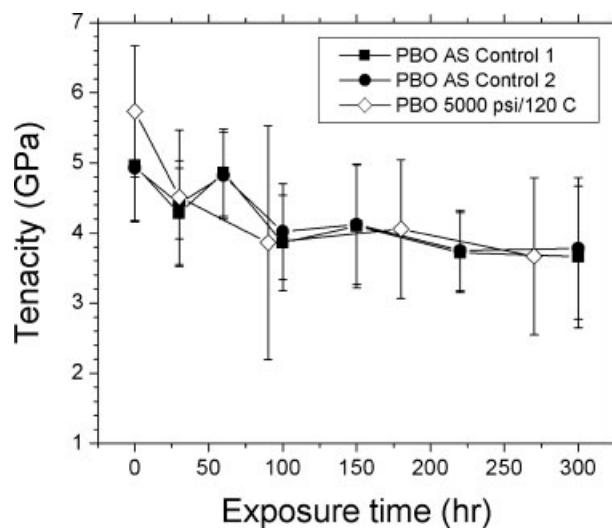
Figure 3 SEM of scCO$_2$ washed PBO AS fiber (A) compared to control fiber (B).

ing results for fibers exposed at 750 W/m^2 over a 300-h duration. The response of the neat fiber and the washed fiber is identical. This result supports the idea presented in Part I in which it is supposed that UV–vis degradation is not related directly to the presence of residual phosphoric acid but is instead due to the intrinsic photoreactivity of the highly conjugated structure of PBO.[4]

## Neutralization and extraction of residual phosphoric acid

A second approach to improving the stability of PBO in aqueous conditions is to consider the possibility of neutralizing any residual phosphoric acid with a small molecule having a more favorable reaction with phosphoric acid than the polymer backbone. An scCO$_2$ environment could be used to both enhance introduction of the small molecule and extract the neutralized phosphoric acid.

Three low molecular weight compounds shown in Scheme 2 were selected to explore this hypothesis. Morpholine (MOR) and pyridine (PYR) were chosen


Figure 4 Tenacity of scCO$_2$ washed PBO AS fibers exposed to UV–vis light at 750 W/m^2 compared to pristine control fiber.

based on their pK_a values relative to the pK_a values for loss of phosphoric acid hydrogens (Scheme 1). Trimethylphosphate (TMP) was selected because it has a chemical structure very close to phosphoric acid and has been shown in other polymers to actually work as a molecular fortifier.[16] For these experiments PBO fiber was soaked in scCO$_2$ at 100°C/5000 psi for 30 h then immersed in 100% concentrations of each compound at room temperature for approximately 160 h. The mechanical properties were initially tested and additional samples were exposed to UV–visible light and subsequently tested.
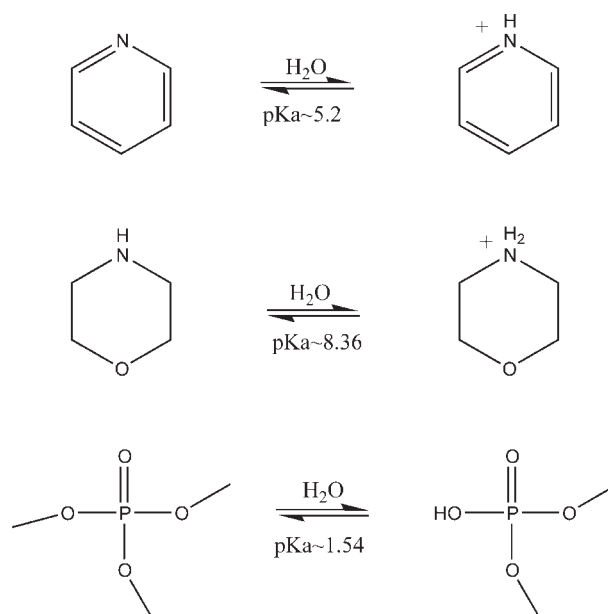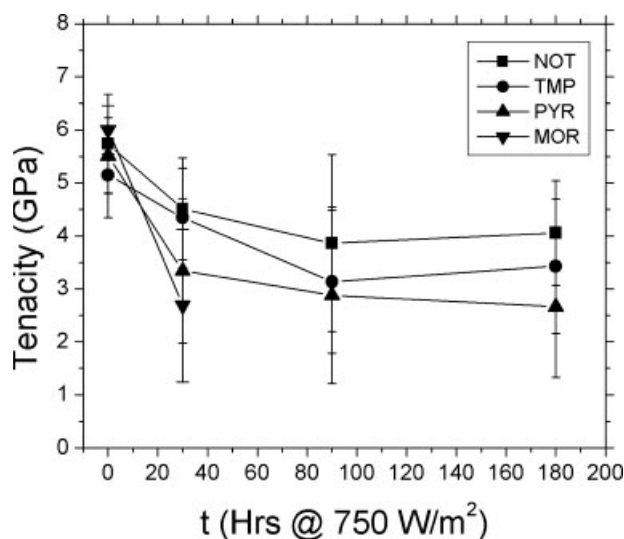

Scheme 2 Small molecules used to treat PBO AS fibers: pyridine, morpholine and trimethyl phosphate.
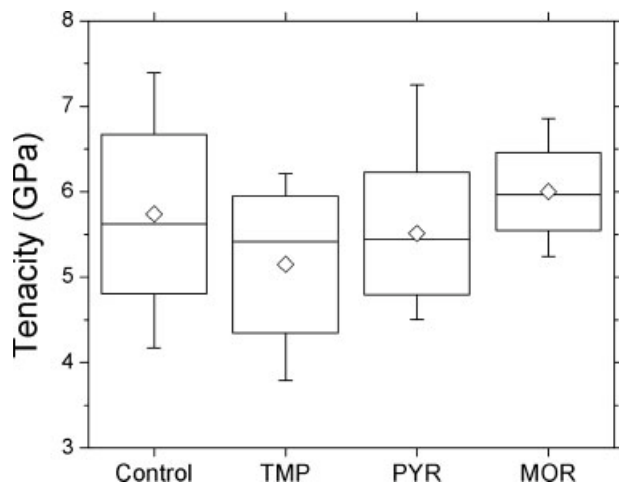
Figure 5 Comparison of initial tenacity for control PBO AS fiber and fiber treated with trimethyl phosphate (TMP), pyridine (PYR) and morpholine (MOR). Whiskers denote minimum and maximum, box denotes median and standard deviation, and the open diamond denotes the mean.

Figure 5 compares the effect these compounds have on the initial fiber tenacity and the indication is that there are no changes in tenacity relative to the control fiber. However, as shown in Figure 6, all three of these compounds negatively affect the UV–vis stability. Both trimethylphosphate and pyridine exposed fiber showed slightly less stability than the control fiber—in fact the response of these two compounds is similar in magnitude to that for fiber exposed to concentrated phosphoric acid (Part I, Fig. 9).[3] After only 30 h, the morpholine treated samples had degraded to the extent that it was not possible to test single fibers.

Information published by Toyobo has already indicated drops in the tenacity of PBO with exposure to strong acids and bases; however, these results are somewhat alarming in that here we have observed that comparatively weak acids and bases in combination with exposure to UV–vis light will also significantly degrade fiber strength.

In further work, PBO AS fibers were exposed to pyridine in an $scCO_2$ environment. The idea here was to more effectively introduce pyridine into the fibrillar bundle and where it could neutralize the residual acid and subsequently be extracted along with the $scCO_2$ upon depressurization. Figure 7 shows the UV–vis stability of these fibers plotted along with that of two control samples and the pyridine exposed sample of Figure 6. The primary point of interest is that the $scCO_2$/pyridine sample shows approximately similar response to UV–vis light as the control groups. This is in contrast to the $nonscCO_2$ data of Figure 6 in which 100% pyridine detrimentally affected the UV–vis response relative to the control. One explanation for this is that it is possible that the $scCO_2$ environment is effective in removing the pyridine without damaging the fiber.

Figure 8 shows the ATR-FTIR spectra for fibers exposed to liquid water, and treated with $1M$ phosphoric acid, 100% trimethyl phosphate, 100% pyridine, and 100% morpholine. While the spectra for the pristine fiber and water-exposed fiber are similar and indicate little or no chemical change near the fiber surface, changes are observed for fibers exposed to the phosphoric acid, trimethyl phosphate, pyridine, and morpholine. In the case of phosphoric acid exposed fiber, a broad peak develops between ~ 3200 and $3300 \ cm^{-1}$. This peak is assigned to a secondary amine on the oxazole ring nitrogen implying some hydrolytic reaction, but because there is no accompanying carbonyl peak, the oxazole ring is probably not disrupted. Exposure to trimethyl phosphate shows evolution of a narrow peak

Figure 6 Tensile testing results for PBO AS fibers treated with pyridine, morpholine, and trimethyl phosphate.
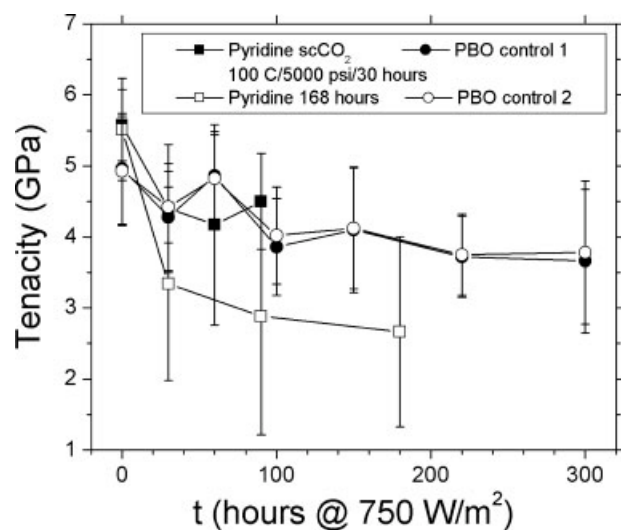
Figure 7 Tensile testing results for PBO AS fibers treated with pyridine in a $scCO_2$ environment.
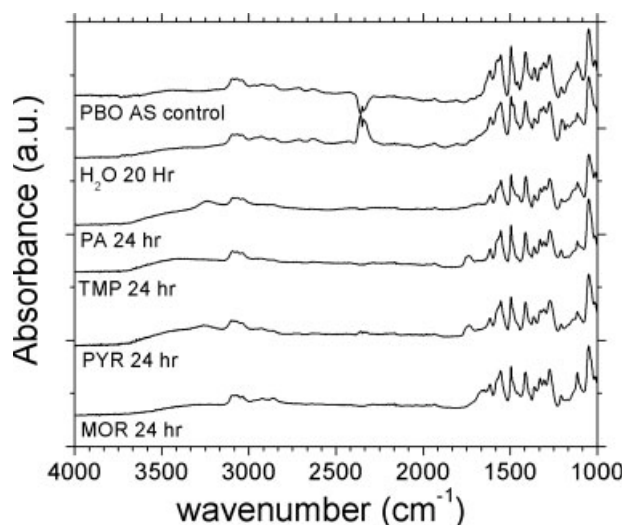
Figure 8 ATR-FTIR spectra of PBO AS fibers treated with phosphoric acid, pyridine, morpholine, and trimethyl phosphate compared to spectra of pristine fibers and water exposed fibers.

at ~ 1700–1800 cm^{-1} that is ascribed to a carbonyl. The pyridine exposed fiber shows development of both an oxazole ring secondary amine peak between ~ 3200–3300 cm^{-1} and a narrow carbonyl peak at ~ 1700–1800 cm^{-1}. The morpholine exposed fiber shows the appearance of a narrow peak at ~ 1690 cm^{-1} that is thought to be due the formation of an amide carbonyl; however, there is no accompanying secondary amine peak. It is not possible to deduce the exact chemical pathway of these degradation reactions from these spectra. Taken together they suggest that hydrolytic reactions originating at the oxazole nitrogen and subsequent alteration or disruption of the oxazole ring around its quaternary carbon center are the most likely route.

All the abovementioned results were somewhat surprising. Since it was initially anticipated that the resid-

ual phosphoric acid played a key role in at least accelerating the degradation of the PBO, and the introduction of a base should neutralize the acid. Nonetheless, the results in Figures 6 and 7 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 seems to support the hypothesis proposed in Part I that the PBO fiber may be intrinsically susceptible to photodegradation. Recent studies show that these polymers do absorb significant amount of energy in the UV–visible spectrum.[4] It should be emphasized that absorption of energy doesn't necessarily indicate instability. However, energy is absorbed nonetheless and, if these fibers are intrinsically unstable in this spectral range, the presence of either an acid or base may catalyze the degradation.

UV–vis Blockers

Both the conjugated structures in PBO chains and the π–π stacking in crystals may make PBO fibers intrinsically photosensitive. For polymeric products, the normal method of improving weathering resistance or photostability is through the use of additives. Light blockers used were carbon black, exfoliated graphite (EG) and glassy titanium dioxide prepared via a sol–gel method.

Both carbon black and the exfoliated graphite flakes were pulverized using an ultrasonic processor in ethanol for 24 h. PBO fiber bundles were immersed in the sonicated solution, taken out and dried for UV–visible light exposure, and subjected to tensile testing. SEM images of PBO fibers coated with carbon black and graphite are shown in Figure 9.

Note that exfoliated graphite does not cover the fiber surface in a consistent manner. Although the thickness of exfoliated graphite is in the range of nanoscale, the
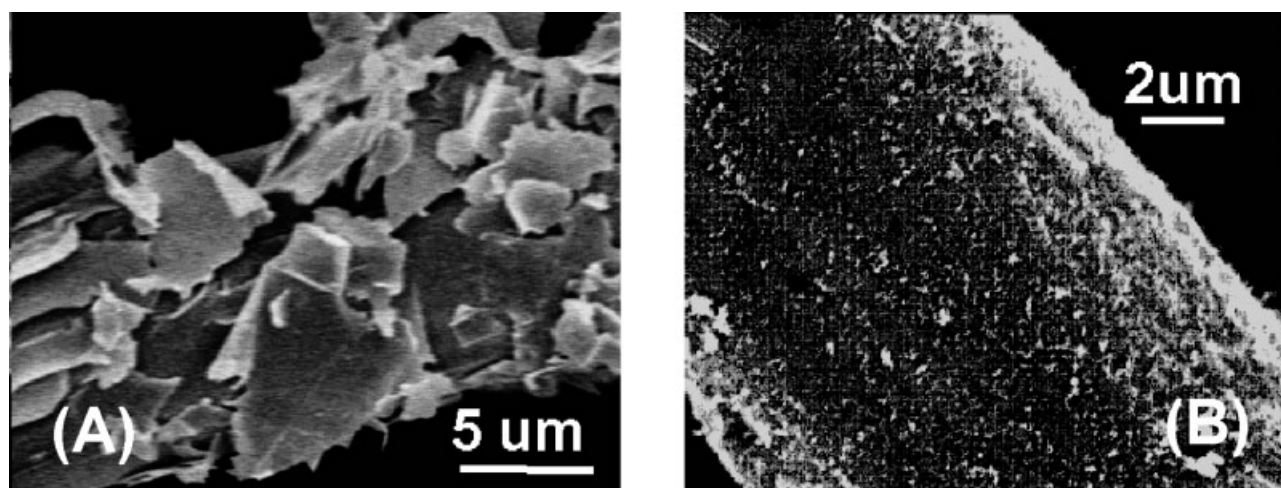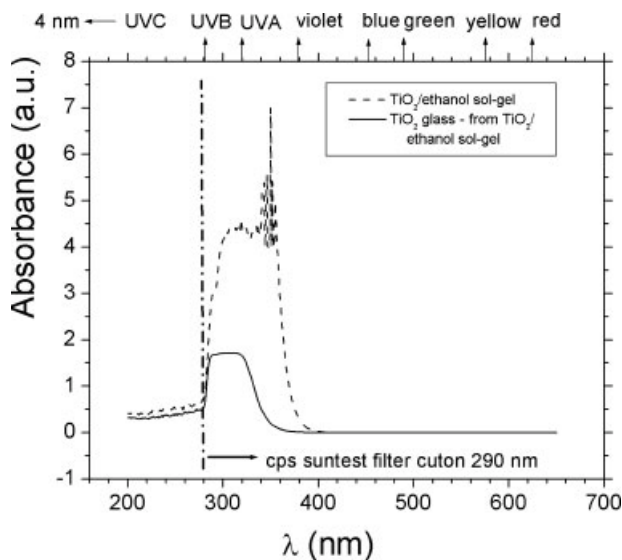

Figure 9 SEM of (A) graphite and (B) carbon black coated PBO AS fibers.
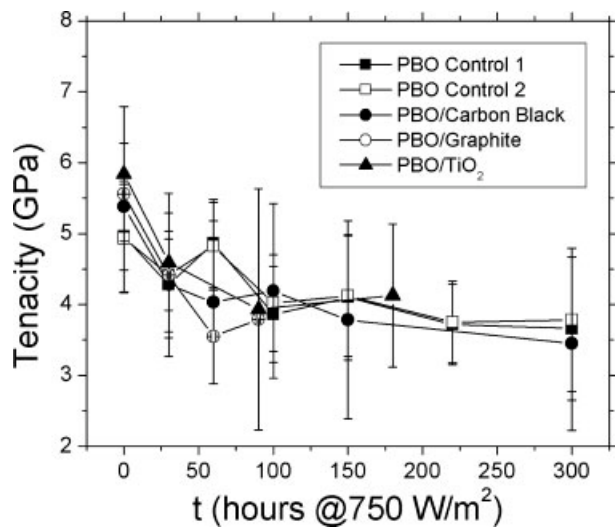
Figure 10 Tensile testing results for carbon black, graphite and TiO$_2$ coated fibers exposed to UV–vis light.

aspect ratio of graphite is much larger and this prevents defect free coating of the fiber. In contrast, carbon black powder does cover the surface of the fiber fairly well. There are at least two reasons for better coating of carbon black. One is that the size of a carbon black particle is about 20–50 nm and their agglomeration is still in the range of a few hundreds of nanometers. The other reason is that carbon black has polar groups such as —C=O, —COOH and —OH. Compared to exfoliated graphite, these polar groups have stronger interactions with PBO fiber, which will result in better coating and coating strength.

As shown in Figure 10, the load-at-break of carbon black coated fibers is very close to those of control samples at the same UV–vis exposure time. Coating PBO

fiber with carbon black does not appear to increase the light stability of PBO fibers. In contrast to carbon black, it seems that exfoliated graphite enhances the light degradation of PBO fibers. In Figure 10, the load-at-break of EG coated fibers decreases more quickly compared to uncoated ones. It is a surprise that carbon black coating does not increase the light stability of PBO fibers. One possible reason is that the coating may be too thin to block the UV–visible light. The exact thickness of coating is not clear from SEM images.

A third blocking material is a glassy coating of TiO$_2$ created using sol–gel chemistry. A sol–gel was made by adding titanium isopropoxide to ethanol with pH brought to ~ 2 using hydrochloric acid. Previously prepared PBO AS single fiber tensile specimens were dipped in the sol–gel and allowed to dry in vacuum at 50°C for 1 h. Figure 11 shows the UV–vis absorbance of the sol–gel and the dry TiO$_2$ film. While the wet sol–gel blocks most of both the UVB and UVA spectrum, the glassy TiO$_2$ film is only effective in blocking the UVB wavelengths. Figure 12 shows an SEM image of the resulting glassy TiO$_2$ coating. The coverage appears

Figure 11 UV-Vis absorption of TiO$_2$ sol–gel and dried glassy TiO$_2$ film.
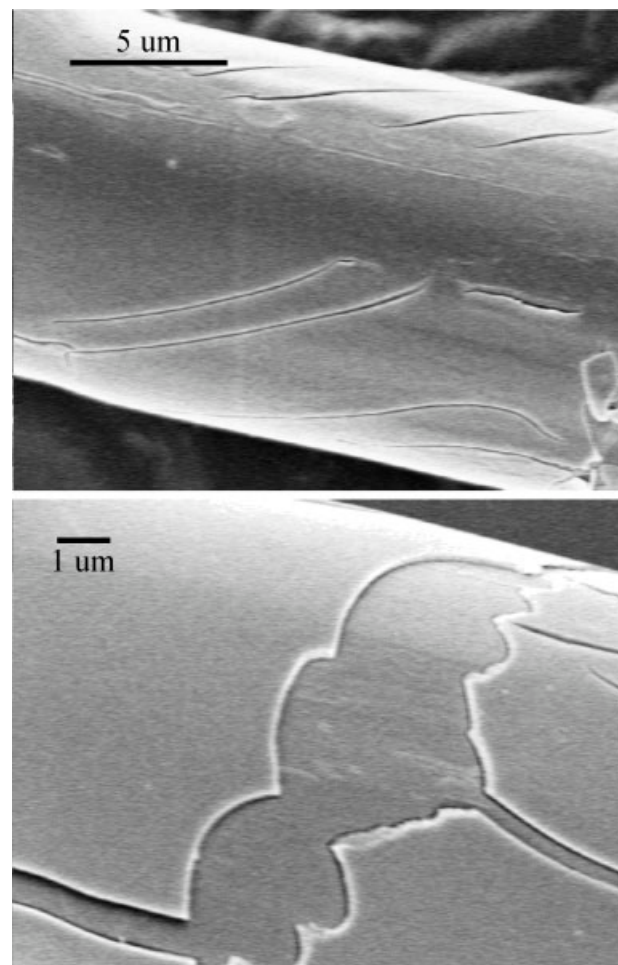
Figure 12 SEM of TiO$_2$ coating showing a thin film with thickness on the order of $\sim$ 100's of nanometers.

very consistent with thickness on the order of 100's of nanometers. However, there are some cracks and defects evident. The cracks aligned with the fiber axis seem to be due to contraction of the glassy TiO_2 as the ethanol solvent evaporates away, while those perpendicular to the fiber axis result from the fracture of the glassy and brittle coating due to handling the fibers after evaporation. The Figure 10 tensile testing results for samples exposed to UV–vis show that the tenacity of the TiO_2 coated fibers is nearly identical to that of two uncoated control groups. Again, it is a surprise that this coating does not enhance the UV–vis stability. This could be due to either inadequate film thickness or defects in coverage due to cracking during drying and handling. Also, given that the TiO_2 film only absorbs strongly in the UVB spectrum, UVA spectrum radiation may still be reaching the fiber surface.

These results clarify some of the attributes needed for successful application of a UV-vis blocking material. The blocker must efficiently either absorb or reflect incident UV–vis radiation over the full UV spectrum. The coating must completely cover the fiber surface and be flexible enough that bending of the fibers does not result in fracture or other defect. Given the results for degradation due to physical expansion of the fibrillar bundle with exposure to water presented in Part I it would be advantageous if the coating also excluded water from the fiber interior.

Improvements in strength via compaction of fiber microstructure

In Part I of this work, exposure to water was shown to result in physical separation of the fibrillar elements within the PBO fiber. In particular, the size of voids between the fibrils was found to increase. SEM evidence indicated that the presence of concentrated phosphoric acid accelerates this swelling and separation perhaps due to the effects of a synergistic chemical reaction. It is useful to also consider that because the loss of strength is primarily due to loosening of the fiber morphology there may be an opportunity to improve the properties of PBO. Any post spinning process we can introduce that compacts the structure of the fiber, increases the size of the fibrillar elements and reduces the volume fraction of voids should be a route to improving the mechanical properties. Three possible approaches are: using twist to compact the fibrillar morphology of the fiber and enhance load transfer between fibrils, using hydrostatic pressure to compact the fibrillar morphology, and using tension and the plasticizing influence of CO_2 to align crystalline domains and decrease the number of defects in the crystalline material.

The initial idea here is to increase the strength of single filament by an interlocking mechanism where the fibrils are held together by radial force and friction due to twist. Fibrils in the twisted fiber can break more than once and still support load via load transfer from fibril to adjacent fibril. There should be an optimum twist since very high degree of twist will result in a transverse compression stress on fibrils and a decrease in strength.

In the tensile results for twisted single fibers presented in Figure 13, the load-at-break of PBO fibers increases very slightly for degree of twist of less than ~ 5 turns. After five turns, the tenacity no longer increases and begins to show significantly increased variability.

In the experiments using scCO$_2$ to extract residual phosphoric acid, fibers were placed under hydrostatic pressure using scCO$_2$ fluid. Figure 2 shows a weak trend of an increase in fiber strength for pressures of 2500 and 3250 psi at a temperature of 100°C. This result encouraged a further look at using scCO$_2$ in combination with hydrostatic stress to compact and increase the perfection of the fiber morphology. Experiments were conducted in which scCO$_2$ and nitrogen was used to apply hydrostatic pressure to the fiber with silicon oil as an intermediate fluid. Subsequently, the influence of hydrostatic stress on the reorientation or the rearrangement of crystals and fibrils should be greater than with the gas phase.

Fibers were placed in a pressure vessel filled with silicon oil and hydrostatic pressure was applied using both nitrogen gas and scCO$_2$. Conditions of temperature and pressure were in both cases 5000 psi and 100°C. Figure 14 shows the results of tensile testing for these fibers. The indication is that there is no increase in fiber tenacity with such treatment, and in fact there is a drop for the fibers with scCO$_2$.

Tension, usually combined with heat, is widely used in the fiber industry to increase the orientation of both
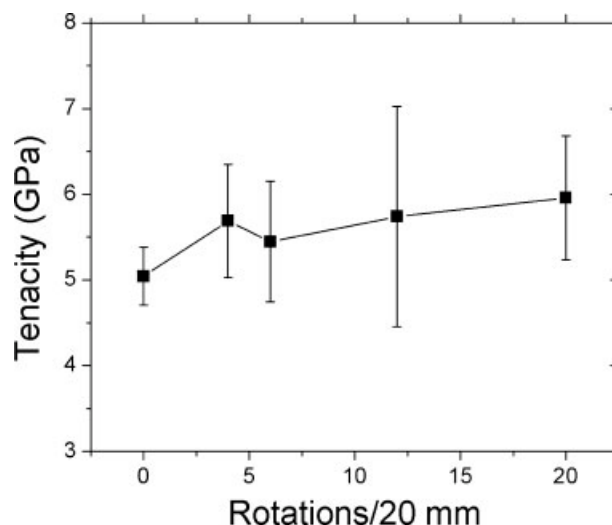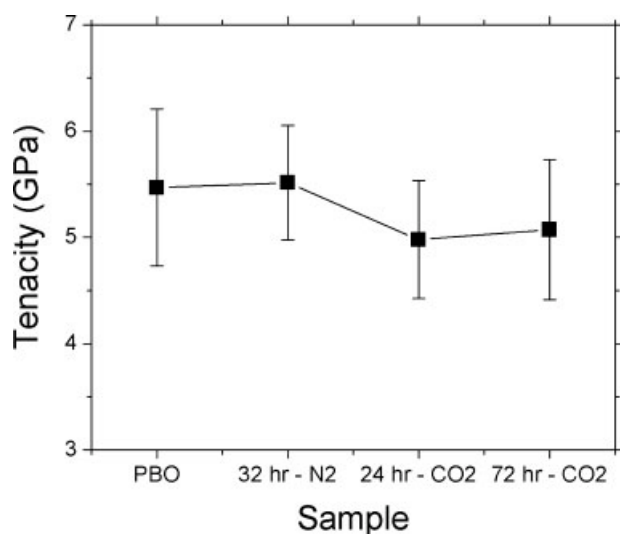

Figure 13 Tensile testing results showing effect of twist on fiber tenacity. Error bars indicate 1 standard deviation on the mean.

amorphous and crystalline regions of fibers. There are two competitive processes during this: fibers tend to become oriented upon tension and lose orientation on heating. If the magnitude of tension is adequate to overcome the influence toward disorder then the crystalline material is forced to align and the heat can have the effect of increasing the perfection of the crystalline material. This is precisely the approach used to manufacture high modulus PBO (PBO HM) fibers from PBO AS fiber. In this work $scCO_2$ is used with the idea that it may partially plasticize the fiber material and enable a decrease in the defects present.

The effect of tension on fiber properties was explored by placing fibers under tension of ~ 40 cN or approximately 80% of the fiber breaking strength. Experiments were conducted in both air at standard pressure and temperature and in sub critical CO_2 at $20°C$ and 5000 psi for a 24-h duration. The results of tensile testing on fibers treated in this way are shown in Figure 15. The fiber placed under tension in air shows the same tenacity as control fibers not held under tension. The fiber held under tension in the $scCO_2$ environment shows a slight increase in tenacity, but given the large degree of variability, this is not a significant effect.

All three of these approaches to compact the fiber morphology and decrease defects using mechanical means of twist, hydrostatic pressure and tension combined with $scCO_2$ conditions resulted in no significant increase in fiber tenacity. One possible explanation for this may be that even if a compacting force is applied to the fiber, once that force is removed the comparatively weak van der Waals and dipole interchain forces are insufficient to maintain the compacted morphology. The observation of little or no increase in properties with application of a compacting force in the pres-
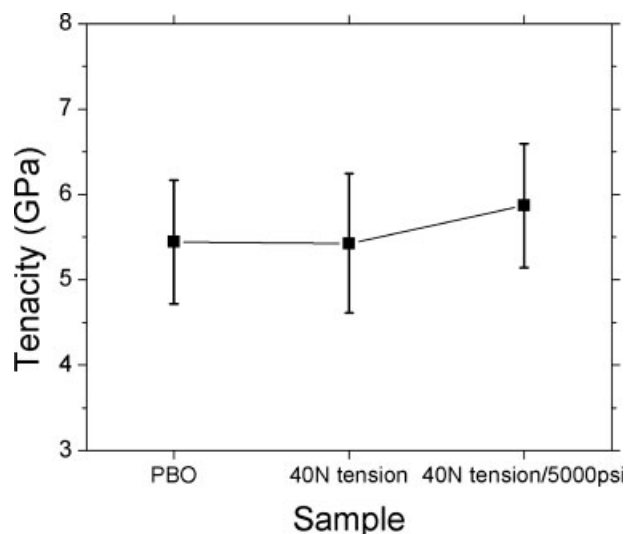
Figure 15 Tensile testing results showing effect tension with and without a room temperature high pressure CO_2 soak on fiber tenacity. Error bars indicate 1 standard deviation on the mean.

ence of $scCO_2$ suggests that $scCO_2$ has little effect on the number of defects present in PBO fibers. This reinforces the previous observations during attempts to extract residual phosphoric acid that the PBO fibers may be only partially permeable to $scCO_2$.

CONCLUSIONS

The use of $scCO_2$ to wash residual phosphoric acid results in a decrease in residual phosphorus from 0.4 to 0.25 wt %. Complete removal of residual phosphorus was not achieved. This is possibly because the highly crystalline PBO microstructure may not be very permeable to $scCO_2$, allowing entry of the fluid only to the larger interconnected voids and not smaller isolated voids. Washing in $scCO_2$ shows no detrimental effect on the fiber strength, in fact, fibers washed in $scCO_2$ show a weak trend to increase the fiber tenacity. This is possibly due to the effect of hydrostatic pressure compacting the fibrillar structure of the fiber and the influence of $scCO_2$ in reducing defects in the fiber microstructure. However, the trend is weak, and the subsequent experiments using hydrostatic pressure in $scCO_2$ and hydrostatic pressure combined with tension in $scCO_2$ show no significant improvement in tenacity. The UV–vis stability of fibers washed in $scCO_2$ is nearly identical to that of the pristine fiber.

Attempts to neutralize and extract residual phosphoric acid using low molecular weight compounds morpholine, pyridine, and trimethylphosphate showed no benefit. ATR-FTIR spectroscopy after exposure to these weak bases and acid showed evidence of hydrolytic reactions involving the oxazole nitrogen and leading to disruption of the oxazole ring structure. While

Figure 14 Tensile testing results showing effect of hydrostatic pressure on fiber tenacity.

the initial mechanical properties of the fiber were not significantly degraded by exposure to these low molecular weight compounds, the degradation by subsequent UV–vis radiation was accelerated by their presence. Pyridine applied in an scCO$_2$ environment was found to not degrade fiber strength suggesting that perhaps scCO$_2$ is effective in extracting the pyridine.

The use of exfoliated graphite, carbon black, and glassy titanium dioxide as UV–vis blockers was not successful. This is most likely due to incomplete coverage by the blocking agents. Desirable attributes in a blocking agent are efficient reflection or absorption of the full UVA and UVB spectrum, the ability to apply a consistent coating with few defects, high compliance and to accommodate bending of the fibers after coating without damage, and the ability to exclude water from the fiber interior.

Efforts to increase the tenacity of PBO AS fiber using applications of external force such as tension, hydrostatic pressure and twist to compact and increase the perfection of the fiber microstructure did show a general tendency to increase strength but not to a very large degree. One possible explanation for this is that once the compacting force is removed the comparatively weak van der Waals and dipole interchain forces are insufficient to maintain the compacted morphology.

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