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14. ABSTRACT

Poly(p-phenylene-2,6-benzobisoxazole) (PBO) is an engineering fiber of extraordinary properties, but has been found to degrade quickly under moisture and ultraviolet light, which is a fatal flaw for soft body armor applications. The present report uses 31P solid-state nuclear magnetic resonance (ssNMR) spectroscopy to investigate the chemical structure and physical state of the residual phosphorous in PBO fiber, which has been long suspected to hydrolyze the benzoxazole bonds of PBO chains and cause the degradation. The residual phosphorous is found to be in the form of phosphoric acid (PA) and its various forms of hydrated or dehydrated derivatives. Moisture would

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Poly(p-phenylene-2,6-benzobisoxazole) (PBO) is an engineering fiber of extraordinary properties, but has been found to degrade quickly under moisture and ultraviolet light, which is a fatal flaw for soft body armor applications. The present report uses 31P solid-state nuclear magnetic resonance (ssNMR) spectroscopy to investigate the chemical structure and physical state of the residual phosphorous in PBO fiber, which has been long suspected to hydrolyze the benzoxazole bonds of PBO chains and cause the degradation. The residual phosphorous is found to be in the form of phosphoric acid (PA) and its various forms of hydrated or dehydrated derivatives. Moisture would drive the reaction along the direction of P2O5 -> polyphosphoric acid -> PA -> water-bound PA, while increasing temperature would reverse the direction. Hydration increases the mobility of PA molecules and increases its damaging power, while higher temperature removes water and immobilizes PA. The residual P species are easily accessible by gas molecules but inaccessible by aqueous media. These studies provide direct evidence to confirm the proposed environmental degradation mechanisms in the literature, and point out future directions for mitigation of this crippling problem for PBO fiber, the otherwise superior fiber of choice for soft body armor applications.

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Nihal Kanbargi	0.50	
FTE Equivalent:	**0.50**	
Total Number:	**1**	

Names of Post Doctorates

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FTE Equivalent:	
Total Number:	

Names of Faculty Supported

NAME	PERCENT_SUPPORTED	National Academy Member
Weiguo Hu	0.09	
Alan J. Lesser	0.03	
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The number of undergraduates funded by this agreement who graduated during this period with a degree in science, mathematics, engineering, or technology fields:...... 0.00

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Names of personnel receiving PHDs

NAME

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Enclosure 1

Abstract

Poly(*p*-phenylene-2,6-benzobisoxazole) (PBO) is an engineering fiber of extraordinary properties, with tensile modulus and strength that nearly double that of poly(*p*-phenylene terephthalamide (PPTA, commercially known as Kevlar® and Twaron®) and ultra-high molecular weight polyethylene (UHMWPE, commercially known as Spectra® and Dyneema®) fibers. However, PBO fiber has been found to degrade quickly under moisture and ultraviolet light, which is a fatal flaw for soft body armor applications. Many studies have suggested that the likely mechanism of the degradation is that the residual phosphorous that was trapped inside the fiber during fiber production reacts with the oxazole bonds and breaks the chains. However, there has been no direct study of the structure and behaviors of the residual phosphorous. The present report investigates the chemical structure and physical state of the residual phosphorous in PBO fiber using ^{31}P solid-state nuclear magnetic resonance (ssNMR) spectroscopy. The residual phosphorous is found to be in the form of phosphoric acid (PA) and its various forms of hydrated or dehydrated derivatives. Moisture would drive the reaction along the direction of P_2O_5 → polyphosphoric acid → PA → water-bound PA, while increasing temperature would reverse the direction. Hydration increases the mobility of PA molecules and increases its damaging power, while higher temperature removes water and immobilizes PA. The residual P species reside on the surface of the nanovoids in the PBO fiber, easily accessible by gas molecules but inaccessible by aqueous media. These studies provide direct evidence to confirm the proposed environmental degradation mechanisms in the literature, and point out future directions for mitigation of this crippling problem for PBO fiber, the otherwise superior fiber of choice for soft body armor applications.

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(2) Statement of the problem studied

Poly(p-phenylene-2,6-benzobisoxazole) (PBO) is an engineering fiber of extraordinary properties, with tensile modulus and strength that nearly double that of poly(p-phenylene terephthalamide (PPTA, commercially known as Kevlar® and Twaron®) and ultra-high molecular weight polyethylene (UHMWPE, commercially known as Spectra® and Dyneema®) fibers. However, PBO fiber has been found to degrade quickly under moisture and ultraviolet light, which is a fatal flaw for soft body armor applications. Many studies have suggested that the likely mechanism of the degradation is that the residual phosphorous that was trapped inside the fiber during production reacts with the oxazole bonds and breaks the chains. However, there has been no direct investigation of the structure and behaviors of the leading role of the play: the residual phosphorous. The present work addresses this unanswered challenge, studying the residual phosphorous in PBO fiber using ^{31}P solid-state nuclear magnetic resonance (^{31}P ssNMR) spectroscopy.

(3) Summary of the most important results

(a) A Brief Summary of Literature Results on PBO Environmental Degradation

After the tragic accidents of two new (less than one year old) soft-body-armor units containing PBO fibers were penetrated by bullets in the early 2000s, many efforts have been conducted to investigate the environmental stability issue of this fiber that had been claimed to be twice as strong as Kevlar®.[1-5] The main suspect was the residual phosphorous (P), which could hydrolyze the oxazole structure and break the polymer chains. The residual P was trapped inside the fiber during the fiber production process, and elemental analysis found that there was between 0.3 and 0.4 wt% of residual P in the fiber.[5] This mechanism was supported by the study of dissolved PBO, which found that the benzoxazole structure is susceptible to hydrolysis, especially at acidic condition.[3] Using Fourier-Transform Infrared (FTIR) spectroscopy, Chin et al. found that PBO yarns exposed to elevated temperature and relative humidity showed opening of the benzoxazole rings and generation of amide functionality.[1] These results seem to tell a consistent story that the residual P is acidic and catalyzes the breakdown of the PBO chains. On the other hand, PBO fibers exposed in high temperature and low humidity (5%) showed very little mechanical property degradation (< 4%) and no opening of the benzoxazole structure.[1]

Amid the extensive array of results, there has been a major missing link: there has been no direct study of the structure and behaviors of the apparent culprit, the residual P species. This has been partially due to experimental challenges: the residual P is of small population and defies any extraction. In the present report, we use ssNMR techniques to directly study the chemical structure and physical behaviors of the residual phosphorous, detect how they react to various environmental factors, and present some preliminary results of possible treatment strategies.

(b) ^{31}P ssNMR: A Brief Introduction

Using solid state NMR (ssNMR) to study the residual P has several unique advantages. First, like liquids NMR, its much-better-known sequel, ssNMR is capable of probing the chemical structure of the P species. Second, it can also detect their physical properties (e.g. liquid vs solid), which play a crucial role in their chemical activities. Third, the NMR-active isotope of P, ^{31}P, is at 100% natural abundance, and has a high gyromagnetic ratio. These traits mean that the P species give high NMR signal strength, enabling detection of low levels of P in the fiber. Finally, NMR is a non-invasive technique, so the P species do not need to be extracted to be studied. In addition, as the fiber matrix is free of phosphorous, the ^{31}P ssNMR spectra of the fiber contain only signals from the residual P species, without any complication from the much more populous fiber matrix.

One of the basic tools for structural identification by NMR is the position of the peaks, or chemical shifts. The ^{31}P NMR peaks of PA and its inorganic salts usually appear between -5 and 5 ppm. In fact, 0 ppm in ^{31}P NMR spectra is defined as the peak position of 85% PA.

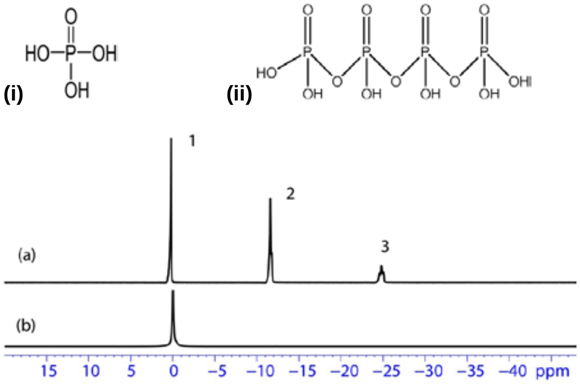

Figure 1. Liquid-state ^{31}P NMR spectra of (a) PPA and (b) PA. The PPA sample was partially hydrolyzed and thus has a high concentration of monomer (PA; structure (i)), which contributes to peak 1 (P that bonds to no P neighbors). Peak 2 is from P that bonds to one P neighbor (end units of oligomers), and peak 3 from P that bonds to two P neighbors (middle units of oligomers). Structure (ii) shows a PPA tetramer.

As an illustration of the NMR signatures of some important P species, Figure 1 shows the ^{31}P NMR spectra of phosphoric acid (PA) and partially hydrolyzed polyphosphoric acid (PPA). Both samples were in the bulk liquid state, thus generating needle-sharp NMR peaks. PPA is an important ingredient in the PBO fiber production process, serving to extract water generated by polymerization. However, part of the PPA eventually gets trapped inside the fibers and cannot be washed off.

PPA is a mixture of oligomer of PA of various lengths. It easily reacts with water and produces PA (monomer) and other smaller oligomers. On the ^{31}P NMR spectrum, PPA shows a 3-peak structure, corresponding to P that bonds to 0, 1, and 2 P neighbors, corresponding to monomer, end units of oligomer, and middle units of oligomer, respectively (Figure 1a).

^{31}P NMR spectra of solid P compounds have additional complexities that need to be considered. Unlike in liquids where molecules tumble quickly and thus do not occupy a fixed orientation, in solids each molecule occupies a fixed orientation, so a complexity – chemical shift anisotropy (CSA) – that goes unnoticed in liquid-state NMR must be discussed in ssNMR. CSA means that the signal frequency, or chemical shift, of an atom is dependent on its orientation relative to the magnetic field. As a typical solid contains molecules in every possible orientation (with the exception of a single crystal), its ssNMR spectrum would consist of very broad peaks instead of needle-sharp ones as seen in liquid-state NMR. Therefore, a special technique, Magic-Angle Spinning (MAS) was invented for ssNMR. When the signal is collected as the sample is spun at high speed (usually 3 - 15 kHz) at the Magic Angle, sharp peaks would result.

In combination with MAS, this report will primarily use two pulse sequences: Direct Polarization (DP/MAS), which directly excites ^{31}P signal, and Cross Polarization (CP/MAS), which excites ^{1}H signal first, then transfers to nearby ^{31}P through nuclear magnetic interaction. These pulse sequences probe different aspects of the P species.

Figure 2 shows the ^{31}P DP/MAS ssNMR spectra of two crystalline solids, ammonium phosphate ($NH_4H_2PO_4$) and phosphorous pentoxide (P_2O_5). $NH_4H_2PO_4$ peak appears at 1.05 ppm (the tallest peak in Figure 2b), which is very close to that of PA (0 ppm). There are several other smaller peaks on the spectrum, which are the spinning sidebands (SSB) of the main peak, generated by the MAS. The SSBs are easy to recognize as their distances to the main peak (termed centerband) are the multiples of the spinning speed. If we spin the sample faster during an experiment, the centerband will stay in the same position, while the SSBs will move away from the centerband and become smaller.

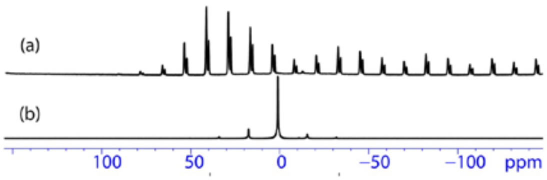

Figure 2. ^{31}P DP/MAS spectra of (a) P_2O_5 and (b) ammonium phosphate. The P in P_2O_5 has a highly asymmetric electron cloud, which generates large SSB intensities. On the other hand, the P in ammonium phosphate has a more symmetric electron cloud and has small SSBs.

The spectrum of P_2O_5 look notably different from that of $NH_4H_2PO_4$ in that the SSBs are much larger and more numerous. This is because the P in P_2O_5 is surrounded by a much more asymmetric electron cloud than that in $NH_4H_2PO_4$. The centerband of P_2O_5 has two peaks, at -45 ppm and -46.5 ppm, respectively, likely due to two different crystal polymorphs. All other peaks on the spectrum are SSBs.

(c) ^{31}P ssNMR of As-Received PBO Fibers

Zylon® HM fiber yarn (1640 Dtex/1500 denier; 996 filament) was purchased and stored in two layers of thick plastic ziplock bags (the outer layer is UV proof), with desiccant added at the bottom of the bags.

Figure 3 shows two ^{31}P ssNMR spectra of as-received PBO fiber. Both spectra show a large peak (centerband) at ca. 3.5 ppm along with several smaller SSBs. The peak position of the centerband means that it is mostly like PA or its phosphate derivatives.

The two spectra were acquired with different recycle delays (RD). Recycle delay is the wait time between two adjacent scans in an NMR experiment. After each scan, T_1 relaxation must occur so that the next scan would result in a signal. If RD is not long enough for T_1 relaxation to complete, the signal intensity will be diminished. T_1 relaxation is an excellent indicator of the physical state of a chemical species in that this relaxation is driven by molecular motion, so the species with low molecular mobility (such as the molecules in a rigid solid) would have long T_1, while those in liquids would have a shorter T_1. Therefore, Figure 3(b), which was acquired with RD = 6 s, contains mostly liquid-like P molecules. The spectrum with RD = 300 s includes both liquid-like (those have relaxed within 6 s) and rigid P (those have relaxed between 6 s and 300 s). The total P content as detected by DP/MAS NMR is ca. 0.4 wt%, consistent with elemental analysis result.

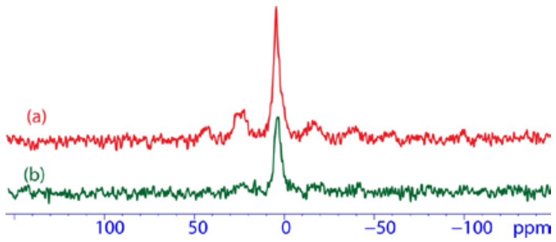

Figure 3. ^{31}P DP/MAS spectra of as-received PBO fiber at RD of (a) 300 s and (b) 6 s. Molecules with liquid-like behavior has a shorter T_1, thus appear on the spectrum with shorter RD. Both liquid-like and rigid molecules appear at longer RD.

As mentioned above, signals appearing between -5 and 5 ppm are usually PA or phosphates. As there is no feasible chemical mechanism that would convert the original PPA that was trapped inside the fiber into phosphates, the liquid-like P that shows up in shorter RD is most likely PA. This assignment agrees with the origin of the residual P species – when they were initially trapped inside the fiber, it was PPA. Then the exposure in moisture hydrolyzes PPA and produces PA. The PA peak appears at 3.5 ppm rather than 0 ppm, and is much broader than those of crystalline solids such as $NH_4H_2PO_4$, likely because the PA molecules in the fiber sample resides on the surface of the fiber nanovoids[6], thus experiencing a different and much more heterogeneous environment than the PA in bulk liquid.

PA in its pure form is a solid, and transitions to liquid upon absorbing water. In other words, the water molecules serve as a plasticizer for PA. Therefore, the liquid-like and the rigid P species may be assigned to water-bound and dry PA, respectively. They would exhibit drastically different reactivity toward the fiber matrix: water-bound PA can intimately adsorb onto the fiber surface and can easily migrate, while dry PA is rigid, thus cannot access reaction sites.

(d) ^{31}P ssNMR of PBO Fibers Treated with Various Environmental Conditions

Next, we examine how these P species respond to moisture and temperature. Figure 4(a) (red) shows the spectrum of a PBO fiber that has been exposed in 40°C and 80% relative humidity (RH) for 6 weeks. The as-received fiber is also shown (Figure 4(b); green) for comparison. Both spectra were acquired with RD = 6 s, thus both mainly contain the liquid-like P species, which we assign to water-bound PA. The rigid P species are invisible on the spectra at this experimental condition. Comparison of the two spectra shows that exposure in moisture significantly increases the liquid PA content. Such an increase can be assigned to the plasticization of the rigid P species, during which the rigid species that are invisible at this experimental condition converts to water-bound PA, which is observable on the spectra.

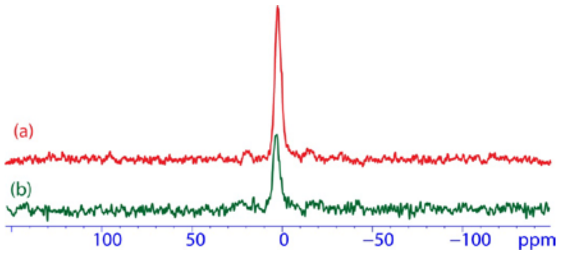

Figure 4. ^{31}P DP/MAS spectra of PBO fiber exposed in 40°C and 80% relative humidity for 6 weeks (a; red) and as-received fiber (b; green). RD = 6 s.

Conversely, heat treatment converts liquid PA back to solids. Figure 5 shows the spectra of PBO fiber exposed in 40°C and 80% RH for 1 week (condition A; red) and the fiber with condition-A treatment followed by 2 days of exposure at 90°C and zero humidity. Both spectra were acquired with RD = 6 s, at which condition the observable signal is mostly liquid-like while the rigid species are invisible. The heat treatment converts most of the liquid-like signal to solids, which is consistent with the well-known behavior of PA, which, at higher temperatures, would lose water and turn into less hydrated structures such as dry PA, PPA, metaphosphoric acid (HPO_3), and P_2O_5. The melting points of these structures increase at increasing level of dehydration. This explains the literature observation that hot and dry environment does not degrade PBO fiber mechanical performances.[1]

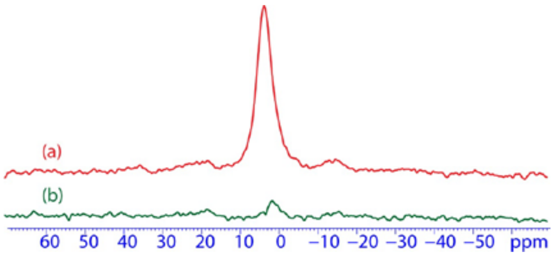

Figure 5. ^{31}P DP/MAS spectra of PBO fiber exposed at 40°C and 80% relative humidity for 1 week ("treatment A")(a; red) and treatment A followed by 2 days exposure at 90°C and zero humidity (b; green). RD = 6 s.

More severe heat treatments continue to drive the P species to more dehydrated structures. Figure 6 shows the ^{31}P CP/MAS spectrum of PBO fiber exposed in 200°C and zero humidity for 24 hours. In contrast to DP/MAS with short RD, which detects mainly liquid-like species, CP/MAS detects mainly rigid species. Three centerbands are observed: peaks 1 (1 ppm), 2 (-7 ppm) and 3 (-19 ppm). Other peaks are SSBs. These three peaks appear at similar positions as those in PPA, as seen in Figure 1(a) as well as in the open literature, so they can be assigned to monomeric (peak 1) and oligomeric (peaks 2 and 3)

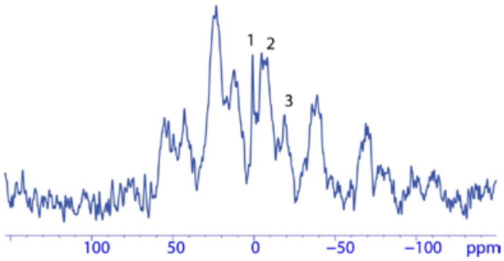

Figure 6. ^{31}P CP/MAS spectrum of PBO fiber exposed in 200°C and zero humidity for 24 hours. Three centerbands are observed (indicated by numbers), while other peaks are SSBs. Spinning speed was 7.5 kHz.

P species. As these all exhibit rigid behaviors, they are likely dry PA and PPA. The large SSB intensities of peaks 2 and 3 also suggest that the structures deviate from the more symmetric monophosphates and transit into polyphosphates, whose P atoms have more asymmetric electron structures.

The DP/MAS experiment for this sample generated no observable signal, confirming that all the liquid-like species have been converted to solids.

(e) Accessibility of Residual P by Moisture

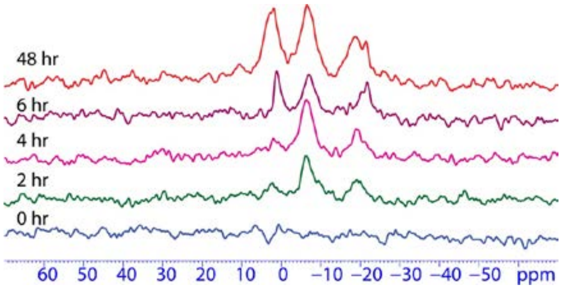

Figure 7. ^{31}P DP/MAS spectrum of PBO fiber exposed in 200°C and zero humidity for 24 hours followed by various exposure time at 40°C and 80% RH. Three centerbands are observed (indicated by numbers), while other peaks are SSBs. RD = 6 s.

The kinetics of moisture diffusing into the fiber can be observed by exposing the heat-treated fibers (which contains no liquid-like P species) in moisture, and watch the increase of the liquid P peaks over time. Figure 7 shows the DP/MAS spectra of PBO fiber exposed in 200°C and zero humidity for 24 hours followed by various exposure time in 40°C and 80% RH. The recycle delay was 6 s for all the spectra, which selectively detects liquid-like species. At zero humidity exposure time, there is no observable liquid-like signal, indicating the heat treatment has effectively immobilized all the P species. However, at moisture exposure of merely 2 hours, the solid P species already begin to mobilize/hydrolyze. The three-peak structure is very similar to that of PPA, thus can be assigned to monomeric PA (ca. 3 ppm), end-units of PPA (ca. -7 ppm), and middle-units of PPA (ca. -19 ppm), respectively. At short exposure times (<= 4 hours), the major hydrolysis products are oligomers, as indicated by a very small peak at 3 ppm and larger peaks at -7 ppm and -19 ppm. At longer exposure time, the monomeric peak begins to increase in intensity. This is consistent with the well-known hydration pathway of PPA oligomers → PA. The results indicate that water molecules can very easily get inside the fiber.

The kinetics of the reactions of residual P species would be determined by two processes: permeation of the water molecules into the fiber nanovoids, and the subsequent reactions between the water and the P species. It is well known that the reaction between highly dehydrated P species such as P_2O_5 and water is extremely fast. On the other hand, less dehydrated P species such as PPA oligomers would react much more slowly with water, especially at lower temperatures. This explains the experimental observation that the mechanical degradation proceeds much faster at higher temperature, given similar high-humidity conditions.[7]

(f) Preliminary Exploration of Treatment Strategies for Environmental Stability Improvement

The results above show that the nanovoids in the PBO fiber can be easily accessed by gas molecules. On the other hand, most of the residual P is inaccessible to aqueous media. This is likely because the residual P resides in the nanovoids of the fiber, and the liquid water cannot overcome the large surface tension due to the limited affinity between water and PBO. Therefore, one possibility of mitigating the PBO fiber environmental stability problem is to treat with gas molecules that would react with the residual P and change its chemical identity. Such a treatment could be easily administered on a commercial scale, e.g., during storage of the fabric.

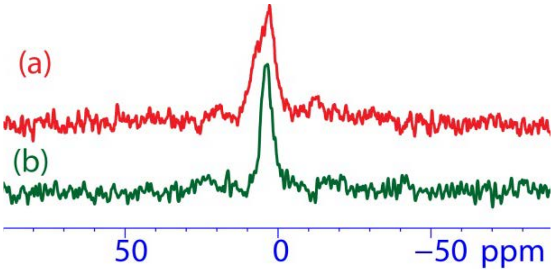

Figure 8. ^{31}P DP/MAS spectrum of PBO fiber exposed in ammonia (ca. 100 psi and 20°C) for one week (a) and as-received fiber (b).

One of the gaseous candidates that could react with the residual P is ammonia. This reaction would increase the pH values of the P species and thus might slow down the mechanical degradation due to acid-catalyzed benzoxazole bond scission. Figure 7(a) (red) shows the DP/MAS spectrum of a PBO fiber that has been exposed to the saturation vapor pressure (ca. 100 psi) of ammonia at room temperature for one week. The experiment was acquired with RD = 6 s, under which condition the spectrum mostly detects liquid-like P species. The spectrum of the as-received fiber acquired under the same condition (Figure 7(b); green) is also shown for comparison. The ammonia-treated sample shows a spectrum that is mainly between 0 and 10 ppm, and notably broadened as compared to the original fiber. The different peak signatures indicate that ammonia has accessed the nanovoids and reacted with the P species. The most likely reaction product would be ammonium phosphate, $NH_4H_2PO_4$.

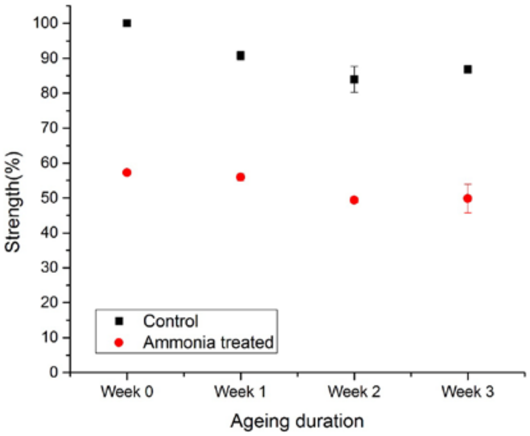

Figure 9. Tensile strength retention of ammonia treated (red circle) and as-received (black square) PBO fiber as a function of exposure time at 40°C and 80% RH. Error bars are indicated (several points have error bars that are within the symbols).

However, our preliminary mechanical measurements indicate that the ammonia treatment (100 psi and room temperature for one week) itself would cause a 40% loss of tensile strength (Figure 9). When exposed in 40°C and 80% RH environment, the ammonia-treated fiber seems to lose strength slower than the as-received fiber (Figure 9), though more data and longer aging periods are needed to further confirm this trend. These data suggest that strongly basic environment also degrades the fiber properties, so an optimization of the ammonia treatment condition or a search for alternate choices of gaseous molecules might be warranted.

(g) Outlook

This study revealed the chemical structure of the residual P, its physical state, its evolution under the influence of various environmental factors such as moisture and temperature, and its accessibility by foreign molecules. The results provided direct evidence that confirmed the proposed environmental degradation mechanisms for PBO fiber in the existing literature, and pointed out future directions for mitigation of this crippling problem. The study shows the promise of ssNMR as a useful technique for fiber environmental stability studies. However, due to the limited scope of this grant, our understandings achieved at this point are preliminary and qualitative. Following this study, several future directions could be taken. First, as the residual P resides on the surface of the fiber nanovoids, the structure of the nanovoids, which is difficult to characterize by other techniques, can be studied by NMR techniques such as Pulsed Field Gradient (PFG) NMR, which could probe the diffusion behaviors of the residual P and infer the properties of the cavities that it resides in. Second, various treatment strategies for PBO fiber stabilization could be explored with the guidance provided by ssNMR. Finally, ssNMR methodologies deployed in this study can be used to study the environmental stability of other important engineering fibers that also use PPA in polymerization, such as M5. Furthermore, the interaction between acidic residues and the fiber matrix learned from studying PBO and M5 could be useful in understanding other fibers that use other acids in production, such as PPTA (Kevlar®), which uses sulfuric acid.

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