

# A Critical Look at Damage Mechanisms in Ballistic Fibers \*

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**Abstract.** The unexpected failure of soft body armor composed of polybenzoxazole (PBO) fibers has led to an intense investigation to identify the mechanisms associated with the reduction in ballistic performance of PBO fibers that comprise the vest. Acid-catalyzed hydrolytic degradation, associated with the presence of residual phosphoric acid from the manufacturing process, has long been suspected of reducing the mechanical properties of the fibers by attacking the benzoxazole ring found in the polymer chain. However, until a recent systematic investigation by Park et al. (2009) there has been virtually no data to support this suspicion. These researchers showed for the first time that the 25 % by mass extractable phosphorus detected by previous researchers was a residual phosphorus compound from the manufacturing process. Furthermore, using information gleaned from model compound studies, the remaining non-extractable phosphorus was found to be chemically bound to the PBO polymer structure as a mono-aryl phosphate ester. This type of phosphate ester was found to be resistant to caustic hydrolysis that is typically used in the manufacturing process.

Folding that occurs during normal wear was also found to be a factor in PBO degradation. Using a device designed to impart localized folding damage, the strain-to-failure (STF) and ultimate tensile strength (UTS) of PBO fibers were found to be reduced with increased folding. In tests designed to simulate 6 months and 10 years of wear, the STFs of the mechanically degraded PBO fibers were reduced by 14 % and 40 %, respectively (Kim 2008). These results coupled with analyses of field returned vests showed that the folding damage creates localized regions in the vest that are weaker than the damage caused by hydrolytic action (Holmes 2009). Similar tests on poly(paraphenylene terephthalamide) (PPTA) fibers indicate that their folding damage is much less severe than that observed in PBO fibers.

## 1. BACKGROUND ON DEGRADATION MECHANISMS

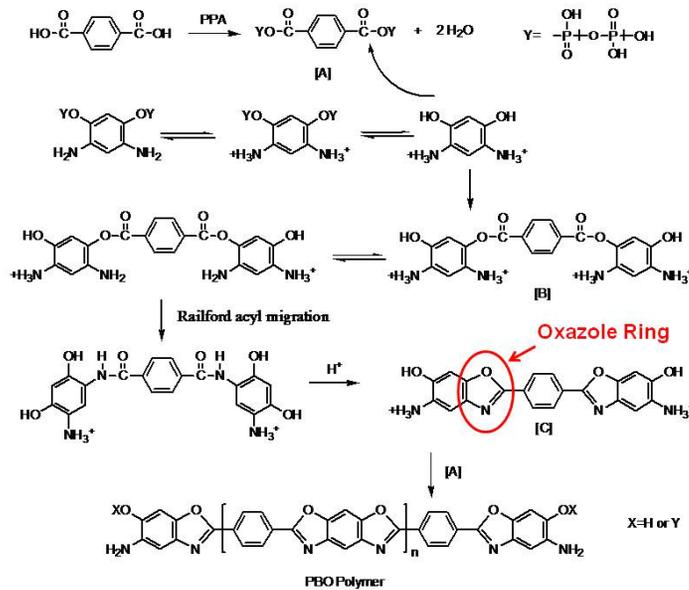
The high performance fiber poly[(benzo-[1,2-d:5,4-d']-benzoxazole-2,6-diyl)-1,4-phenylene] (PBO) is prepared by the reaction of 1,3-diamino-4,6-dihydroxybenzene (DADHB) dihydrochloride with terephthalic acid (TA) in a reaction medium consisting of poly(phosphoric acid) (PPA) enriched with P<sub>2</sub>O<sub>5</sub> as a dehydrating agent (see Figure 1) [1]. Although PBO fibers have superior tensile strength, modulus, cut and abrasion resistance, and flame retardation relative to other high performance fibers, the unexpected failure of a 6 month old vest worn by a police officer in Forest Hills, Pennsylvania in 2003 initiated a critical investigation into the long-term durability of high performance fibers used in soft body armor (SBA).

The hydrolytic stability of the oxazole ring, the characteristic structure of PBO, is susceptible to acid-catalyzed hydrolysis and the hydrolysis rate is most probably pH sensitive [2]. From model compound studies, the oxazole ring in PBO is hydrolyzed into an amide linkage like that found in PPTA fibers (compare Figure 2 and Figure 3). In addition, it is known that amides can undergo acid catalyzed hydrolysis by the A<sub>AC</sub>2 mechanism [3]. The A denotes acid catalysis, the AC designation indicates that acyl-oxygen bond cleavage occurs, and the 2 indicates the bimolecular nature of the rate-determining step

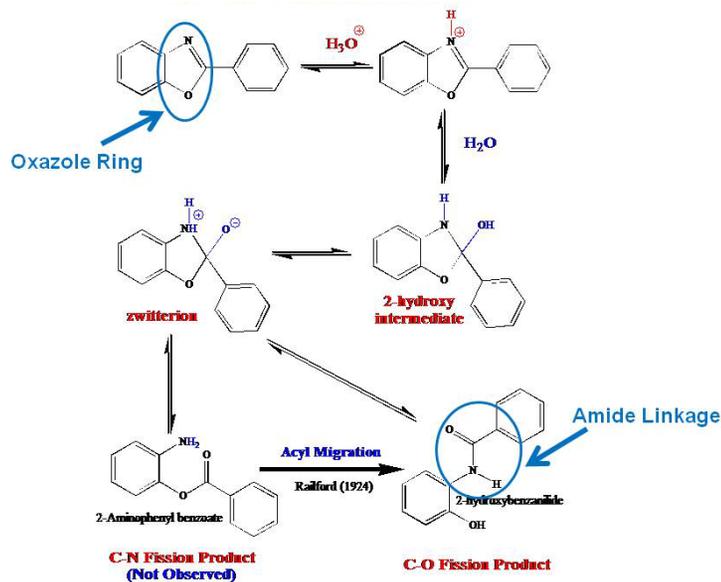
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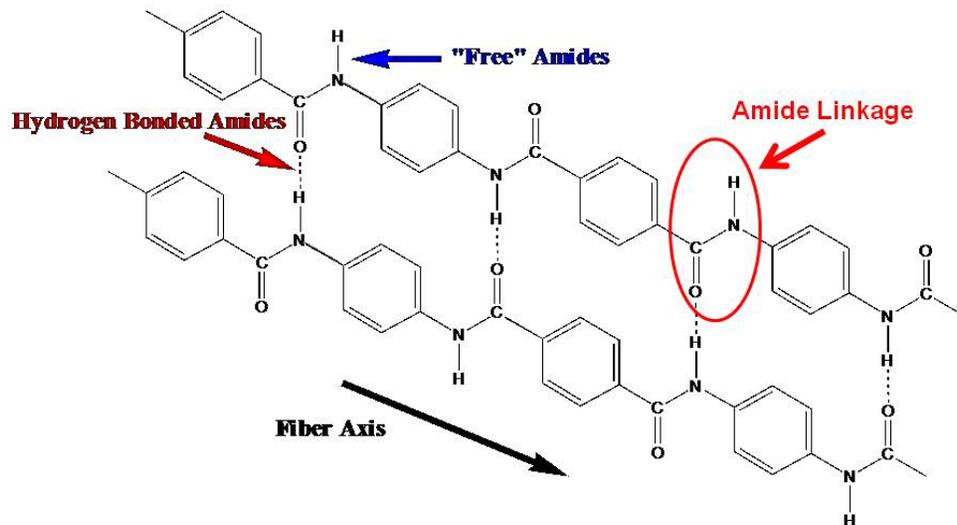
[4]. Kinetic data suggests that three molecules of water are involved in the rate-determining step (see Figure 4) [5,6]. Consistent with this reaction mechanism, the acid-catalyzed hydrolysis of the amide linkage in PPTA-100 % H<sub>2</sub>SO<sub>4</sub> dopes has been shown to be catalyzed by small quantities of absorbed moisture, with the hydrolysis rate being influenced by the resonance effects induced on the amide linkage by the attached aromatic rings and any substituent attached to the aromatic ring [7]. Therefore, the PBO polymer chain is likely to undergo macromolecular chain scission after the formation of the amide linkage shown in Figure 2. Extensive chain scission can result in the reduction of a polymer's mechanical integrity, as manifested in strain-to-failure (STF) and ultimate tensile strength (UTS). PBO fibers from hydrolytically aged vests are known to exhibit reductions in STF and UTS [8].



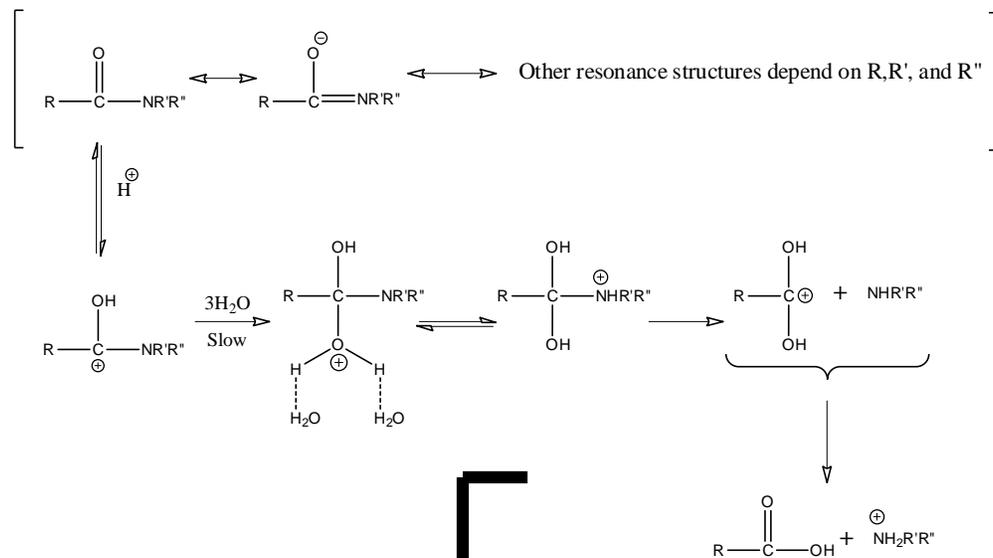
**Figure 1.** Accepted reaction scheme for the formation of the oxazole ring that characterizes the PBO polymer (adapted from [1]).



**Figure 2.** Hydrolysis of oxazole ring structure to amide linkage. (adapted from [9])



**Figure 3.** Chemical structure of poly(paraphenylene terephthalamide) (PPTA). (adapted from [2])



**Figure 4.** Acid Catalyzed Amide Hydrolysis. (adapted from 3,5,6)

Since PBO is formed in a PPA/ $\text{P}_2\text{O}_5$  reaction medium and approximately 0.34 % by mass phosphorus (P) is routinely detected in process fibers by soxhlet extraction, solid state NMR and P-31 NMR [8], it is generally believed that the acid catalyzed hydrolysis reaction is initiated by residual phosphoric acid (PA). Because processing aids that contain P are often used in the manufacturing process, the detection of only P in the processed fibers does not definitively indicate the presence of PA. Furthermore, only 25 % by mass of the residual P can be removed by the various extraction techniques that have been used [8,10-13].

In addition to hydrolytic action, folding has been put forth as a possible degradation mechanism, presumably because of the known low compressive strength of PBO fibers relative to other high performance fibers [14-16]. A preliminary test [17] revealed that a single fold in a PBO fiber can result in a significant decrease in the STF of PBO fibers. From these results, a study was initiated to reproduce the

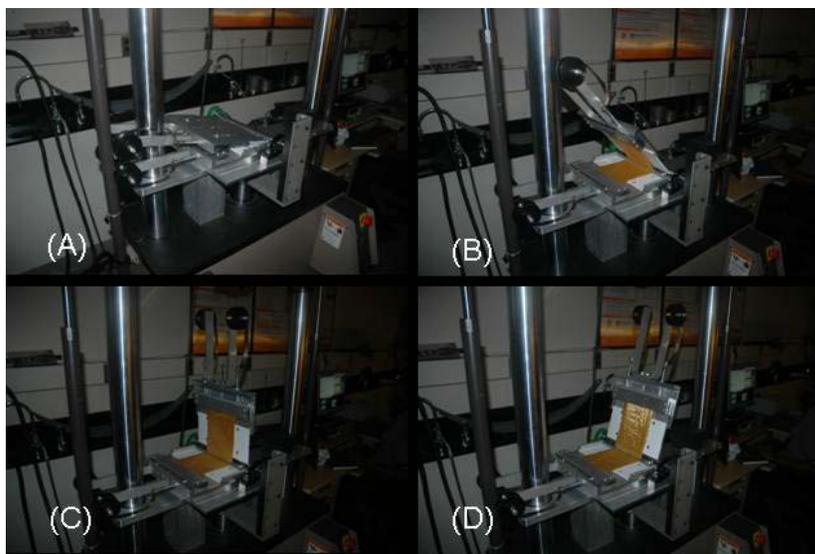
type of folding generally observed when SBA is worn and to quantify the influence of repeated folding on the mechanical properties of high performance fibers.

## 2. EXPERIMENTAL

Aqueous soxhlet extraction was used to determine the chemical structure of the residual P in processed PBO fibers. The extracts were methylated using an in-situ diazomethane generator to convert extracted acids to their corresponding methyl esters. The phosphorus containing species in the methylated extracts were then identified using electron impact (EI) and methane chemical ionization (CI) gas chromatography (GC) mass spectrometry (MS) in conjunction with flame ionization detection (FID), nitrogen-phosphorus detection (NPD), and flame photometric detection (FPD). NPD and FPD are commonly used to detect P in phosphorus containing species as they elute from the GC column.

To identify the non-extractable P remaining in PBO fibers, low molecular mass PBO oligomers were synthesized using a procedure analogous to the industrial process and analyzed by matrix assisted laser desorption ionization (MALDI) – time of flight (TOF) MS. To support the non-extractability of the identified P containing PBO structure by the NaOH wash used in the manufacturing process, the stability of monophenyl phosphate was evaluated by NaOH washes. The extracts were methylated and analyzed by the GC/MS procedure mentioned above. X-ray fluorescence was used to quantify the amount of P remaining in the extracted fibers and the model PBO oligomers. The details of the experimental procedures can be found elsewhere [1,18].

A folding apparatus was designed to use the fatigue testing features inherent in a Flex Test SE controlled 250 kN (55 Kip) model 810.25 Material Testing System<sup>†</sup>. A two-piece clamshell concept was used to effect the repeated folding of a strip of woven ballistic fabric at the same location without frictional sliding. To maintain a constant force on the fabric during the folding cycle constant force springs were used. An example of the folding sequence is shown in Figure 5, with the specific details of the design available in reference 17.



**Figure 5.** Collage showing the repeated folding of woven PBO fabric under constant tension.

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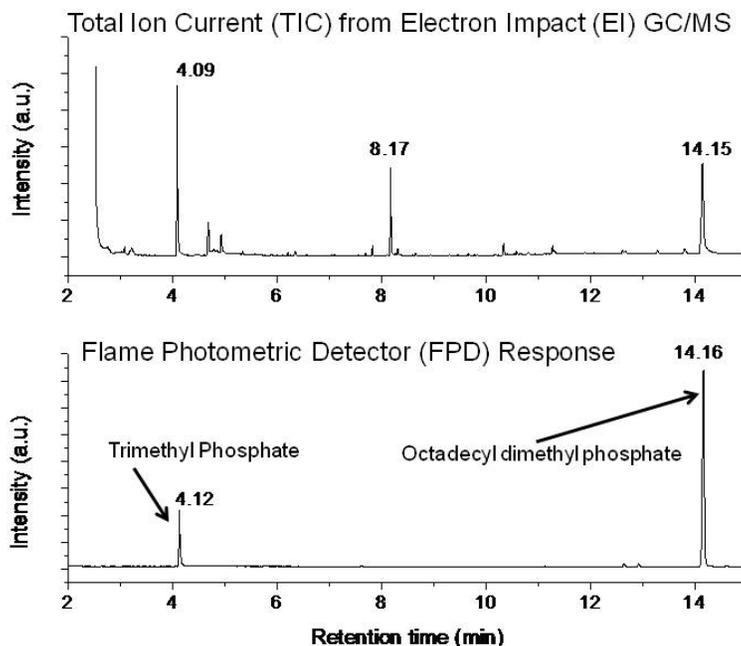
<sup>†</sup> "Certain commercial equipment, instruments, or materials are identified in this paper in order to specify the experimental procedure adequately. Such identification is not intended to imply recommendation or endorsement by the National Institute of Standards and Technology, nor is it intended to imply that the materials or equipment identified are necessarily the best available for the purpose."

### 3. RESULTS AND DISCUSSIONS

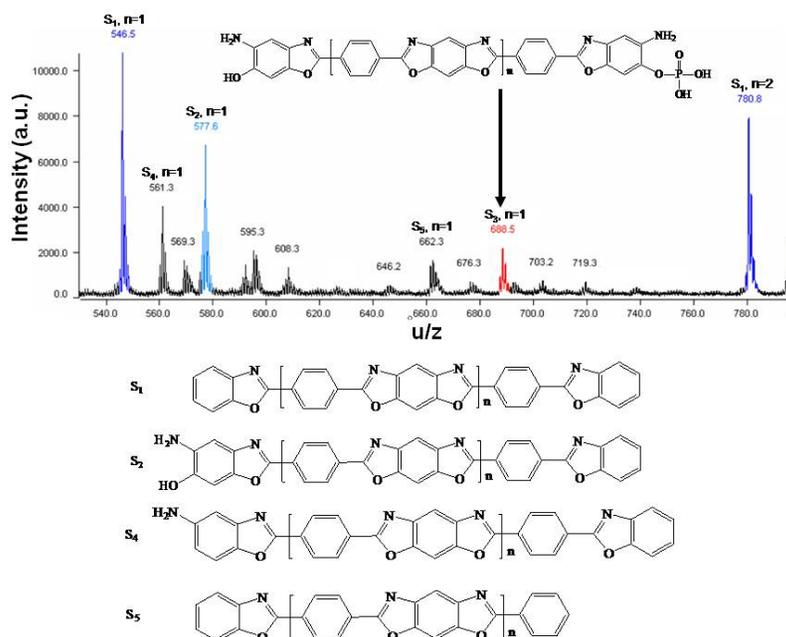
#### 3.1 Chemical Degradation Studies

Consistent with prior studies, the P mass fraction decreased from 0.38 % to 0.28 % mass fraction in the PBO fibers with water extraction. No additional reduction in P was observed when these fibers were subsequently extracted with NaOH solution. Analysis of the methylated extracts by GC/MS coupled with simultaneous FPD detection and off-line NPD detection showed the extracts to contain two P containing compounds eluting at 4 min and 14 min (see Figure 6). The peak at 4 min was identified as trimethyl phosphate, thereby indicating the presence of extracted phosphoric acid. The larger peak at 14 min was identified as octadecyl dimethyl phosphate. Noting that the methyl groups arise from the methylation procedure, the second peak corresponds to the presence of octadecyl phosphate, most probably the disodium variant – used as a processing aid in the fiber manufacturing process. The limited solubility in water of this long chain alkyl phosphate resulted in most of the material precipitating out of solution as the extraction solution was concentrated. Thus the predominant amount of the 25 % extracted P corresponds to the processing aid.

Since no additional P was extracted by washing the fibers with NaOH solutions, low molecular mass PBO oligomers were analyzed by MALDI-TOF MS to search for compounds with chemically bound P. A mono-aryl phosphate ester based on the PBO structure was identified (see Figure 7). The surprising stability of the mono-aryl phosphate species to NaOH washes was verified by refluxing trimethyl phosphate (TMP) in a 1 mol/L NaOH solution for 7 d. After methylation, 95 % of the converted TMP corresponded to monophenyl dimethyl phosphate and only 4 % was converted to TMP, which indicates the presence of PA. To verify this finding, monophenyl phosphate (MPP), made from its disodium salt, was then refluxed in a 1 mol/L NaOH solution for 7 d. Only 2 % of the MPP was converted to TMP. These results support the identification of the non-extractable P in PBO fibers as a mono-aryl phosphate.



**Figure 6.** Electron Impact (EI) GC/MS analysis with simultaneous flame photometric detection (FPD) of water extract from PBO fiber (typical example).



**Figure 7.** MALDI-TOF MS of molecular mass model PBO oligomers with identification of  $S_3$ ,  $n=1$  oligomer as being a monoaryl phosphate.

### 3.2 Mechanical Degradation Studies

The effect of repeated folding of PBO and PPTA fibers is shown in Table 1, where the  $\pm$  represents 1 standard deviation of the mean value which is taken as a measure of the uncertainty. The 5,500 folds (5.5 k for short) and 80,000 folds (80 k for short) are estimated to reflect damage caused by folding during the wearing of the SBA for 6 months and 10 y, respectively. The virgin fibers of PPTA and PBO are shown to have different modulus values than their woven counterparts. This difference may reflect human variation and inaccuracies in the optical method used to measure fiber diameters required in the data analysis of the results from the manual test procedure. Data from the industry standard Favimat testing machine, which uses a vibration method to extract a measure of the fiber diameter, yields consistently lower values than obtained by the optical method. Although the differences between the two methods will affect the modulus and UTS values, the STF values from the two methods agree to within 5%. Irrespective of these differences, the test data for the woven fabric indicate that the modulus does not change with repeated folding for the woven PPTA and PBO fibers. Additionally, the UTS and STF values of the woven PPTA fibers remain unchanged with repeated folding. In contrast, the woven PBO fibers exhibit a consistent and statistically significant reduction in the UTS and STF with repeated folding.

**Table 1.** Change in Mechanical Properties of PPTA and PBO Fibers with Folding

Sample	Diameter, $\mu\text{m}$	Ultimate Tensile Strength, GPa	Modulus, GPa	Strain-to-Failure, %
PPTA (Virgin)	$13.0 \pm 0.5$	$2.8 \pm 0.2$	$70 \pm 4$	$3.7 \pm 0.3$
PPTA (Woven)	$12.9 \pm 0.3$	$3.1 \pm 0.3$	$85 \pm 6$	$3.6 \pm 0.4$
Woven PPTA (5.5 k folded)	$13.0 \pm 0.3$	$3.1 \pm 0.4$	$83 \pm 5$	$3.5 \pm 0.5$
Woven PPTA (80 k folded)	$13.0 \pm 0.4$	$3.1 \pm 0.4$	$85 \pm 5$	$3.5 \pm 0.4$
PBO (Virgin)	$12.5 \pm 0.2$	$4.5 \pm 0.5$	$163 \pm 10$	$3.5 \pm 0.4$
PBO (Woven)	$13.1 \pm 0.6$	$3.4 \pm 0.4$	$143 \pm 10$	$3.0 \pm 0.4$
Woven PBO (5.5 k folded)	$13.0 \pm 0.5$	$2.9 \pm 0.4$	$146 \pm 9$	$2.5 \pm 0.5$
Woven PBO (80 k folded)	$13.3 \pm 0.4$	$2.0 \pm 0.3$	$136 \pm 8$	$1.7 \pm 0.3$

The reduction in the STF and UTS mechanical properties of PBO fibers may be related to their low compressive strength ( $0.19 \pm 0.04$  GPa) relative to that of PPTA fibers (between  $0.29 \pm 0.03$  GPa and  $0.35 \pm 0.04$  GPa) [15]. A contributing factor to the compressive strength differences may be the extensive hydrogen bonding between the amide linkages of PPTA fibers versus the complete absence of this type of inter-chain interaction in the PBO fibers (compare the chemical structure of the PBO polymer chain in Figure 1 to the PPTA polymer chain structure in Figure 3).

### 3.3 Correlating Changes in Mechanical Properties with Ballistic Performance

From the previous sections, the chemical and mechanical degradation mechanisms in PBO result in similar reductions in STF and UTS with hydrolytic exposure time and folding. A desirable outcome of these results is to equate the observed changes in material properties of a high performance fiber with changes in ballistic performance. It is worth noting that empirical [19,20] and theoretical [21,22] studies for the transverse impact of SBA by a flat right circular cylinder (RCC) projectile show that the relative ranking of ballistic performance is related to the fiber's UTS, STF, and Young's modulus (see Equation 1). Although plausible, using this model to track changes caused by environmental and mechanical actions has not been validated. Furthermore, the solution is restricted to one type of ballistic threat.

#### Equation 1

$$[\Omega]^{1/3} = \left[ \frac{\sigma_y^{\max} \varepsilon_y^{\max}}{2\rho} \sqrt{\frac{E_y}{\rho}} \right]^{1/3}$$

where

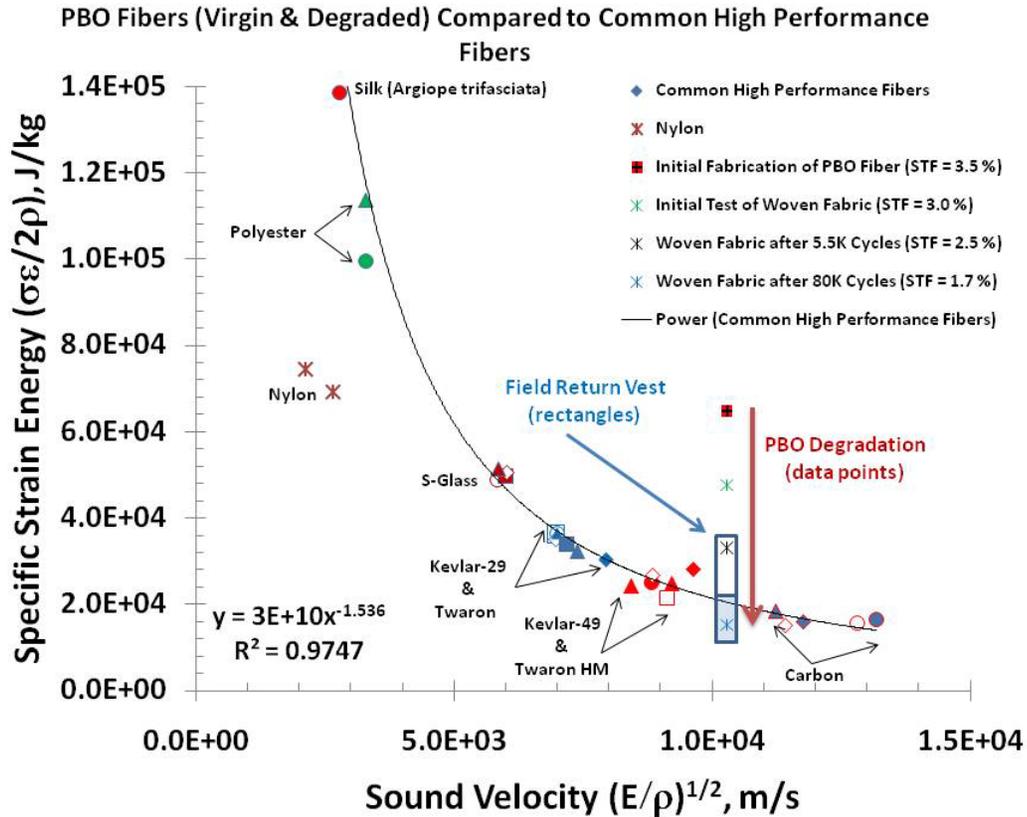
$[\Omega]^{1/3}$	denotes a normalizing velocity
$m$	denotes meters
$s$	denotes seconds
$\sigma_y^{\max}$	is the yarn (fiber) maximum axial tensile strength
$\varepsilon_y^{\max}$	is the yarn (fiber) maximum tensile strain
$\rho$	is the yarn (fiber) density
$E_y$	is the yarn (fiber) longitudinal linear elastic modulus

An important observation from Equation 1 is that  $\Omega$  is the product of the elastic energy storage capability of the fiber per unit mass ( $\sigma_y^{\max} \varepsilon_y^{\max} / 2\rho$ , a measure of toughness) and the fiber's tensile wave speed (or sound velocity),  $a_{0y} = \sqrt{E_y / \rho}$ . As described by Phoenix [21], increasing the elastic energy storage (often believed desirable for improved impact resistance) is not beneficial if  $a_{0y}$  is greatly reduced in the process. Another consequence of greatly lowering  $a_{0y}$  is the need for a much larger distance to stop the projectile, thereby greatly increasing the bulk of the body armor or allowing larger undesirable armor deformations that increase the risk of blunt force trauma.

Similarly, the concept that ballistic resistance results from a balance between high performance fibers producing faster wave speeds and lower strains and the fiber STF has been advanced from a numerical simulation [23] of the transverse impact of woven fabrics. Simulations of nylon, two types of PPTA fibers, and carbon fibers showed that the rate of energy absorption increased monotonically with the fiber modulus. However, the high modulus carbon fibers exhibited poor impact resistance due to low STF. Furthermore, the level of strain at the impact point and the rate of propagation of the stress wave (energy) away from the impact location were observed to be governed by the fiber modulus and density. Therefore,

as the modulus decreases, the strain level at the impact point increases and the wave speed and rate of energy dissipated away from the impact zone decreases.

From these observations a graphical approach that compares changes in the sound velocity of a fiber to its potential for storing elastic energy was recently advanced as a means of qualitatively monitoring changes in ballistic performance [24]. As a benchmark, a select group of high-performance fibers [(a) S-glass, (b) PPTA (Kevlar, Twaron), (c) carbon fiber, (d) polyester, (e) nylon, and (f) silk] that span a wide range of sound velocities were chosen (see Figure 8). Although the choices of the benchmark fibers are somewhat arbitrary, these fibers have been considered for, are being used in, or are of historical interest for ballistic applications. Excluding the nylon data points, a power function trend line was fit through these data ( $R^2 = 0.97$ ) to aid in interpretation.



**Figure 8.** Specific strain energy versus sound velocity plot for PBO fibers compared to common high performance fibers: (a) virgin - (rectangle data point), (b) degraded - (asterisk data points), and (c) 6 y field return vest (rectangles). The rectangles denote the range of values from the field return vest with the shaded rectangle denoting the location of 75% of the 8 sets of tested fibers.

Noting that silk is no longer used in SBA, the reference data captures the general observation [21] that increasing the elastic energy storage does no good if  $a_{0y}$ , the sound velocity, is greatly reduced in the process. The reference data also underscores the observation that PPTA fibers, as embodied by Kevlar 29, which is widely used in SBA, achieves a balance between wave speed and energy absorption [23].

From this reference frame, the exceptional properties of PBO fibers are initially achieved by having a sound velocity comparable to carbon fibers and an initial specific strain energy absorption potential comparable to S-glass fibers (see Figure 8). Both of these properties exceed those of PPTA fibers. While the sound velocity of PBO remains comparable to that of carbon fibers, the reduction in STF caused either by the chemical and/or mechanical degradation mechanisms, reduces the potential of these fibers to absorb strain energy.

Using the reduced STF values caused by folding from Table 1 and the industry standard for the modulus of PBO fibers, the potential amount of strain energy that PBO fibers can absorb is reduced to that of carbon fibers. Such a reduction results in inferior ballistic performance from degraded PBO fibers as compared to PPTA fibers (see asterisk data points in Figure 8 labeled as PBO degradation). Interestingly, the STF values of fibers tested from a six year old field return vest composed of PBO fibers ranged from 1.6 % to 2.6 %, with 6 of the 8 sets of 50 fibers yielding average values  $\leq 2.0$  %.

In contrast to the PBO results, the PPTA fibers are not degraded by folding. This suggests that the primary degradation mechanism in PPTA fibers is the hydrolytic degradation mechanism that may be caused by the residual sulfuric acid that is believed to be in the processed fibers. It is worth noting that unacceptable levels of residual acid in PPTA fibers (which may contain 0.24 % by mass) are detected by an indirect procedure that quantifies the amount of degradation observed from a standard exposure protocol [25].

#### 4. CONCLUSIONS

The presented data indicate that material properties of high performance fiber poly[(benzo-[1,2-d:5,4-d']-benzoxazole-2,6-diyl)-1,4-phenylene] (PBO) are degraded by chemical and mechanical mechanisms. The PBO chemical degradation mechanism is the result of acid catalyzed hydrolysis of its characteristic oxazole ring structure to an amide linkage of the type that is typically found in poly(paraphenylene terephthalamide) (PPTA) fibers. The acid that catalyzes this reaction was found to be chemically bound to the polymer chain and not hydrolyzed by NaOH washes used in the manufacturing process to remove unwanted impurities from the process fibers.

Literature results indicate that the amide linkage is susceptible to further acid catalyzed hydrolysis promoted by the presence of H<sub>2</sub>O. The hydrolysis of the amide linkage in hydrolyzed PBO results in macromolecular chain scission, thereby reducing the polymer's mechanical properties, such as strain-to-failure (STF) and ultimate tensile strength (UTS). Although the amide linkage is dominant in PPTA fibers and these fibers are believed to contain residual sulfuric acid, quality control procedures apparently keep the residual acid below a level where excessive degradation occurs.

Folding experiments on PBO and PPTA fibers indicate that PBO, and not PPTA, fibers are susceptible to this degradation mechanism. Presumably this susceptibility is a result of the weak compressive strength of the PBO fibers, which may be associated with the absence of inter-chain interactions between the polymer chains.

A graphical approach based on a plot of the potential strain energy absorption of the high performance fiber relative to its sound velocity is presented as a qualitative metric for assessing changes in ballistic performance that result from these degradation mechanisms. By referencing the initial properties of PBO fibers against a set of benchmark high performance fibers, the increased ballistic performance of virgin PBO fibers appears to be a result of increased ability to absorb strain energy, relative to PPTA fibers, while dissipating this energy away from the impact zone at a rate comparable to carbon fibers. Therefore, the resulting deterioration in ballistic performance of these fibers is caused by a reduction in the potential of these fibers to absorb strain energy as the STF of the fibers is decreased by chemical and mechanical degradation mechanisms.

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