

THE EFFECT OF ENVIRONMENTAL AND MECHANICAL MECHANISMS ON THE PERFORMANCE OF SOFT BODY ARMOR*

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SUMMARY

Research on soft body armor has shown that ballistic resistant textile fibers can be susceptible to environmental and mechanical degradation that results in a non-uniform reduction in ballistic performance throughout the armor. Test procedures that quantify the rate of degradation in areas of critical concern are presented.

Keywords: degradation, mechanical properties, ballistic fiber, polybenzoxazole, soft body armor, PBO

INTRODUCTION

The use of high-performance fibers (such as, poly[(benzo-[1,2-d;5,4-d']-benzoxazole-2,6-diyl)-1,4-phenylene]¹ (PBO), ultra-high molecular weight polyethylene² (UHMWPE), and poly(p-phenylene terephthalamide)³ (PPTA)) in soft body armor (SBA) is well documented. The susceptibility of the ballistic fibers to environmental degradation, however, became the subject of intense concern after two new units (< 1 year old), containing PBO fibers, failed when hit by bullets the SBAs were designed to resist. These premature failures resulted in the National Institute of Standards and Technology's (NIST's) Office of Law Enforcement Standards (OLES), at the behest of the National Institute of Justice (NIJ), initiating a research program designed to understand the root causes of these premature failures and to develop testing methodologies to ensure that unexpected failures of this type did not occur again in SBA worn by police officers and other first responders.

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A review of the literature by Holmes et al.⁴ revealed that PBO and PPTA are susceptible to degradation by ultraviolet (UV) radiation, while UHMWPE is resistant due to its structure. Noting that the susceptibility of PBO and PPTA to UV radiation is overcome by encasing the woven ballistic fabrics in a breathable UV resistant pouch, the research initially focused on the hydrolytic stability of the PBO benzoxazole ring (see Figure 1) to acid-catalyzed hydrolysis, since the premature failures were associated with the use of this fiber.

PPTA (also referred to as Kevlar[†] or Twaron) was also found to be susceptible to hydrolytic attack at its amide linkage. However, quality assurance tests designed to detect “unacceptable” residual acid levels in PPTA had previously been established.³

The hydrolytic instability of the benzoxazole ring of PBO has been associated with the level of residual phosphoric acid (PA), as detected by residual phosphorus (P) analyses, since PBO is synthesized by the reaction of terephthalic acid (TA) with 1,3-diamino-4,6-dihydroxybenzene (DADHB) dihydrochloride in a reaction medium consisting of polyphosphoric acid (PPA) enriched with P₂O₅ as a dehydrating agent. Manufactured PBO fibers are known to contain about 0.34 % mass fraction of P.⁵⁻⁷ Using this information, researchers have surmised that all of the residual P in the PBO fiber is due to residual PA and that PA is the acid source that catalyzes the benzoxazole ring hydrolysis reaction and degrades the ballistic properties of the PBO fiber. But there is little direct evidence that PA exists in PBO fibers. Furthermore, this supposition is complicated by the observation that P processing aids are used in the manufacture of PBO fibers.

Although the hydrolysis mechanism is significant in PBO fibers, tests in the NIST laboratories⁷ indicate that it is unlikely that this mechanism alone resulted in the premature failure of the vests in question and for that reason further research was directed toward examining how folding affects the mechanical properties of PBO fibers. This observation led to an examination of folding as a potential degradation mechanism in PPTA fibers, since this material is the preferred ballistic fiber for SBA applications. This report summarizes NIST’s research on the contribution of both chemical and mechanical degradation to the performance of PBO fibers and the impact of mechanical degradation on the ballistic performance of PPTA fibers.

EXPERIMENTAL

Materials

All PBO materials were obtained from NIST/OLES and included virgin PBO fibers, the back panel of a failed vest, a field returned vest, a newly manufactured vest and a

[†] Certain commercial materials and equipment are identified in this paper to specify adequately the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Institute of Standards and Technology, nor does it imply necessarily that the product is the best available for the purpose.

hydrolytically aged vest. The PBO fibers from the vests were obtained by a procedure designed to minimize degradation of the fibers from handling.⁷ A complete listing of the compounds needed to effect the synthesis and analysis of low molecular mass PBO oligomers and the methylation of acids that may be extracted from PBO fibers can be found elsewhere.⁸

Instrumentation

A gas chromatograph mass spectrometer (GC/MS) operated under electron impact (EI) and chemical ionization (CI) conditions were used to identify unknown phosphorus species extracted from the PBO fibers. To unequivocally verify the presence of phosphorus in an unknown compound the effluent from the GC column was split between the MS and a flame photometric detector (FPD) (parallel detection). An identical column was connected to a nitrogen phosphorus detector (NPD) to provide additional evidence for the unknown compound containing phosphorus (non-parallel detection). Matrix-assisted laser desorption ionization-time of flight mass spectrometry (MALDI-TOF-MS) was used to identify species in low molecular mass model PBO oligomers that contained phosphorus since PBO oligomers are intractable in most solvents. An X-ray fluorescence (XRF) spectrometer was used to quantify the level of phosphorus in PBO fibers, PBO model oligomers, and extracts from PBO fibers and model oligomers.⁸

Synthesis of Low Molecular Mass PBO Oligomers

PBO oligomers were synthesized in the laboratory by using DADHB, TA, PA, P₂O₅, and 2-aminophenol (2-AP) according to a procedure known to mimic that used in the manufacture of PBO fibers.⁹ Since PBO is intractable in most organic solvents, the 2-AP was added to the reaction mixture to keep the molecular mass of the oligomers in a mass range where MALDI-TOF-MS could be used.⁸

Controlled Folding of Woven PBO Fabrics

To quantify the effect of repeated folding on the ballistic performance of PBO fibers a device was built that attaches to a standard MTS servohydraulic testing machine. The device effectively converts the linear motion of the MTS into rotational motion to simulate the repeated folding that may occur when a vest is worn. (see Figure 2).¹⁰

RESULTS AND DISCUSSION

Chemical Degradation of PBO Ballistic Fibers

A coherent approach was developed to detect and identify the types of residual P found in PBO fibers by taking advantage of the fact that previous research groups had shown, without identifying the extracted P species, that only 25 % of the 0.34 % mass fraction of residual P typically found in PBO fibers could be removed by aqueous Soxhlet

extraction.⁸ Defining the removed material as extractable P, the Soxhlet extracted fibers were then subjected to a series of procedures designed to discriminate between P that might be trapped in the microvoids of PBO fibers and P that may be chemically bound to the polymer structure. The P compounds found in the extract from the Soxhlet extraction procedure were identified using the EI and CI modes of the GC/MS with parallel FPD detection and non-parallel NPD detection as phosphoric acid and octadecyl phosphate.

Since PBO fibers are insoluble in most organic solvents, low-molecular mass PBO oligomers that were synthesized in a manner consistent with the manufacture of PBO fibers were analyzed by MALDI-TOF-MS. These analyses indicated the presence of an aryl-phosphate ester that is resistant to the NaOH treatment that is used to remove residual impurities from the processed fibers (see Figure 3).

The stability of the aryl-phosphate ester to NaOH was verified by subjecting the compounds triphenyl and phenyl phosphate to 1 mol/L NaOH treatments. The susceptibility of the aryl-phosphate ester to acid hydrolysis was verified by hydrolyzing phenyl phosphate in a pH 4 HCl solution in a sealed chamber. Within 24 h only phosphoric acid was detected by GC/MS. Additional evidence supporting the presence of chemically bound P attached to the PBO oligomers can be found in the research of So et al.¹¹ They deduced the presence of an aryl-phosphate ester attached to PBO oligomers from their model compounds studies using nuclear magnetic resonance. Consistent with the findings in this report, they observed that by placing one drop of water on the sample, the aryl-phosphate they detected in the model compound studies slowly hydrolyzed under acid conditions.

Mechanical Degradation of PBO Ballistic Fibers

In a parallel study designed to determine if a mechanical mechanism contributes to a reduction in ballistic performance during the use of PBO-based SBAs, the impact of repeated folding that may occur during use was investigated. A preliminary study showed that a single fold of a PBO fiber could result in a 10 % reduction in the strain-to-failure and ultimate tensile strength, as tested by the modified-single fiber test, of a PBO fiber.^{10,12} The damage induced by the single fold is shown in Figure 4. Repeated folding of woven PBO fabrics placed in the device shown in Figure 2 indicated a 15 % and 40 % reduction in the strain-to-failure under test conditions designed to simulate 6 months and 10 years of folding, respectively. This change in mechanical properties was also accompanied by a change from fibrillar to brittle failure (see Figure 5).

Tests were then performed, again using the modified-single fiber test,¹² on a field returned vest, a new vest, a hydrolytically aged vest, and the back panel from the compromised vest.¹³ Data from the new vest showed that there is minimal damage to the PBO fibers during the manufacturing process, while hydrolytic ageing can result in a significant reduction in ballistic performance caused by the residual phosphoric acid that exists as free and chemically bound P. More importantly, data from the field return

vest showed that the folding mechanism works in addition to the chemical (hydrolytic) damage mechanism to create localized weak spots in the vest that have even lower ballistic performance. Also these results indicate that the back panel of the compromised vest is not a good indicator of the ballistic performance of the front panel, because of the additional folding that occurs to the front panel.

Mechanical Degradation of PPTA (Kevlar) Ballistic Fibers

Unlike the behavior observed for PBO, a single fold of PPTA fibers resulted in no measureable loss of mechanical properties as quantified by the modified single fiber test. These results may be associated with the absence of inter-chain interactions in the PBO fibers. In Figure 1, the polymer chains of PPTA molecules are shown to hydrogen bond to each other through the amide linkage that characterizes this polymer. The structure of PBO does not afford this type of inter-chain interaction and may be the reason for its compressive strength being lower than PPTA, even though PBO has a higher initial tensile strength and modulus than PPTA. Additional tests that simulate 6 months and 10 years of repeated folding are being conducted.

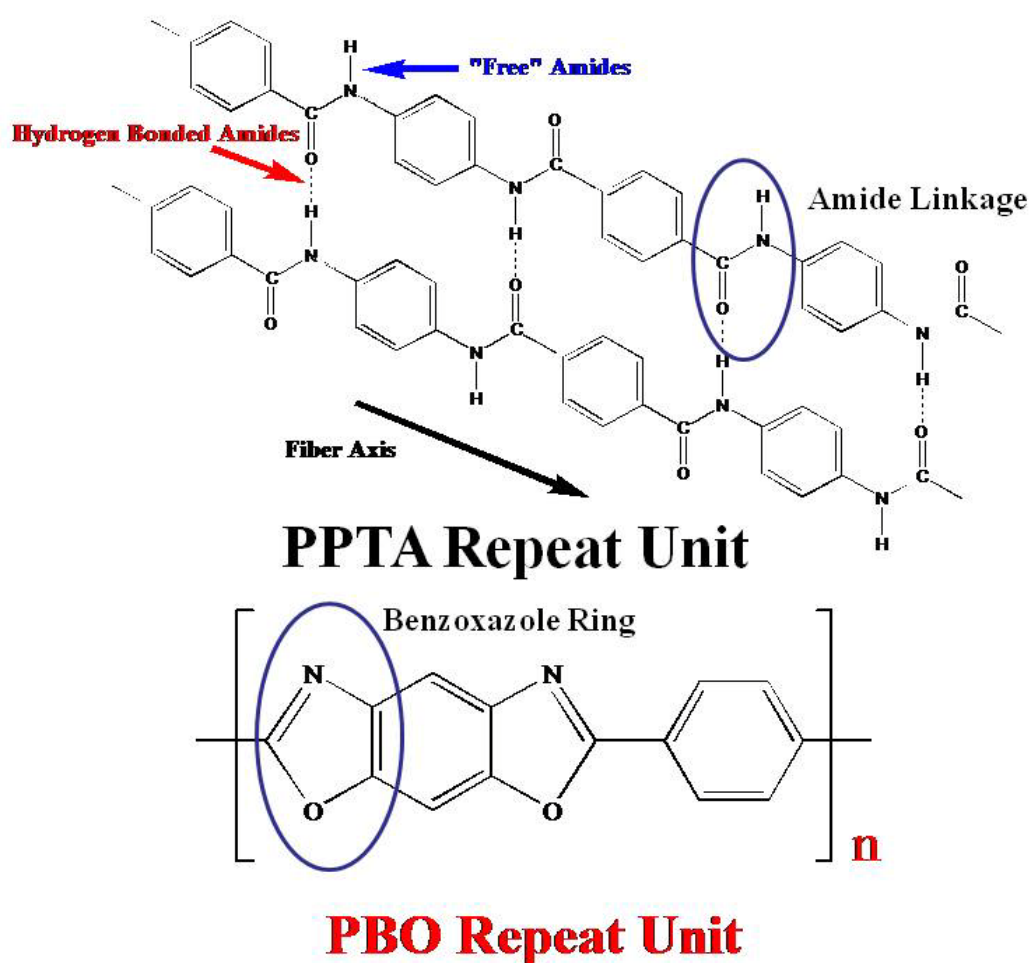


Figure 1. Polymer repeat units of poly(p-phenylene terephthalamide) (PPTA) and poly[(benzo-[1,2-d;5,4-d']-benzoxazole-2,6-diyl)-1,4-phenylene] (PBO).

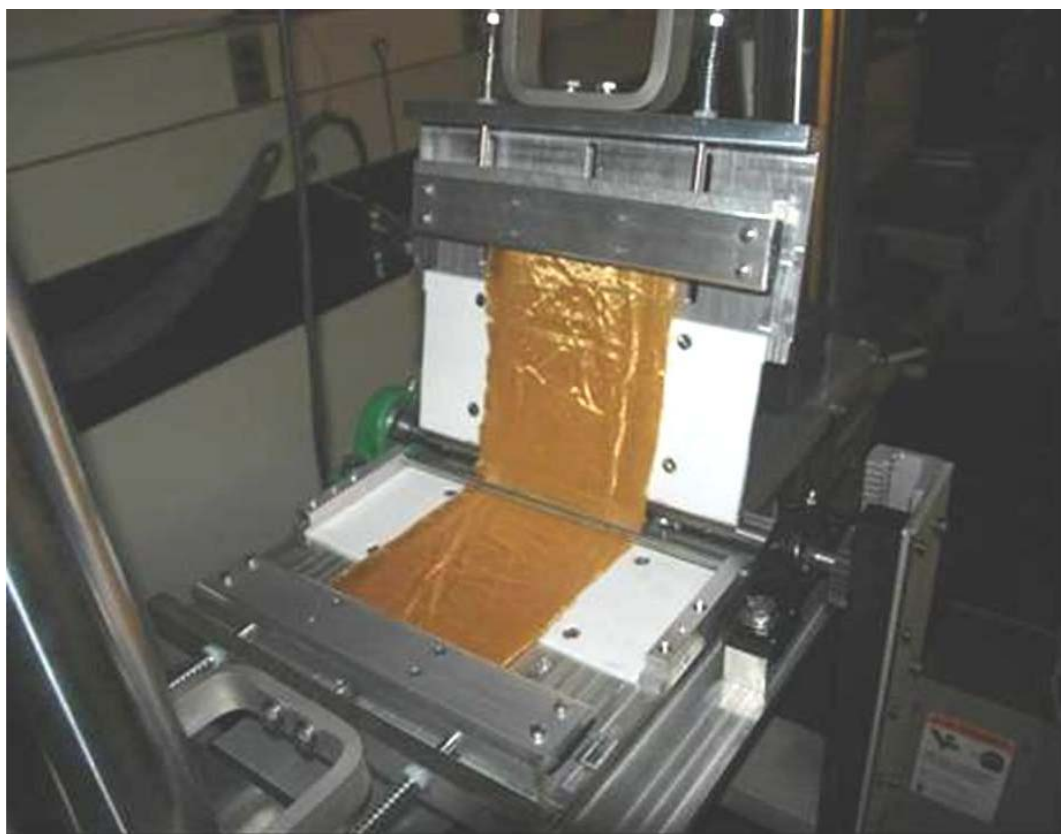


Figure 2. Folding apparatus with woven PBO fabric clamped in the sliding brackets and around the folding rod.

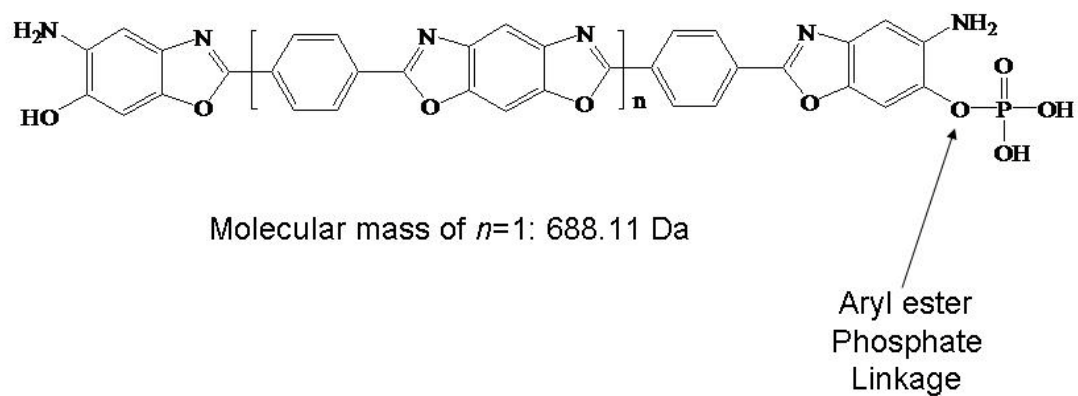


Figure 3. Chemical structure aryl-phosphate ester identified by MALDI-TOF-MS in low molecular mass PBO oligomers.

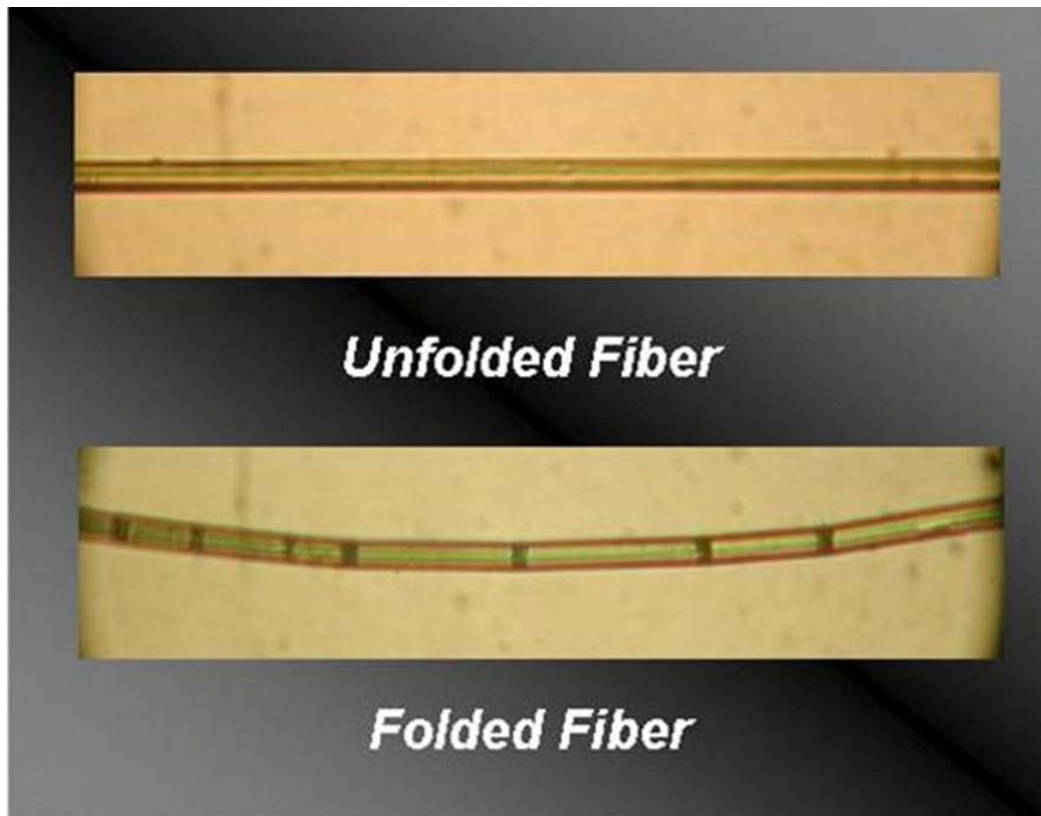


Figure 4. Damage induced by a single fold of PBO fibers. (Fibers are 12 μm in diameter).

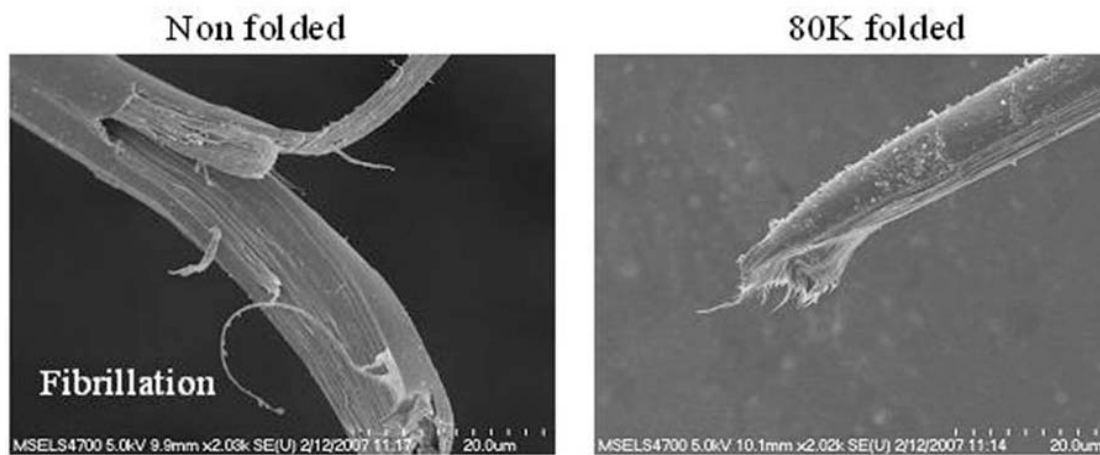


Figure 5. Effect of repeated folding on the failure behavior of PBO fibers.

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