

Degradation of Polymeric Ballistic Materials *

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Introduction There is great interest in the degradation of ballistic fibers from sunlight and high humidity, since it directly affects the lives of people who use protective ballistic armor. Polybenzoxazole (PBO), a rigid rod polymer developed by the Air Force Materials Laboratory [1], is a ballistic fiber material that has excellent strength, high mechanical modulus, good thermal stability, and superior chemical resistance. Recently, concerns have been expressed about the long-term stability of PBO fibers when exposed to hydrolytic environments [2]. The impact of pH and other factors on the stability of the benzoxazole ring structure found in PBO have recently been reviewed by Holmes et al. [3], with literature results indicating that the acid catalyzed hydrolysis degradation pathway of the benzoxazole ring of PBO is feasible but pH sensitive. However, to date, no mechanisms have been found to explain how these fibers degrade in the presence of sunlight or humidity. In this study, we investigated two hypotheses for the degradation mechanism of PBO fiber in the presence of phosphoric acid inclusion in PBO molecule using mass spectrometry. The first hypothesis suggests that residual phosphoric acid, if present, may be trapped in microvoids that are known to exist along the length of the PBO fiber [4]. In the presence of moisture, the trapped phosphoric acid in these microvoids is suspected of lowering the localized pH in the PBO material surrounding these voids, thereby creating a localized environment conducive for hydrolytic degradation. The second hypothesis suggests that the residual phosphoric acid, if present, may be chemically bound to the PBO polymer chain structure as a monoaryl phosphate ester

Methods Three model compound of PBO (called AF1, AF2, and AF3) were supplied by Thuy Dang of the Wright Patterson Air Force Base Research Laboratories (Molecular structures of these are shown in Figure 1). PBO fibers were obtained from a used vest that was returned to the NIST/OLES Division for analysis. PBO oligomers were synthesized in polyphosphoric acid following a method similar to that used commercially [5]. By adding 2-aminophenol to the procedure, we obtained oligomers of molecular mass suitable for analysis by Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS). MALDI-TOF MS, gas chromatography/mass spectroscopy (GC-MS), and X-ray fluorescence spectrometry (XRF) were used to confirm the presence of phosphoric acid and PBO oligomers that contain phosphoric acid moieties. Soxhlet extraction using distilled water was initially carried out to elute residual unbound phosphoric acid that may be present in the PBO fibers and synthesized PBO oligomers. After the initial extraction the fibers were then cut, crushed using a LN₂ mortar and pestle, and re-extracted to remove residual phosphoric acid that may be trapped in the microvoids of the fibers. A second extraction was also applied to the synthesized PBO oligomers. Extractants were analyzed by MALD-TOF MS, GC-MS, and XRF.

Results and Discussion To demonstrate the feasibility of using MALDI-TOF to analyze PBO oligomers, mass spectra of AF1, AF2, and AF3 were obtained from the mixture of sample powder with tetrahydrofuran/hydrochloric acid (THF/HCl) (2 mL/1 drop) using a dry sample preparation method and the plate covered with parafilm. These showed mono-dispersed peak without any matrix peak in lower molecular weight range. Using the same method a MALDI-TOF mass spectrum of the PBO oligomers was obtained (shown in Figure 2). An analysis of this spectrum shows the major PBO peaks in the oligomeric series to be end capped with 2-aminophenol. A second major species was also observed with only one end capped with 2-aminophenol and the other end uncapped. Additionally there were several other minor series. One of these was tentatively identified as a phosphate ester end cap. Phosphate esters are known to be resistant to hydrolysis by neutral water. Fluorescence analysis of the fibers before and after extraction revealed that only 25 % of the phosphorus in the fibers was removed on the initial soxhlet extraction (see Table 1). Methylation of the soxhlet extract showed there was no phosphoric acid in it. This suggests that the phosphorus containing species in the initial extract are associated with the processing aids used during the manufacturing process. Therefore, primary attention was focused on the second extract of these fibers, that extraction after the fibers were cut into smaller pieces and damaged with a LN₂ mortar and pestle. GC/MS analysis of the concentrated and methylated second extract also showed no presence of

phosphoric acid. A parallel analysis of the extractant from the soxhlet extraction of the synthesized PBO oligomers did indicate the presence of phosphoric acid. However, a MALDI analysis of these extracted oligomers showed that the peaks series tentatively identified as having a phosphate ester end cap were unaffected by the soxhlet extraction process. Consistent with these results, fluorescence analysis of the damaged PBO fibers indicated that no additional phosphorus was removed by the second soxhlet extraction. Therefore, 75 % of the phosphorus originally in the fibers remained in the fibers after two soxhlet extractions. Future research will involve the heating of the twice extracted PBO fibers and the extracted PBO oligomers in 1 N NaOH solution to hydrolyze any phosphorus that may be bound as phosphate esters to the PBO polymer chains. These extractants will then be concentrated, acidified, and methylated to check for phosphoric acid. Parallel analyses by fluorescence will be performed on the PBO fibers and oligomers to determine if the phosphorus level in these specimens were reduced by the caustic hydrolysis process.

Figures 1 to 2: (From left to right)

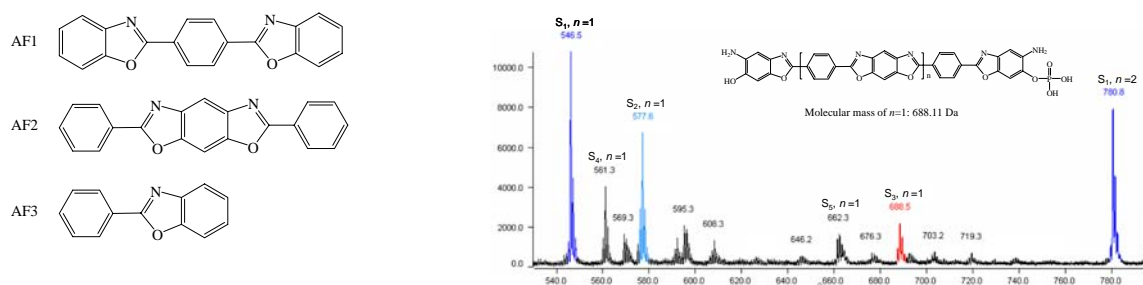


Table 1. X-ray fluorescence results from soxhlet extraction of PBO fibers

	P (% by mass)
Fiber Samples	
PBO Fibers (As received)	0.38
PBO Fibers (After cut)	0.28
PBO damaged (After cut using LN2)	0.30
PBO Model Oligomers	
PBO before extraction	1.4
PBO after extraction	0.062
Liquid Samples	
Blank Solvent	0.024
Extracted soln from PBO oligomer	0.80
Extract from Damaged PBO Fibers	0.026

* Estimated uncertainty is 0.02 % by mass

Conclusions The MALDI-TOF MS results of small model compound (AF1, AF2, and AF3) demonstrated the feasibility of using the MALDI technique for identifying oligomers of PBO and PBO oligomers that may contain bound phosphorus. Although no phosphoric acid was detected by extracting the PBO fibers with distilled water, the presence of phosphoric acid in the extractant obtained from the synthesized PBO oligomers attests to the feasibility of the soxhlet extraction process with subsequent concentration and methylation of the extractant for detecting residual free phosphoric acid. These negative results suggest that the residual phosphorus in the fibers may be bound to PBO oligomers as a phosphate ester. Future research is being designed to test this hypothesis.

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