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Effect of moisture on copolymer fibers based on 5-amino-2-(*p*-aminophenyl)-benzimidazole

Guillaume H.R. Messin[a], Kirk D. Rice[a], Michael A. Riley[a], Stephanie S. Watson[b], John R. Sieber[c], Amanda L. Forster[a,*]

[a] *Law Enforcement Standards Office, National Institute of Standards and Technology, Gaithersburg, MD, USA*
[b] *Engineering Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA*
[c] *Material Measurement Laboratory, National Institute of Standards and Technology, Gaithersburg, MD, USA*

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ABSTRACT

In recent years, there has been concern in the soft body armor community that copolymer fibers based on 5-amino-2-(*p*-aminophenyl)-benzimidazole can release hydrochloric acid, which is present in these fibers as a by-product of the manufacturing process. The presence of acids could potentially be detrimental to other fibers that might come in contact with these materials. In an effort to examine this issue, a study was designed to investigate the release of acid in different environments from these fibers. During the first phase of the study, fibers were exposed to water and pH decreases were observed. While immersed in deionized water, two of the fiber samples studied released a sufficient amount of acid to drop the pH of the solution from approximately pH 6.0 to approximately pH 3.0 in less than 10 d at room temperature. Further ion-selective electrode studies of chloride ion released from these fibers indicated that hydrochloric acid may not be the species responsible for this pH reduction. In a second phase of the investigation, fibers were exposed to water vapor in an elevated temperature environment (conditions were 65 °C, 80% RH). While the pH reduction released by the water vapor exposure was substantially less than observed in the submersion phase, a reduction in the yarn tensile strength of some of the fibers was observed during this phase of the study. In a third phase, fibers were exposed in a dry oven (less than 5% RH) at 65 °C. Almost no pH reduction or strength reduction was observed. Molecular spectroscopy was also performed to better understand the effect of elevated temperature and moisture environments on these fibers.

1. Introduction

Modern body armor utilizes a wide range of polymers to provide the level of performance required for these applications. The materials most commonly used in body armor are poly(*p*-phenylene terephthalamide) (PPTA) and ultra-high molecular weight polyethylene (UHMWPE); however, in an effort to expand consumer choices, several additional fibers have been recently introduced into the United States body armor marketplace. These fibers were developed in the former USSR in the late 1970s, and are based on several starting monomers [1]. Several of these fibers were investigated in this study, including Artec[1], Rusar, SVM, and Armos. PPTA and poly-(*p*-phenylenebenzobisoxazole) (PBO) fibers were used as comparison fibers. Artec, Rusar, and Armos all have the same basic chemical composition, as depicted in Fig. 1, and are formed by polycondensation reaction of two diamines, p-phenylene diamine and 5-amino-2-(*p*-aminophenyl)-benzimidazole with terephthalic acid (or anhydrides or acid chloride derivatives of these monomers).

PPTA fibers, sold under trade names Kevlar and Twaron, are manufactured by polycondensation of *p*-phenylenediamine with terephthalic acid. The structure of PPTA fibers is shown in Fig. 2. For the purposes of this work, linkages between terephthalic acid and 5-amino-2-(*p*-aminophenyl)-benzimidazole will be referred to as benzimidazole linkages and linkages between *p*-phenylene diamine and terephthalic acid will be referred to as PPTA linkages.

PBO, sold under trade name Zylon, is a member of the benzazole-polymer family and is characterized by the heterocyclic benzobisoxazole group in its main chain structure, as shown in Fig. 3. The conjugated benzobisoxazole and phenyl rings in the PBO repeat unit contribute to extended π electron delocalization and molecular

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* Corresponding author.
E-mail address: amanda.forster@nist.gov (A.L. Forster).

[1] 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 this purpose.

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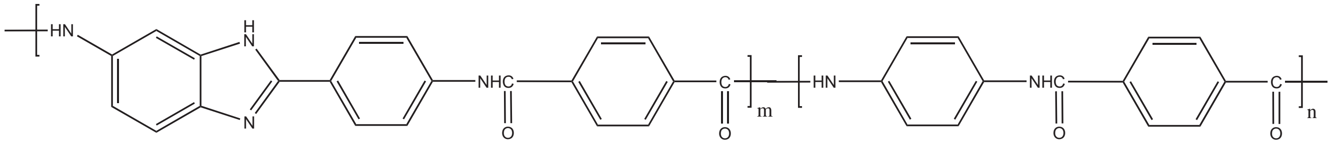

Fig. 1. Basic chemical structure of the copolymer fibers (Armos, Rusar, and Artec).

rigidity, which provides high thermal stability and outstanding mechanical properties to this class of polymers.

The main difference between these fibers is the ratio of benzimidazole linkages to PPTA linkages [2]. While specific information on these ratios is difficult to obtain, one weaver of these fibers supplied information indicating that in the case of Artec, the ratio of PPTA to benzimidazole linkages was 2:1, and in the case of Rusar, the ratio of PPTA to benzimidazole linkages was 1:1. Additionally, Rusar is made with raw materials sourced from Eastern Europe, and Artec is made with raw materials sourced from the United States [3]. Late in the course of the completion of the study, it was discovered that Rusar and Artec fibers may actually be the same [4]. Since no official data was published to confirm that these two fibers were similar, it was then decided to keep considering them as two different materials.

Another fiber that was investigated in this study is sold under the trade name SVM. This homopolymer fiber is manufactured by direct polycondensation of 5-amino-2-(*p*-aminophenyl)-benzimidazole with terephthalic acid [5]. The structure of SVM fiber is shown in Fig. 4.

In a communication to the body armor community released in January 2006, there was an allegation by a competing fiber manufacturer that copolymer fibers based on 5-amino-2-(*p*-aminophenyl)-benzimidazole can release hydrochloric acid, which could potentially be detrimental to other fibers that might come in contact with these materials [6]. Despite the fact that these allegations came from a competing manufacturer, due to recent issues with degradation of another fiber in field use, it was decided that this allegation should be investigated to see if it was an officer safety issue.

1.1. Fiber manufacture

While details of the specific processes by which these fibers are made is difficult to find in the literature, a general idea of the fabrication of Armos fiber can be determined from a paper published by Machabala et al. in 2000 [7]. One can readily assume that the general processing steps would apply to the other fibers as well. The homopolymer (SVM) or copolymer (Armos, Rusar, Artec) is manufactured by polycondensation of terephthalic acid chloride and some combination of para-aromatic diamines (p-phenylenediamine or 5-amino-2-(*p*-aminophenyl)-benzimidazole) in an amide-salt solvent system (specified as dimethylacetamide and lithium chloride in the Machalaba paper) [7]. The polymer formed from this reaction is then filtered and degassed prior to being spun into a filament yarn. This yarn is then drawn and heat treated to form the final finished product. PPTA and PBO fibers were used as reference fibers in this study, and their specific processing information will not be detailed in this report [8,9].

1.2. Structure, moisture sorption, and other properties

Slugin et al. published two papers in 2006 related to the use of Rusar fibers for composites and ballistic protection applications. Additional information is given regarding the rationale for use of the co-monomer 5-amino-2-(*p*-aminophenyl)-benzimidazole. A paper published by Perepelkin in 2001 compares the properties of Armos and SVM with commercial polyamide yarns. The primary difference between these fibers is in their structural properties. Polyamide fibers have a fibrillar structure with stretched chains and three-dimensional order. SVM fibers also have a fibrillar structure with stretched chains, but only one-dimensional crystalline order. The Armos fiber has a fibrillar structure with stretched chains, but no crystalline order. The strength at break of the Armos fiber is reported at 4.5 GPa–5.5 GPa as compared to 2.7 GPa–3.5 GPa for the polyamide fibers, leading the authors to conclude that crystallinity is not a prerequisite for preparing fibers with good mechanical properties [10]. It appears that the Armos fiber has been investigated for use in composite applications due to its unique transverse mechanical properties. A paper by Leal et al. from 2007 attributes the ability to achieve greater draw ratios, better molecular orientation, and improved mechanical properties to lack of three-dimensional organization in the Armos fibers. Additionally, Armos develops intermolecular hydrogen bonds that allow for stress transfer between adjacent chains. This improves the compressive properties of the fiber and makes it attractive for use in composite applications [2,11]. Studies on the moisture sorption properties of several fibers as compared to PPTA have shown that Rusar has very similar sorption isotherms to PPTA. Differences in the sorption properties of these materials are attributed to the lower crystallinity of SVM and Rusar as compared with PPTA. As previously discussed, the benzimidazole linkages in these polymers do not crystallize as readily as the more linear polyamide linkages do [12,13].

Much work [14–17] has been performed to investigate the thermal stability of these fibers for use in high-temperature environments and fire applications. These materials are chemically similar to other fibers used in fire-resistant applications, such as para-aramid and meta-aramid fibers, so interest in their thermal properties is not surprising. The decomposition temperatures in air for Armos showed that it was stable to oxidation and onset of degradation to approximately 400 °C [15]. A separate study on the thermal stability of PPTA, SVM, Rusar, and Armos fibers in which

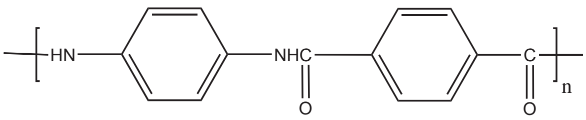

Fig. 2. Basic chemical structure of PPTA fibers.

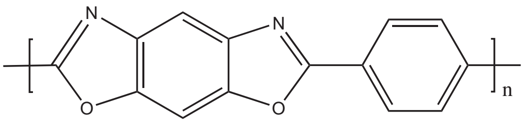

Fig. 3. Basic chemical structure of PBO fibers.