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Review

Ballistic fibers: A review of the thermal, ultraviolet and hydrolytic stability of the benzoxazole ring structure*

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The penetration of a bullet proof vest worn by a first responder in 2003, resulted in the establishment of a research program designed to investigate the long-term stability and durability of all fibers that are used and have the potential to be used in ballistic applications. The Office of Law Enforcement Standards (OLES) of the National Institute of Standards and Technology (NIST) was charged with conducting this program under the auspices of the National Institute of Justice (NIJ). Because of the urgent need to understand the factors that contributed to this unexpected body armor penetration, the initial focus of this research program is on the ballistic fiber material that composed the compromised vest, i.e., poly[(benzo–[1,2-d:5,4-d′]-benzoxazole-2,6-diyl)-1,4-phenylene] (PBO) fiber. Since data related to the susceptibility of PBO fibers to environmental attack are limited and sometimes contradictory, this review also focuses on the susceptibility of the benzoxazole ring structure, a major component of the PBO chain structure, to environmental exposure conditions. A somewhat detailed discussion of the formation and degradation chemistry of this ring structure is presented to increase the reader's understanding of how chemical structure and environmental factors may influence ballistic fiber degradation. To balance this discussion, the susceptibility of key linkages in other ballistic fibers to similar conditions is also presented. Therefore, this review seeks to link chemical structure to ballistic performance and provide a fundamental basis for predicting the long-term durability of existing and future ballistic fibers.

Glossary

PBX	polybenzazole
PPT	poly(*p*-phenylene terephthalamide) or Kevlar
PPTA	poly(*p*-phenylene terephthalamide) or Kevlar
PBO	poly[(benzo–[1,2-d:5,4-d′]-benzoxazole-2,6-diyl)-1,4-phenylene] or poly(benzoxazole)
PBT	poly[(benzo–[1,2-d:4,5-d′]-benzothiazole-2,6 -diyl)-1,4-phenylene] or poly(benzothiazole)
PBI	polybenzimidazole

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PIPD	poly[2,6-diimidazo-(4,5-b:4′5′-e)pyridinylene-1,4-(2,5-dihydroxy)phenylene] or M5
PPA	poly(phosphoric acid)
DADTB	dihydrogenchloride of 1,4-diamino-2,5-dithiobenzene
DADHB	dihydrogenchloride of 1,3-diamino-4,6-dihydroxybenzene
TA	terephthalic acid
DHTA	2,5-dihydroxyterephthalic acid
BO	benzoxazole
2-MeBO	2-methylbenzoxazole
2-PhBO	2-phenylbenzoxazole
2-MeBT	2-methylbenzothiazole
2-MeBI	2-methylbenzimidazole
MSA	methanesulfonic acid
NMR	nuclear magnetic resonance
U*	normalizing velocity as defined by Cunniff and Auerbach

1. Introduction

Although poly(*p*-phenylene terephthalamide) (PPT, PPTA, or Kevlar) ballistic fibers, the industry standard, are known to be susceptible to ultraviolet (UV) and hydrolytic degradation [1, 2], the more recently commercialized poly[(benzo–[1,2-d:5,4-d′]-benzoxazole-2,6-diyl)-1,4-phenylene] (PBO) fiber, which is considered an alternative to Kevlar in ballistic applications, has been the focus of recent discussions concerning the life expectancy of ballistic-resistant armor. PBO evolved out of the pioneering research of Vogel and Marvel [3, 4] on thermally stable polybenzimidazole (PBI) polymers. Their research was extended by the U.S. Air Force (USAF) and National Aeronautics and Space Administration (NASA) to address specific aerospace and defense needs in the 1970s and 1980s [5]. As a result the rigid-rod research program was formed and directed toward the development of new structural materials having low density, high strength, high modulus, and long-term retention of these properties at elevated temperatures [6, 7]. PBO is part of a sub-class of rigid-rod polymers known as polybenzazoles (PBX) polymers of which polybenzimidazoles (PBIs) and poly[(benzo–[1,2-d:4,5-d′]-benzothiazole-2,6-diyl)-1,4-phenylene] (PBT) are also members. Fibers prepared from PBX polymers have been reported to have superior tensile strength and modulus, cut and abrasion resistance, and flame resistance [7], although at least one report suggests that the abrasion resistance of PBO is poor [2, 8].

To better understand the driving force for using PBO fiber in ballistic applications, it is worthwhile reviewing the criterion proposed by Cunniff and Auerbach for assessing the performance of ballistic fibers [9]. From a dimensional analysis study, these researchers concluded that the principal fiber property of interest in relating the V_{50} performance of any armor system material to any penetrator, independent of the system areal density, is the $(U^*)^{1/3}$parameter, which is the product of the elastic energy storage capability of the fiber per unit mass ($\sigma\varepsilon/2\rho$, fiber specific toughness) and strain wave velocity ($\sqrt{E/\rho}$, where Poisson's ratio, ν, has been ignored) and is expressed in terms of *m/s* (i.e., meters per second). A theoretical basis for using this equation was recently established by Phoenix and Portwal [10].

$$[U^*\{m^3/s^3\}]^{1/3} = \left[\frac{\sigma\varepsilon}{2\rho}\sqrt{\frac{E}{\rho}}\right]^{1/3}$$

(Cunniff and Auerbach Equation)

where, σ is the fiber ultimate axial tensile strength, ε is the fiber ultimate tensile strain, ρ is the fiber density, E is the linear elastic fiber modulus

Using this criterion, the performance of any ballistic fiber can be estimated from its fundamental mechanical properties, and since the fibers are assumed to be linear elastic (i.e., $\sigma = E\varepsilon$), the $(U^*)^{1/3}$parameter can be obtained from a fiber's ultimate tensile strength, strain-to-failure, and density (experimentally measurable variables). An example of such calculations is in the cited paper by Cunniff and Auerbach, where they, using standard material properties, calculated the theoretical ballistic performance of PBO fibers, Kevlar fibers, and many of the other known fibers considered for ballistic applications (see Table I).

For completeness, the single fiber density was back calculated from the data provided using the Cunniff and Auerbach equation. These results were found to be consistent with published densities [9, 11], except for the density obtained for the Kevlar 49 fiber. This difference seems to be associated with the use of an incorrect value for the failure strain. Results from another publication [1] indicate a 2.3% failure-strain for this fiber rather than 1.2%. Using this value, a density of approximately 1.41 g/cm^3 is obtained, which is closer to the published value of 1.45 g/cm^3. Included in this list is a new fiber made from poly[2,6-diimidazo-(4,5-b:4′5′-e) pyridinylene-1,4-(2,5-dihydroxy)phenylene] (PIPD or M5), a PBI rigid-rod polymer. The Army has considered the M5 fiber as an alternative to PBO. However, the $(U^*)^{1/3}$ parameter of PBO still exceeds the predicted performance of all currently available fibers (see Table I).

These data suggest that protective vests composed of PBO and Spectra 1000 fibers can be made 25% lighter than the corresponding Kevlar vest, while still providing the same ballistic protection [9]. If the conservative goal of the M5 fiber is achieved, ballistic-armor mass can be reduced by over 40% relative to the mass of Kevlar body armor. However, it should be noted that the exceptional ballistic performance predicted for Spectra 1000, i.e., ultra high molecular weight polyethylene (UHMWPE), fibers is not realized in ballistic testing. This discrepancy is likely due to the apparent melting of the fibers during the

TABLE I Theoretical Ballistic Performance of Common Fibers

Fiber	Density (Calc.) (ρ) (g/cm^3)	Strength (σ) (GPa)	Failure Strain (ε) (%)	Modulus (E) (GPa)	$(U^*)^{1/3}$ (m/s)
PBO (as spun)	(1.56)	5.20	3.10	169	813
Spectra 1000	(0.97)	2.57	3.50	120	801
600 den. Kevlar KM2	(1.44)	3.40	3.55	82.6	682
850 den. Kevlar KM2	(1.44)	3.34	3.80	73.7	681
840 den. Kevlar 129	(1.44)	3.24	3.25	99.1	672
1500 den. Kevlar 29	(1.44)	2.90	3.38	74.4	625
200 den. Kevlar 29	(1.44)	2.97	2.95	91.1	624
1000 den. Kevlar 29	(1.44)	2.87	3.25	78.8	621
1140 den. Kevlar 49	(0.91)	3.04	1.20	120	612
Carbon fiber	(1.80)	3.80	1.76	227	593
E-glass fiber	(2.89)	3500	4.70	74	559
Nylon		0.91	N/A	9.57	482
M5 (2001 Sample)	(1.74)	3.96	1.40	271	583
M5 Conservative	(1.70)	8.50	2.50	300	940
M5 Goal	(1.70)	9.50	2.50	450	1043

impact event [9], suggesting that the glass transition temperature of the polymer fiber and/or the temperature at which the polymer undergoes strain induced melting may be important. In other words, although the modulus properties in the Cunniff and Auerbach equation are assumed to be linear elastic (i.e., mechanical properties independent of temperature and deformation rate), in reality most ballistic fibers are viscoelastic (i.e., properties dependent on temperature and deformation rate). Noting that the M5 fiber is a PBX fiber, the resistance of M5 fibers to UV exposure and hydrolytic action suggests that a fundamental understanding of the structure-property relationship of ballistic fibers is warranted.

Although there has been preliminary data suggesting that PBO fibers, like other ballistic fibers, are susceptible to reductions in strength due to UV and hydrolytic exposures [2, 9], there has been no fundamental investigation linking these results to structural changes within the fiber structure and its mechanical properties. Because the use of PBO fibers in ballistic applications is relatively new, this report will review what is known about the chemical structure of PBO and similar fibers. Therefore, PBO chemistry will be reviewed, followed by a discussion of the environmental stability of the chemical units that comprise PBO and related polymers. This review will conclude with some speculation of how subtle changes in the chemical structure of PBX type polymers may influence ballistic properties and environmental stability.

2. Chemistry of PBX and related ballistic fibers

The two most widely known PBX fibers, PBT and PBO, are prepared by the reaction of the dihydrogenchlorides of 1,4-diamino-2,5-dithiobenzene (DADTB) and 1,3-diamino-4,6-dihydroxybenzene (DADHB) with terephthalic acid (TA) or its derivatives in poly(phosphoric acid) (PPA) [6, 7, 12–16] (see Fig. 1).

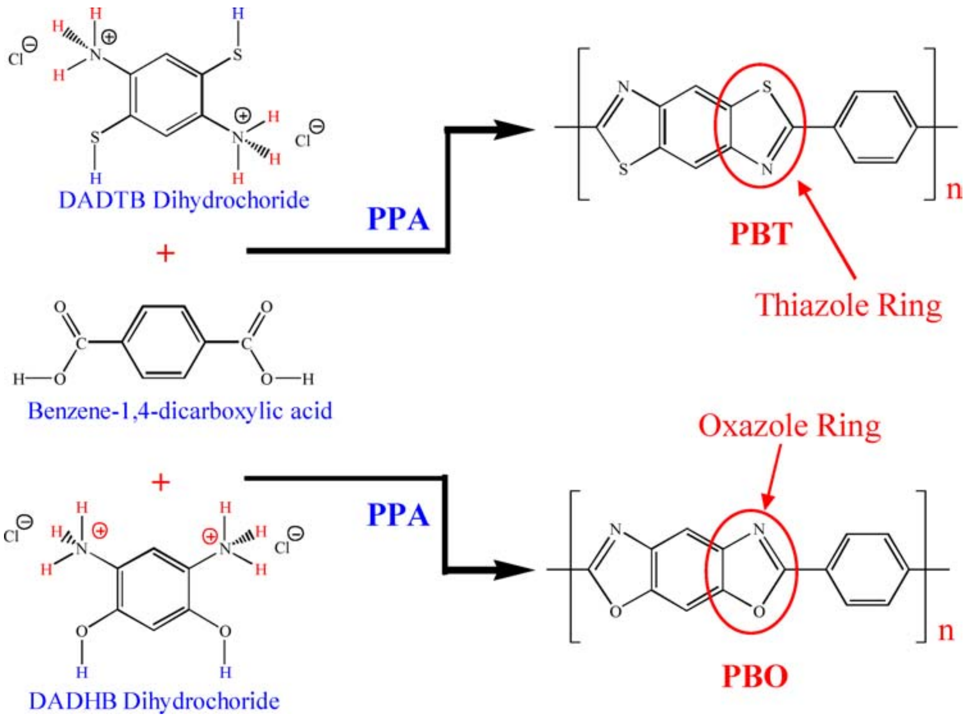


Figure 1 Chemistry for benzothiazole (PBT) and benzoxazole (PBO).

The key structural feature of these two polymers is the formation of the benzothiazole and benzoxazole ring structures. Using ^{13}C and ^{31}P nuclear magnetic resonance (NMR), So and Heeschen [7, 15] contributed to the existing knowledge base of benzoxazole ring formation [6, 12, 13, 17, 18] by investigating, through model compound research, how poly(phosphoric acid) (PPA) works as a reagent. Using the model compounds: benzoic acid, 2-aminophenol and 4-aminophenol, these researchers observed that benzoic acid is activated through the formation of benzoic-phosphoric anhydride that is in dynamic equilibrium with benzoic acid and PPA. In addition, the amino group of 2-aminophenol is protonated and about 90% of the hydroxyl groups exist as phosphate esters. Therefore, the 2-aminophenol derivatives and PPA are in dynamic equilibrium. These researchers propose that the free hydroxyl portion of the protonated 2-aminophenol reacts with the benzoic-phosphoric anhydride to generate the ester, 2-aminophenyl benzoate. This intermediate undergoes rapid acyl migration to form (2-hydroxyphenyl)benzanilide, which then undergoes acid-catalyzed ring closure to generate 2-phenylbenzoxazole (see reaction scheme in Fig. 2). These results are consistent with the reaction pathway deduced by Choe when terephthaloyl diacid chloride is the reacting species [17]. In addition, the research of Wolfe *et al.* [6, 12] suggests that the reaction mechanism for PBT is similar.

In the PBO reaction, the ratio of benzoic acid to mixed anhydride was found to increase dramatically as the P_2O_5 content increased from 77% to 87%. As a result, the reaction proceeds most effectively using PPA whose P_2O_5 content is greater than 85% [15]. In addition to activating benzoic acid and 2-aminophenol for reaction, PPA, with a high P_2O_5 content, reacts with the water generated during the acid catalyzed ring closure step and drives the polymerization reaction toward completion. Therefore, the dynamic equilibrium that would normally exist between 2-hydroxybenzanilide and 2-phenylbenzoxazole is driven toward the benzoxazole ring structure by the continued elimination of the water generated during the ring closure reaction. As will be shown, this provides a basis for understanding the hydrolysis mechanism of the benzoxazole ring structure.

Elemental analysis of commercial PBO fibers indicates a residual phosphorus content of 0.34% atomic mass fraction [9]. Although the impact of residual phosphorus on the stability of the PBO ring structure has not been established, it is interesting to note that the M5 fiber contains only 0.11% residual phosphorus. Again, M5 has the PBX structure and is reportedly stable to UV and hydrolytic action [9]. From the reaction mechanism proposed by So *et al.* [15], it is plausible that the residual phosphorus may exist in the polymer fiber as phosphoric anhydride or phosphate esters of the aromatic amine.

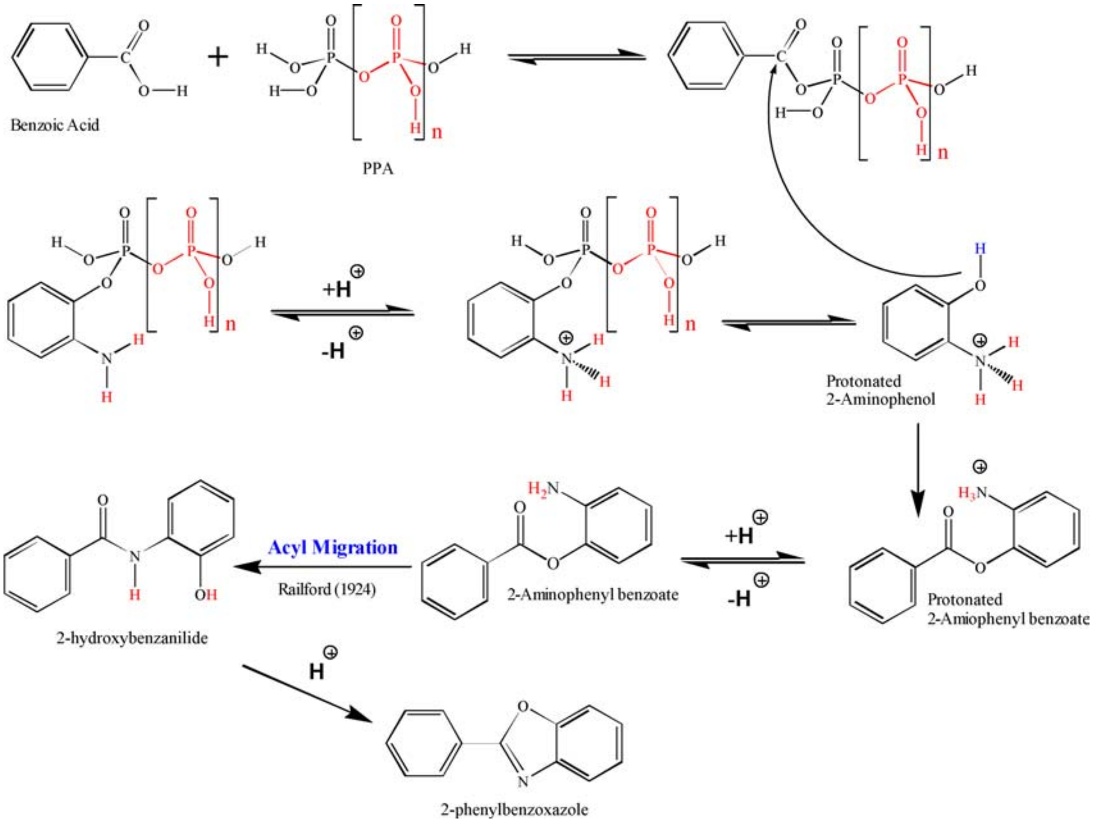


Figure 2 Reaction of benzoic acid and 2-aminophenol in poly(phosphoric acid) (PPA). (*after* So and Heeschen [7, 15]).

Although PBIs are a member of the PBX rigid-rod polymer class (with X = NH), these polymers have a greater solubility and capability of absorbing water than PBO or PBT. Traditionally, these polymers have been synthesized by reacting diphenyl isophthalate with a tetraaminoaromatic such as tetraaminobiphenyl (TAB) [3, 4, 19]. However, in 1998 Sikkema [20] reported the synthesis of poly[2,6-diimidazo-(4,5-b:4′5′-e)pyridinylene-1,4-(2,5-dihydroxy)phenylene] (PIPD or M5) from 2,5-dihydroxyterephthalic acid (DHTA) and 2,3,5,6-tetraaminopyridine (TAP) (see Fig. 3). TAP was prepared by aminating 2,6-diaminopyridine, while Sikkema obtained DHTA by aromatizing diethyl succinoylsuccinate in acetic acid at reflux with 30% aqueous hydrogen peroxide with a sodium iodide catalyst, followed by hydrolysis. Tan *et al.* [21] note two other methodologies for preparing DHTA.

In comparing Figs. 1 and 3, one can readily see that M5 is similar to PBO and PBT with the following exceptions: (a) the central aromatic ring for M5 is pyridinyl rather than benzenyl, (b) a hydroxyl group is located at the 2- and 5-positions of the contributing diacid, and (c) the "X" group in the benzazole ring structure is NH rather than O or S. As will be discussed in subsequent sections, the key features of M5 are that it has a higher compressive strength than PBO or PBT, and it is more stable to UV and hydrolytic action than PBO. It is reasonable to assume that the NH group contributes to the greater solubility and water absorbing capability of this polymer relative to PBO or PBT.

Kevlar, poly(*p*-phenylene terephthalamide) (PPT or PPTA), is a rod-like aramid fiber. The generic term aramid is defined as a synthetic polyamide in which at least 85% of the amide –(CO–NH)– linkages are attached directly to two aromatic rings. Consistent with this definition, the Kevlar polymer is a polycondensation product of terephthaloyol diacid chloride and *p*-phenylenediamine [22] (see Fig. 4).

The rigid character of Kevlar has been attributed to the carbon-nitrogen bond of the amide group having considerable double bond character. This partial double bond character is the result of a resonance-conjugated system that increases the rotational activation energy of the carbon-nitrogen bond to approximately 22 kcal/mol; whereas the rotational activation of the single bond would be between (2 and 4) kcal/mol. Therefore, the restricted rotation contributes greatly to the stiffness of the molecule [23]. In addition to having a medium-to-ultrahigh tensile strength, medium-to-low elongation, and moderately high-to-ultrahigh modulus, the rigid linear molecular chains of Kevlar fibers are highly oriented in the fiber-axis direction and are held together in the transverse direction by hydrogen bonding [1, 22].

To summarize this section, the key structural features of the PBO (benzoxazole ring), M5 (benzimidazole ring), and Kevlar (amide linkages) rigid rod polymers that are currently targeted for ballistic applications are highlighted in Fig. 6, by suppressing the benzene type ring structures.Note that the structures of PBO, PBT, and PBI are similar except that the oxygen (O) atoms in the PBO structure are *cis* to each other, while the sulfur (S) and saturated nitrogen (NH) atoms of PBT and PBI, respectively are *trans* to each other. Interestingly, the structure of M5, which is reportedly hydrolytic and UV stable, has

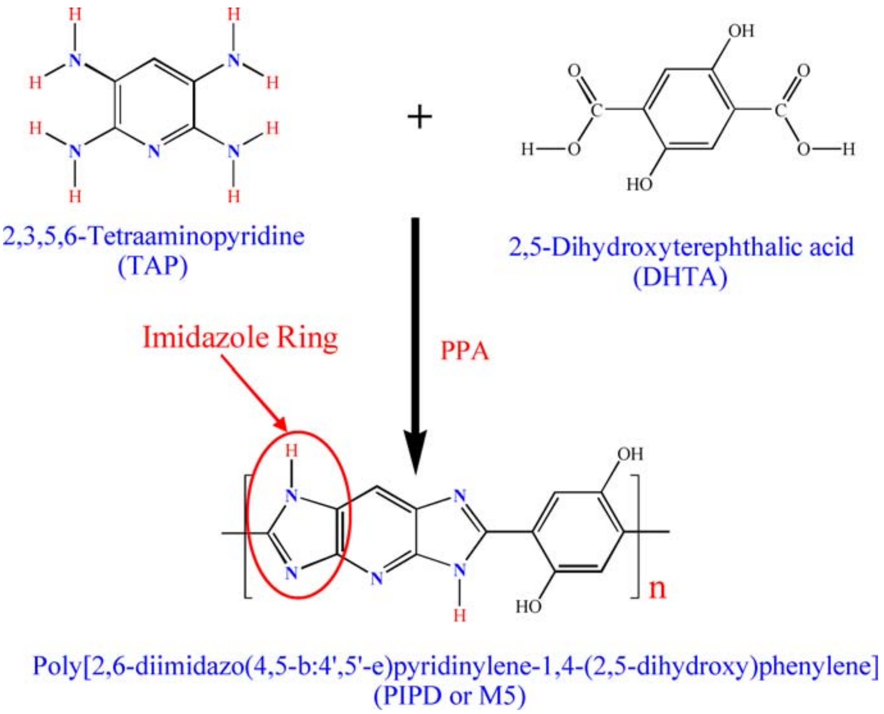


Figure 3 Chemistry for forming the poly[2,6-diimidazo-(4,5-b:4′5′-e)pyridinylene-1,4-(2,5-dihydroxy)phenylene] (PIPD or M5) benzazole.

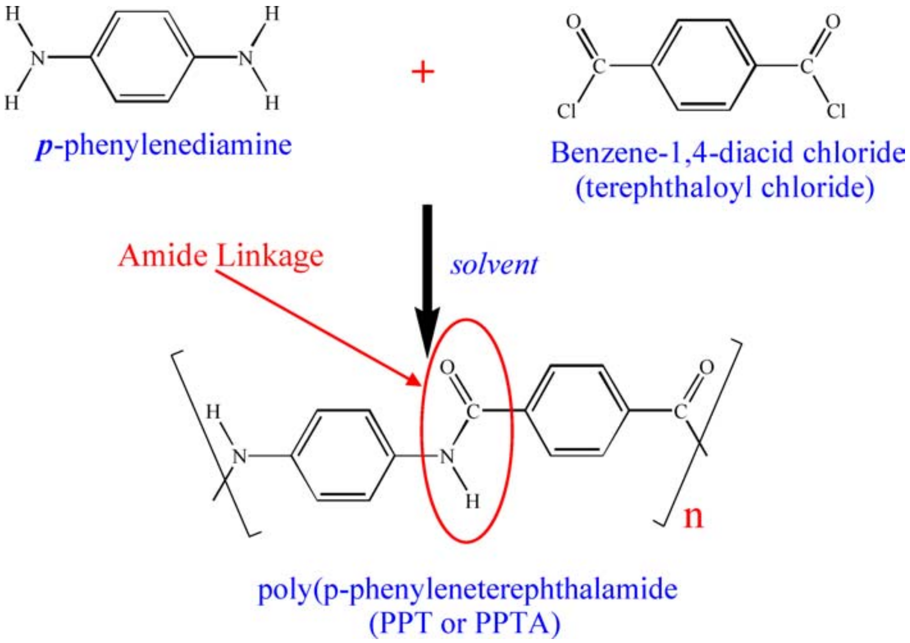


Figure 4 Chemical structure of Kevlar or poly(p-phenyleneterephthalamide).

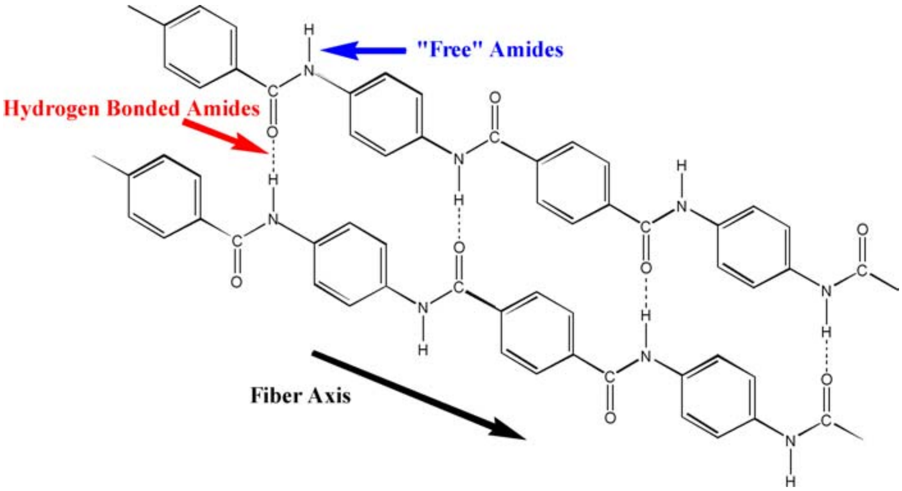


Figure 5 Hydrogen bonding in Kevlar fibers. (*adapted from* [1]).

a structure very similar to PBI, except that the benzene ring structure between the two imidazole rings contains a nitrogen (N) atom and the diacid used to form the imidazole ring structure in the M5 polymer contains two hydroxyl groups. Kevlar differs from the PBX polymers by having repeat amide linkages (NHCO) as the key structural unit that forms the polymer chain. This is particular interesting since one of the proposed hydrolytic degradation pathways of the benzoxazole ring (see next section) suggests the generation of this amide linkage prior to complete chain scission.

3. Hydrolytic stability of the benzazole ring

The 1930 research of Phillips [24] appears to be the first indication that the benzoxazole ring structure (found in PBO) may be more unstable in aqueous conditions than benzimidazoles (contained in the M5 fiber) and benzothiazoles (PBT fiber). In 1972, Jackson *et al*. [25] investigated the ring cleavage of the benzoxazole ring under mild conditions. The effect of pH on the first-order rate constant for the hydrolysis of benzoxazole (BO) and 2-methylbenzoxazole (2-MeBO) is shown in Fig. 7. The peak maxima at pH = 0.35 and 1.35, respectively, are consistent with the hydrolysis behavior exhibited by aliphatic oxazolines and aliphatic thiazolines [26, 27] (i.e., a reduction of hydrolysis rate at very low and very high pH). The low aqueous solubility of 2-phenylbenzoxazole (2-PhBO), which is most applicable to the PBO structure of interest, precluded a direct comparison with BO and 2-MeBO. However, a comparison study between 2-PhBO and 2-MeBO in 80% aqueous methanol showed that replacement of the methyl group by a phenyl group produced a dimunition of reactivity of ca. 100 for solutions (0.05 to 1.00) mol/L hydrochloric acid. The results suggest a dependency of the hydrolysis rate and peak maxima on the substituent that is at the 2-position of the benzoxazole ring.

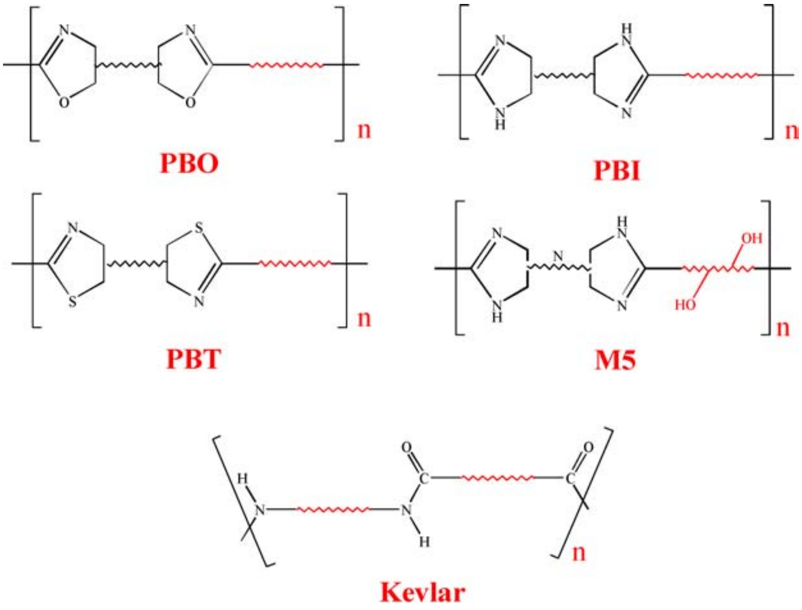


Figure 6 Key structural features of PBX (i.e., PBO, PBT, PBI, and M5) and Kevlar fibers.

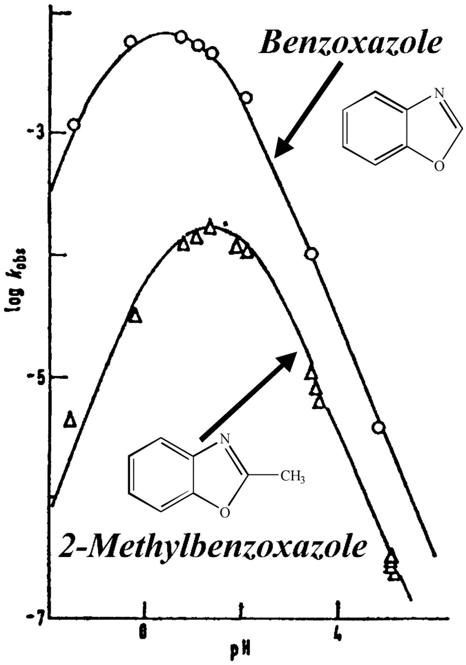


Figure 7 Effect of pH on first-order rate constant for the hydrolysis of benzoxazole and 2-methylbenzoxazole. Experimental values are marked as points; the curve was calculated by Jackson *et al.* (*adapted from* [25]).

From the computations of Dewar *et al.* ([28] and discussion in [25]), the increased reactivity of benzoxazoles relative to benzimidazoles and benzothiazoles seems to parallel the lower aromatic stability of the oxazole ring system and suggest that the hydrolytic process may proceed by nucleophilic attack on the polar carbiminyl bond. Consistent with these data, Skraup and Moser in [29] speculated that an intermediate 2-hydroxy-benzoxazoline is formed during benzoxazole hydrolysis. Since this intermediate can also be found in imidazoles and thiazoles, Jackson *et al.* [25] found several literature references indicating that this intermediate collapses in imidates, oxazolines, iminolactones, and thiazolines to the expected mixture of degradation products corresponding to C–N and C–O fission.

However, these researchers observed that benzoxazole and its 2-methyl and 2-phenyl derivatives are abnormal in giving only the product of C–O fission. The abnormal behavior is best understood pictorially using the hydrolysis mechanism for 2-phenylbenzoxazole (see Fig. 8). Recall that this compound was used by So and Heeschen [7, 15] to elucidate the catalytic role of PPA in benzoxazole ring formation (see Fig. 2). In Fig. 8, the C–N and C–O fission products for 2-phenylbenzoxazole are shown. In exact agreement with the mechanism shown in Fig. 2, the C–N fission product undergoes rapid acyl migration to yield 2-hydroxybenzanilide, i.e., the C–O fission product. Therefore, it is probable that both pathways are viable with the subsequent acyl migration of the C–N product resulting in the final distribution of hydrolysis products.

In 1989, Werstiuk and Ju [30] exposed 2-methyl benzothiazole (2-MeBT), 2-methyl benzimidazole (2-MeBI), and 2-methyl benzoxazole (2-MeBO) to neutral D_2O at elevated temperatures. Although 2-MeBT and 2-MeBI were found to undergo deuterium exchange at 145°C, 2-MeBO underwent facile hydrolysis to 2-acetamidophenol, the C–O fission product, at 115°C with the incorporation of deuterium into the methyl group. This result is consistent with the speculations of Dewar *et al.* [28] and Jackson *et al.* [25], that the oxazole ring system has lower aromatic stability than thiazole and imidazole ring systems (see Fig. 6).

At higher temperatures Werstiuk and Ju note that the amide 2-acetamidophenol undergoes further hydrolysis

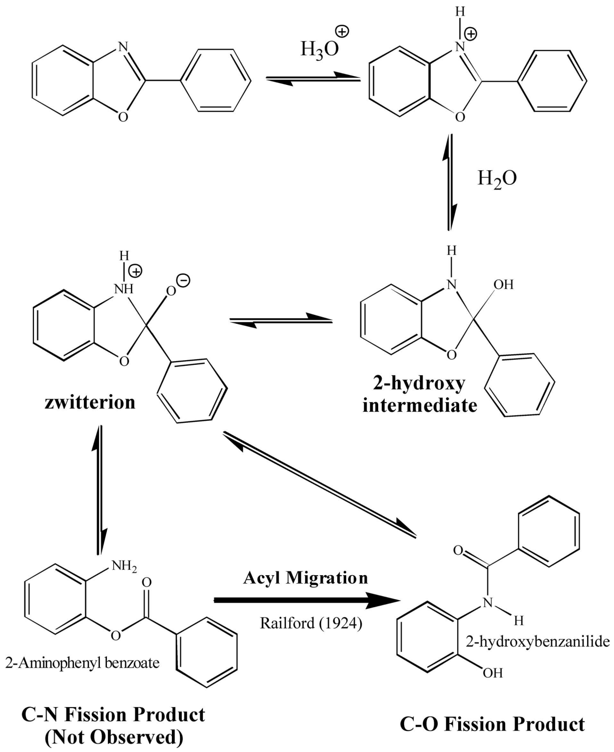


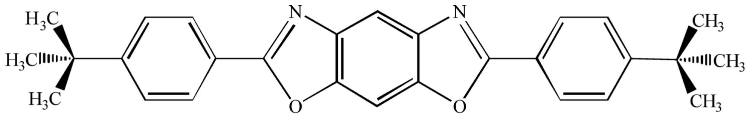
Figure 8 Hydrolysis pathway for 2-phenylbenzoxazole. (*after Jackson et al.* [25]).

to 2-aminophenol and acetic acid. This finding is consistent with March [31] who states that "Water alone is not sufficient to hydrolyze most amides, since NH_2 is even a poorer leaving group than OR. Prolonged heating is often required, even with acidic or basic catalysts." The above observations leave open the question of whether PBO fibers, under the normal use expected of protective vest, degrade with chain scission to the o-phenol and acid byproducts. Furthermore, these results and observations suggest that hydrolysis of PBO fibers under normal use in protective equipment may stop at the amide linkage depicted in Fig. 8. Since the strength of a PBO microfiber will be controlled by the strength of the weakest link, this further suggests that PBO's strength, if strongly acidic or basic conditions are not present, during hydrolytic degradation may reach a lower bound comparable to the aramid, Kevlar.

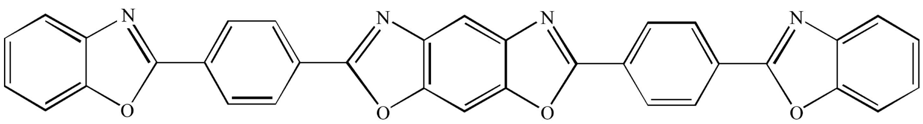
The model compound research performed by So *et al.* in [32] led these authors to suggests that PBO is stable to acid and base hydrolytic conditions, thereby contradicting the results obtained from the above model compounds. So *et al.* reported no degradation in model compound (1), shown in Fig. 9, after it was heated in acetonitrile with dilute sulfuric acid for 30 d at 80°C. In addition, no degradation was observed by FTIR spectroscopy and ^{13}C-NMR spectroscopy in model compound (2) after it had been stirred in 1% PPA aqueous solution or 0.1 N NaOH solution at 100°C for 3 weeks. The lower limit of detection for carboxylic acid groups using ^{13}C-NMR spectroscopy was estimated to be 178 ppm.

However, model compound (2) was found to degrade with the formation of carboxylic acid groups (see Fig. 10) in methanesulfonic acid (MSA) followed by water coagulation. In this procedure, the MSA contained 5% mass fraction of water that was heated, under atmospheric conditions, to 80°C. Paralleling these results, PBO was also found to degrade in MSA or PPA followed by coagulation in water. It was also observed that the carboxylic acid peak at 1680 cm^{-1}, which forms during the degradation process, is weaker when the experiment is performed in the absence of light or air. These researchers speculated that conditions such as this would not be experienced in normal use and therefore, PBO should be hydrolytically stable under normal conditions.

Since PBO fibers, like PPT fibers, are made though a coagulation process from strong acid polymer solutions, then the drying of these fibers during the manufacturing process is an important issue. Kitagawa and Yabuki [33]



2,6-Bis(4-tert-butylphenyl)benzo[1,2-d;5,4-d']bisoxazole
(Model Compound #1)



2,6-Bis[4-(2-benzoxazoyl)phenyl]benzo[1,2-d;5,4-d']bisoxazole
(Model Compound #2)

Figure 9 Model compounds used by So *et al.* [32] to investigate the hydrolytic stability of PBO.

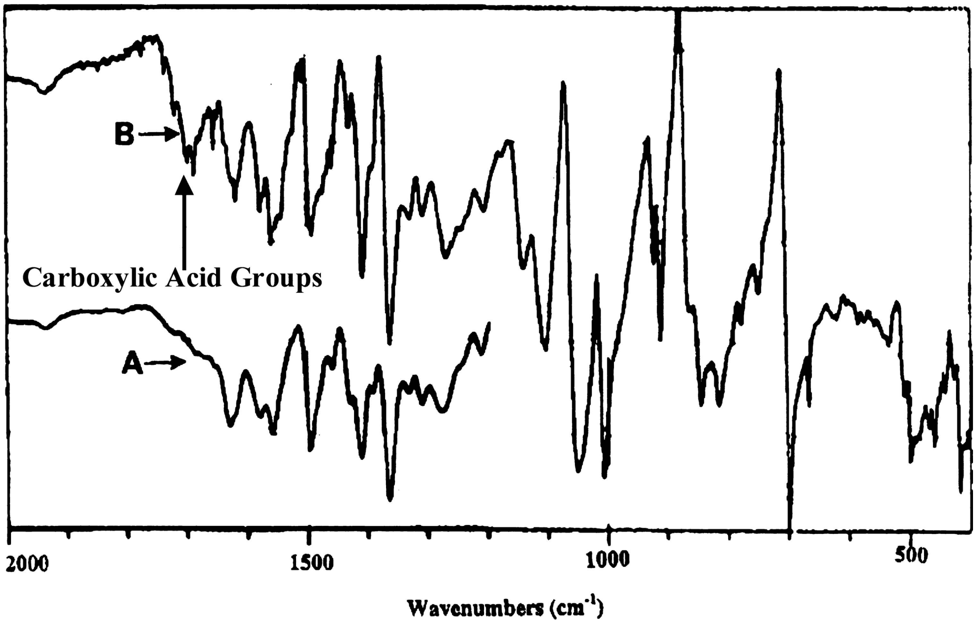


Figure 10 FTIR spectra of PBO samples isolated from methanesulfonic acid solution by coagulation with water. (A) Intrinsic viscosity of sample = 15 dL/g and (B) intrinsic viscosity of sample = 2 dL/g. Note the presence of carboxylic acid groups in the degraded (B) sample. (*taken from* [32]).

recently investigated by differential scanning calorimetry (DSC) the mass loss of wet PBO fibers and found that the weight goes down rapidly up to 120°C, which corresponds to evaporation of surface water. Above 120°C, the fiber mass drops more slowly until a temperature of 230°C is reached (see Fig. 11). These researchers estimated that the mass loss above 120°C accounted for approximately 30% of the wet fiber mass. From spin-lattice (T_1) and spin-spin (T_2) ^{1}H-NMR relaxation measurements it was deduced that the trapped water is packed into capillary voids whose diameter is approximately (2 to 3) nm. It is known that as-spun (AS) PBO has a moisture regain of 2.0% [16]. Therefore, the role that empty capillary voids and/or residual capillary water may have on the hydrolytic stability of PBO is unknown at this time.

From the preponderance of hydrolytic studies at 80°C, there seems to be a consensus that PBO fibers can be exposed to this extreme temperature during summer months when the protective equipment is stored in the trunk of an automobile. Cunniff and Auerbach [9], in 2002, performed a comparative study by exposing PBO and M5 fibers to 82°C (180°F) and 85% relative humidity (R.H.). Under these conditions PBO lost 20% of its initial fiber strength as measured by the single fiber test in 2000 h (83 d) (see Fig. 12). In contrast, M5 was found to be hydrolytically stable. Since M5 is a PBI (imidazole) type polymer, its stability relative to PBO may be associated with its structure. Recall that Dewar *et al.* [28] and Jackson *et al.* [25], speculated that the oxazole ring system has lower aromatic stability than thiazole and imidazole ring systems (see Fig. 6).

4. Thermal stability of the benzazole ring

There is general agreement that the thermal stability (under pyrolytic or thermo-oxidative conditions) of PBO is

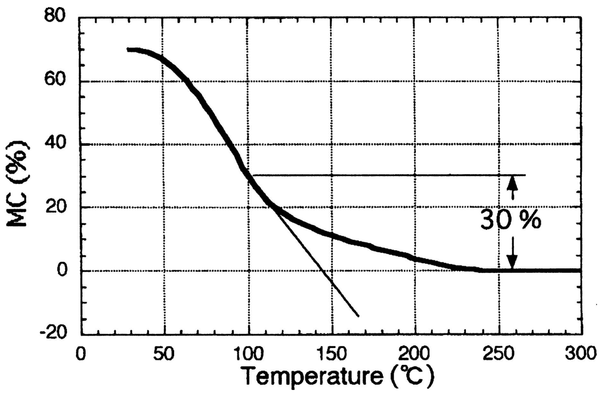


Figure 11 Differential Scanning Calorimetry (DSC) curves of wet PBO fiber. (*taken from* [33]).

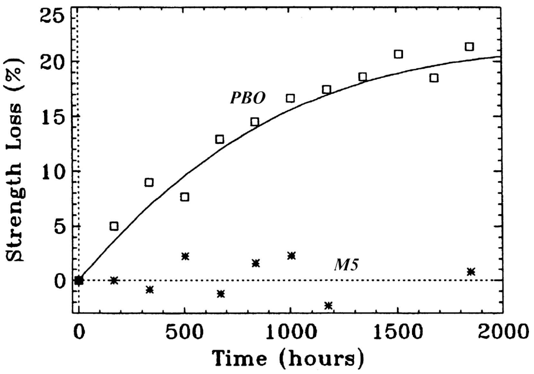


Figure 12 Strength loss of PBO and M5 fibers after exposure to 82°C and 85% relative humidity (R.H.). (*taken from* [9]).

150°C higher than that of PPT, with the presence of oxygen playing a critical role in the onset of degradation in both polymers [34]. Consistent with the DSC results reported in Fig. 11 that characterized the loss of water around 100°C, the data in Fig. 13 shows that PPT contains more water than PBO. In addition, the onset of thermal degradation for both polymers is shown to be above 400°C, therefore it is doubtful that thermal degradation will be a major factor under the normal use conditions of protective body armor.

However, it is well known that thermal aging, without thermal degradation, can result in a reduction of a polymer's mechanical properties. The classic example is that of a polycarbonate part whose fracture toughness immediately after manufacture diminishes with exposure to thermal heat that is well below the glass transition temperature of the material (physical aging) [35]. Since heat may be an important factor in accelerating hydrolytic degradation and because protective equipment may see temperature excursions up to 80°C, it is worth addressing the effect that thermal aging may have on the mechanical properties of PBO fibers.

Although very little research has been specifically directed toward the thermal aging of PBO fibers, it is known that that the properties of high-modulus (HM) PBO fibers and the experimental high-modulus plus (HM+) fiber are obtained by heating the as-spun (AS) PBO fibers under tension, with the specifics of this process being proprietary [36]. However, So [16] notes that the modulus of the AS PBO fiber is increased substantially when the fiber is heat-treated in a tube furnace at 580°C for 10 s under nitrogen with 0.55 GPa tension, while Kitagawa *et al.* [36] give similar but slightly different conditions. This procedure has the net effect of increasing the modulus, changing the ultimate tensile strength, and reducing the treated fiber's strain-to-failure relative to the AS PBO fiber (see Fig. 14).

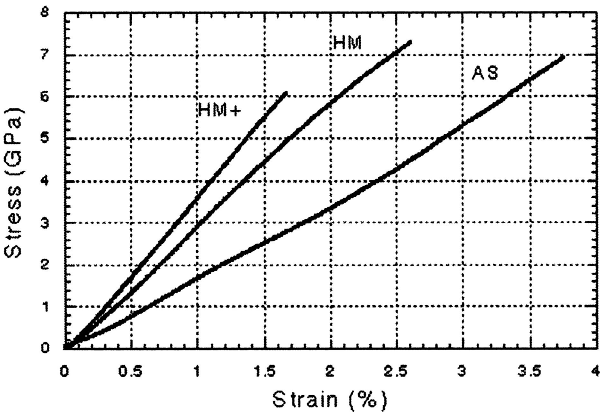


Figure 14 Stress-strain curves for the as-spun (AS), high-modulus (HM), and high-modulus plus (HM+) PBO fibers. (*taken from* [36]).

Recalling that the modulus, ultimate tensile strength, and strain-to-failure of ballistic fibers are the key material properties in estimating a fiber's theoretical performance in ballistic applications (see Cunniff and Auerbach equation in the Introduction), these calculations are done in Table II for the data Kitagawa *et al.* [36] obtained from single fiber tests and tests on yarns.

From the calculations in Table II, it should also be noted that the yarn data for the AS PBO fibers yield values similar to those obtained by Cunnif and Auerbach (see Table I). Therefore, data from single fiber tests appears to over-predict the ballistic performance by approximately 10%. However, the modulus values obtained by these researchers were derived by using strain values determined from measuring the gauge length of the specimen and crosshead displacement, with the latter being an approximate methodology for determining strain. The Kitagawa *et al.* data [36] also suggests that one should expect, even with an increase in modulus, a 20% decrease in ballistic performance if the HM+ fibers are used rather than AS

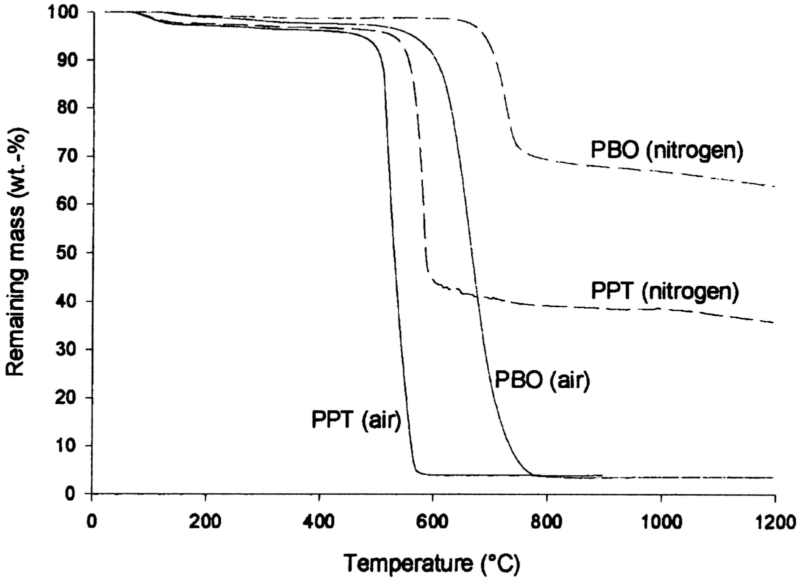


Figure 13 Thermogravimetric curves of PPT and PBO fibers under nitrogen (dashed lines) and air (full lines) (heating rate, 10°C/min). (*taken from* [34]).

TABLE II Theoretical Ballistic Performance of PBO Fibers (after Kitagawa *et al.* [36])

Fiber	Density (ρ) (g/cm^3)	Strength (σ) (GPa)	Failure Strain* (ε)	Modulus (E) (GPa)	$(U^*)^{1/3}$ (m/s)
Single Fiber Data					
AS PBO	1.54	6.30	(0.036)	173	924
HM PBO	1.56	5.90	(0.023)	260	821
HM+ PBO	1.56	5.10	(0.016)	320	720
Yarn Data					
AS PBO	1.54	5.55	(0.030)	187	838
HM PBO	1.56	5.59	(0.022)	258	793
HM+ PBO	1.56	4.72	(0.013)	352	673

∗Values obtained from Modulus and Strength data by assuming linear elastic behavior

fibers. This appears to be associated with a reduction in the strain-to-failure of the material as it is heat treated to increase the fiber stiffness (see Table I). Therefore, these data suggests that if the thermal aging rate becomes significant between room temperature (R.T.) and 80°C one may expect a loss in performance of the PBO fibers without thermal or hydrolytic degradation. So [16] notes that the tensile strength and modulus of PBO fiber were unchanged after 200 h at 300°C under nitrogen atmosphere, and 60% PBO fiber tensile strength was retained after 200 h at 300°C in air.

5. Ultraviolet (UV) stability of the benzazole ring

Although the UV instability of Kevlar has been known since before 1979 [37], the precursor monomer for PBO was not made until the mid-1980s, with commercialization of PBO fibers being announced in October 1998. In 1995, Orndoff published data showing that exposure of PBO and Kevlar yarns to 340 nm wavelength light for 450 h resulted in a loss of over 98% and 89%, respectively, of these fibers' original tensile strength [2]. Knowledge that the benzoxazole ring, the critical linkage in PBO, is unstable to UV light dates back to 1973 [38–41]. In this research Kasai and McLeod [38] deduced that the electron spin resonance (ESR) spectra of oxazole and benzoxazole corresponded to a spectra of an anion radical intermediate of the ruptured oxazole ring (see Fig. 15). Support for this assignment was obtained using INDO (Intermediate Neglect of Differential Overlap), a semi-empirical quantum mechanical method for studying molecules.

However, the instability of this ring system did not receive considerable attention until 1982, when clinical studies were conducted on 2-(4-chlorophenyl)-α-methyl-5-benzoxazole acetic acid (benzoxaprofen), a non-steroidal anti-inflammatory agent. Exposure of the skin of benzoxaprofen-treated subjects to UV-A irradiation produced intense itching and burning followed by the development of a weal and flare response. Using electron spin resonance (ESR), Reszka and Chignell [42] showed that UV irradiation of this benzoxazole derivative produces free radicals. Subsequent research [43] on 2-phenylbenzoxazole also produced free radicals and supported the earlier research of Kasai and McLeod [38].

Therefore, PBO fibers like Kevlar fibers are sensitive to UV radiation (e.g., sunlight, etc.). However, no studies were found that quantify the relative rates of the 2 materials to UV degradation.

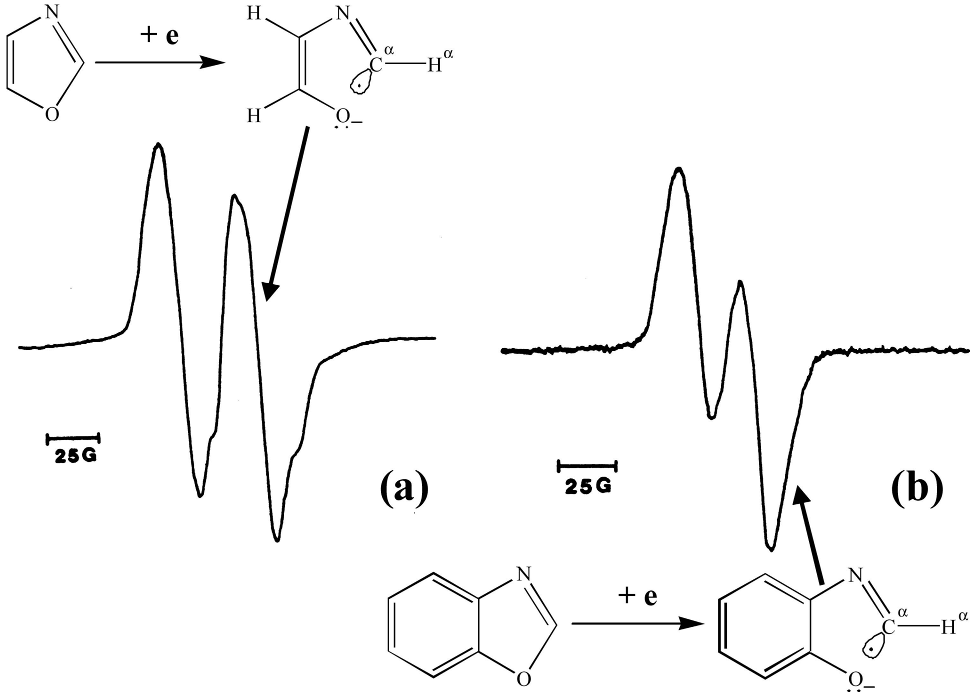


Figure 15 Electron Spin Resonance (ESR) spectra photoinduced in an argon matrix containing sodium plus (a) oxazole and (b) benzoxazole. Spectra were interpreted as anion radical intermediates of the respective the ring-ruptured structures. (*adapted from* [38])

6. Conclusions

Although the hydrolytic instability of the benzoxazole ring has been established in research conducted on small molecules [24–30], the model compound research of So *et al.* [32] contradicting these results and the results by Cunniff and Auerbach [9] indicating that PBO does degrade when exposed to moisture and heat indicates that further research in this area is needed. For future research to be successful in resolving this issue, the impact of thermal exposure and the composition of residual phosphorus and its role in any hydrolysis mechanism must be determined. In addition, the role of residual moisture and microvoids that may be present in the PBO fibers must be investigated. Current data suggests that PBO may degrade in two steps, with the first step resulting in the formation of an amide structure similar to that found in Kevlar (see Fig. 8), followed by amide hydrolysis that will result in chain scission. Establishing the extent of these two mechanisms in PBO hydrolysis will provide insight into the lower bound of this fiber's strength under normal use conditions, where hydrolytic action and heat are presumed to be the major factors.

Although UV degradation seems assured, the rate of this degradation mechanism in PBO relative to Kevlar has not been established. Heat treatments of PBO indicate that physical aging through thermal excursions may also degrade ballistic fiber performance. Therefore, there are several research areas where the response of PBO to environmental stimuli must be better understood before an accurate assessment can be made about the long-term performance of this polymer fiber in ballistic applications.

Disclaimer: Certain commercial materials are identified in this paper. 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 identified are necessarily the best available for the purpose.

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