

# Study on Photoaging of Poly(*p*-phenylene benzobisoxazole) Fiber

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**ABSTRACT:** As a kind of rig-rod-like polymer, poly(*p*-phenylene benzobisoxazole) (PBO) has received great interest because of its excellent mechanical properties and good thermal stability. The use of PBO fibers, however, is limited due to its low sunlight stability. In this work, the photoaging of PBO fibers, as well as the effects of oxygen and moisture on their photoaging, is investigated by tensile strength measurements, infrared spectroscopy, molecular mass determination, and scanning electron microscopy. It is first time to find that the photoaging of PBO fibers includes two development stages. The physical aging is the dominate factor at the first stage of photoag-

ing relative to the second stage, in which the chemical aging is the dominate factor. In the first degradation stage, long defects appear and develop parallel to the fiber axis. Little chemical change occurs in this stage. In the second degradation stage, the molecular mass of PBO decreases and chemical degradation occurs. Oxygen accelerates the occurrence of chemical degradation. It is also found PBO fibers are more stable for photoaging when moisture and oxygen are isolated. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 124: 1050–1058, 2012

**Key words:** high performance fiber; PBO fiber; photoaging

## INTRODUCTION

As a kind of rig-rod-like polymer, poly(*p*-phenylene benzobisoxazole) (PBO) has received great interest because of its excellent mechanical properties and good thermal and environmental stability.<sup>1–7</sup> PBO fibers have exceptionally high tensile strength, stiffness, relatively low density, and good chemical resistance. Typical PBO fibers are used in high strength applications, such as in body armor and ropes. The chemical structure of PBO is shown in Scheme 1.

In 2001, Toyobo published some disconcerting results regarding the susceptibility of PBO fibers to degradation when exposed to relatively mild conditions.<sup>8</sup> Problems became apparent to the law enforcement community in the summer of 2003, when ballistic penetration of PBO-based body armor occurred in two separate incidents.<sup>9</sup> Subsequent data from Toyobo show that PBO fibers are also suscepti-

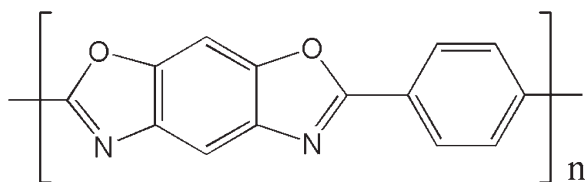
ble to degradation when exposed to sunlight. PBO fibers lost more than 60% of their strength after only 4 months of exposure at Ohtsu, Japan.<sup>8</sup>

Some studies of the degradation of PBO fibers have been reported, including thermal degradation, hydrolysis, and photodegradation.<sup>9–15</sup> Walsh et al. found that exposure to moisture results in loosening of the PBO fiber morphology, leading to an increase in the number and size of defects.<sup>10</sup> The presence of aqueous acids causes both loosening of the fiber structure and hydrolysis of the oxazole ring structure. UV–Vis radiation primarily hydrolyzes the material near the fiber surface with the attendant formation of amide linkages. So et al. found that aryl benzobisoxazole and aryl benzobisthiazole compounds both in the solid state and in solution have completely different photoreactivities.<sup>11</sup> In the solid state, excimers form and undergo photo-induced electron transfers to generate an ion radical pair. In solution, photo-induced electron transfer and its subsequent reactions do not occur. The compounds in solution are stable even after prolonged irradiation. Yong et al. found that PBO undergoes a self-sensitized photo-induced electron transfer reaction during photolysis.<sup>14</sup> According to this mechanism, an excited polymer repeating unit undergoes electron transfer with another unit to generate a radical-cation and radical-anion pair. In the presence of oxygen, the radical-anion transfers an electron to the oxygen molecule to generate a superoxide.

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**Scheme 1** The chemical structure of PBO.

Since knowledge about the photodegradation of PBO fiber is important, the effects of environmental factors, such as UV–Vis light, moisture, and oxygen, on the photoaging of PBO fibers is investigated in this article by tensile strength measurements, infrared spectroscopy (IR), molecular mass determination, and scanning electron microscopy (SEM).

## EXPERIMENTAL

### Materials

All reagents, unless otherwise specified, were obtained from Aldrich and used as received. PPA was purchased from Shanghai Chemical Reagent Company and used without further purification. 4,6-diamino-1,3-benzenediol dihydrochloride (DAR) was obtained from commercial sources and purified before use. PBO was synthesized in the laboratory by polycondensation in poly(phosphoric acid) (PPA) as solution following the procedure described in the Ref.<sup>16</sup>. PBO fibers were spun in our laboratory by the dry-jet wet-spun method.<sup>17</sup>

### Photoaging

Photoaging of PBO fibers was performed in an SN-500 xenon lamp weather-resistant chamber, where the intensity of UV–Vis light was 1100 W/m<sup>2</sup> and the wavelength range of UV–Vis light was from 290 to 800 nm, the relative humidity was 65%, and the temperature was 54°C.

Photoaging of PBO fibers isolated from oxygen and moisture was performed. Before UV–Vis exposure, the fibers were placed inside a quartz glass tube, which was subsequently vacuumed, and then filled with argon. Finally, the tube was sealed.

Photoaging of PBO fibers isolated from moisture was performed. Before UV–Vis exposure, the fibers were placed inside a glass quartz tube, then were heated at 100°C to eliminate moisture; last, sealed the tube.

Photoaging of PBO fibers isolated from oxygen was performed. Before UV–Vis exposure, the PBO fibers were placed inside a xenon lamp weather-resistant chamber filled with argon. Argon was continuously pumped into the chamber to eliminate air.

### Measurements

The mechanical properties of the fibers were tested using an electronic yarn strength tester (Instron Tensile Tester, Model YG020B) with a crosshead velocity of 10 mm/min and a gauge length of 20 mm. All reported results are the averages of at least 30 specimens.

The attenuated total reflectance infrared spectra (ATR-FTIR) of the fibers were obtained using a Nicolet 5700 FTIR Spectroscopy with resolution of 0.09 cm<sup>-1</sup>.

Molecular mass was measured by intrinsic viscosity (IV), which was carried out by dissolving about 6 mg polymer in 25 mL methanesulfonic acid (MSA).<sup>18</sup>

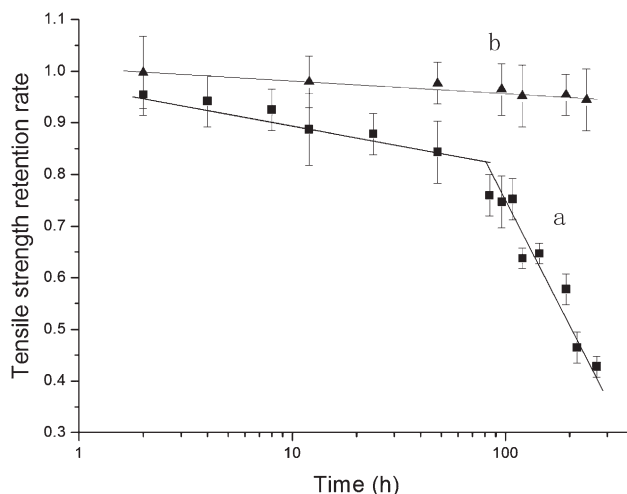
The morphologies of the fiber surface and its cross section were examined by SEM (Model TS5136MM). Samples were sputter-coated with gold in an argon atmosphere before testing.

Wide-angle X-ray diffraction (WAXD) diffraction patterns were collected in the range of 5°–50° on a Rigaku D/MAX-2550 X-Ray diffractometer with Ni-filtered Cu K<sub>α</sub> radiation.<sup>19</sup>

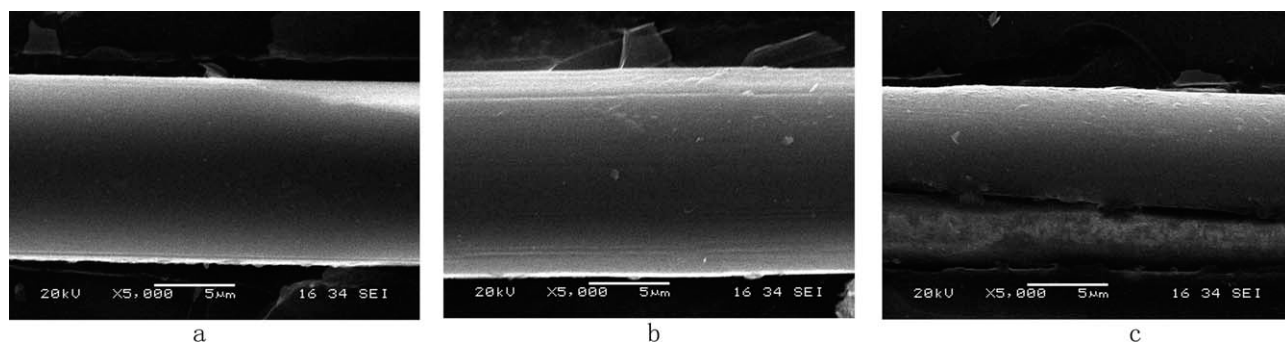
## RESULTS AND DISCUSSION

### The UV–Vis light exposure of PBO fiber

To investigate the photoaging of PBO fibers, the fibers were first aged with and without UV–Vis light. Figure 1 shows the results of tensile retention for PBO fibers aged under (a) UV–Visible light irradiation, 65% relative humidity, and 54°C and (b) the same temperature and humidity but no UV–Vis light. As shown in Figure 1, the tensile strength decreased quickly when the fibers were exposed to UV–Vis light. Strength retention was only about 44% after 240 h. For the fibers aged without UV–Vis light,



**Figure 1** Tensile strength of PBO fibers aged (a) with UV–Vis light and (b) without UV–Vis light.



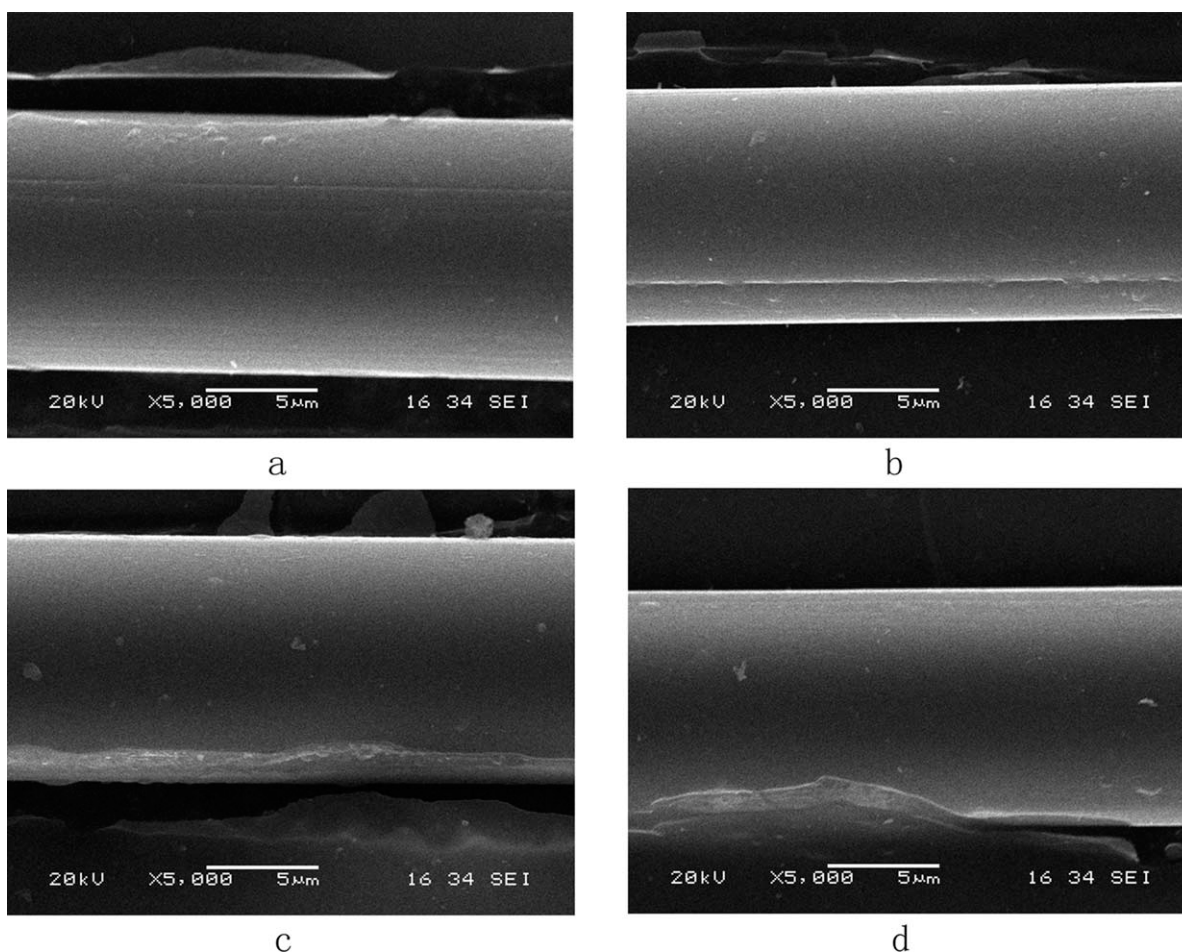
**Figure 2** SEM micrographs of (a) unaged PBO fibers, (b) PBO fibers aged for 300 h without UV-Vis light, and (c) PBO fibers aged for 300 h with UV-Vis light.

tensile strength declined slowly. After 240 h, the strength retention of these fibers was 96%. These findings indicate that the tensile strength of PBO fibers is sensitive to UV-Vis light.

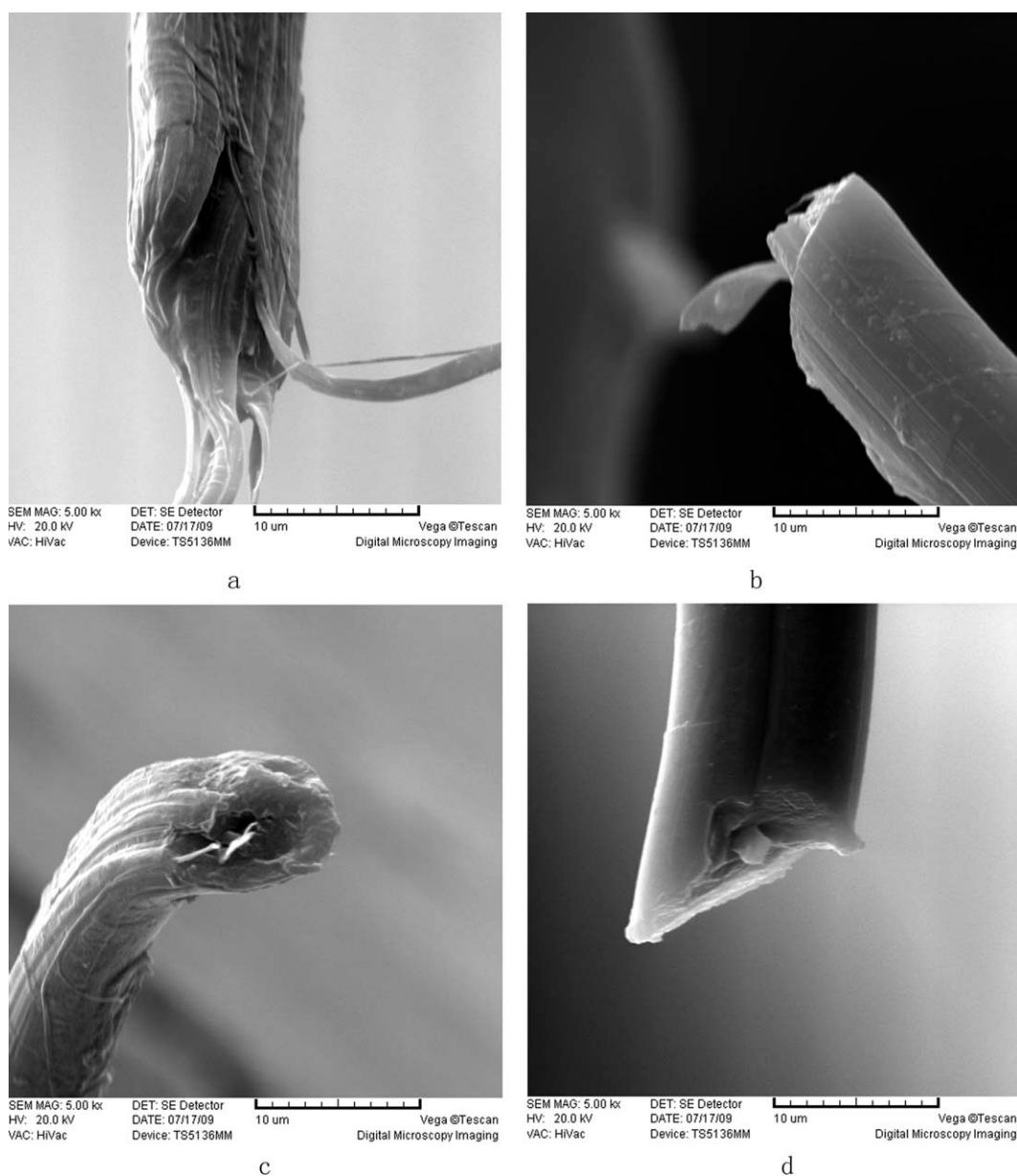
Figure 1 also shows that the decrease in tensile strength of PBO fibers exposed to UV-Vis light behaves in two developmental stages: (i) slow decline of fiber strength of fiber and (ii) fast decline of fiber

strength. The point of inflection in the tensile strength rate curve is located at about 110 h.

Figure 2 compares the surface morphology for PBO fibers aged for 300 h with and without UV-Vis light. The surface of the PBO fibers shows no obvious change when they are aged without UV-Vis light, whereas aging with UV-Vis light produces serious fiber surface damage.



**Figure 3** SEM micrographs of PBO fibers exposed to UV-Vis light for different time: (a) 12 h, (b) 96 h, (c) 120 h, and (d) 216 h.



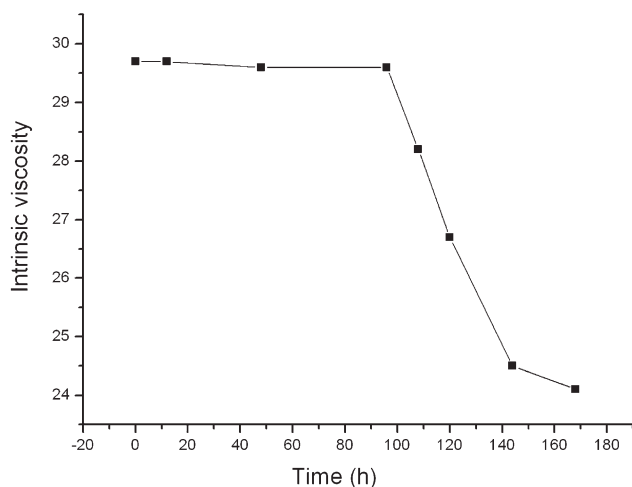
**Figure 4** SEM micrographs of cross sections of PBO fiber exposed to UV-Vis light for different time: (a) unaged fibers, (b) 96 h, (c) 120 h, and (d) 216 h.

Figure 3 shows the surface morphology of PBO fibers exposed to UV-Vis light for different time. When the aging time was less than 120 h, only long defects parallel to the fiber axis were observed, which was regarded by Kitigawa as the scattering of needle-like voids oriented parallel to the fiber axis.<sup>20</sup> After 120 h aging, slight exfoliation was observed on the fiber surface. The time observations correspond to the time at which the fiber strength decreases faster (Fig. 1). Kitigawa demonstrated that PBO fibers have a core-shell structure, in which the shell of  $\sim 1\text{--}2\ \mu\text{m}$  thickness has fewer voids and a higher degree of order compared with the core.<sup>20</sup> As a result, even small damages to the PBO fiber's cortex may bring about disproportionately large effects to its fiber strength.

Figure 4 shows the SEM morphologies of tensile cross sections of PBO fibers aged for different time. The fracture character of the fibers was cleavage fracture for unaged fiber, whereas the fiber aged for 216 h behaved obviously brittle fracture. This suggested that the aged PBO fibers had a higher degree of brittleness.

#### Chemical character of PBO fibers during photoaging

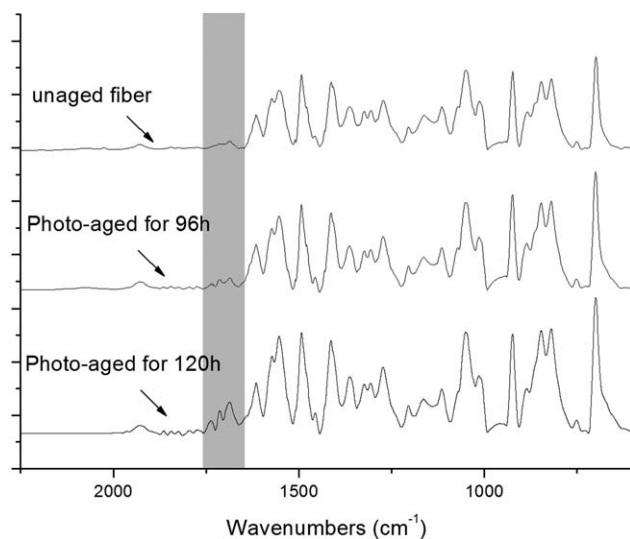
Changes to the molecular mass of the PBO fibers during photoaging were also investigated since molecular mass is directly associated with chemical chain scission, rather than the mechanical properties



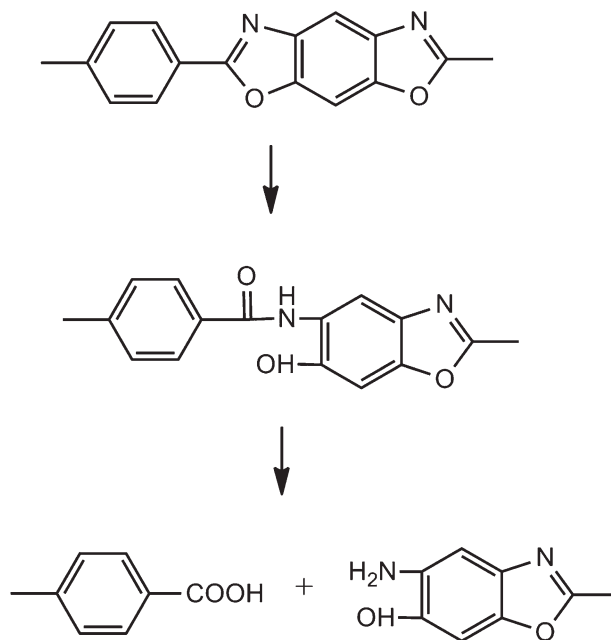
**Figure 5** Intrinsic viscosity of PBO fibers exposed to UV-Vis light for different time.

of the fiber. Figure 5 shows changes of the intrinsic viscosity of PBO fibers during photoaging. The intrinsic viscosity of the fibers remained almost constant until about 96 h after initiation of photoaging, after which it showed a sharp decline. This suggests that extensive chain scission may have occurred at this point.

ATR-FTIR was used to study the chemical changes near the fiber surface during photoaging. The ATR-FTIR spectra of fibers aged for different time are baseline corrected, normalized, and shown in Figure 6. The spectra of unaged fibers were similar to those of fibers aged for 96 h, which suggest that no chemical changes occur near the fiber surface when the aging time is less than 96 h. However, the spectra of fibers aged for 96 h was different from the spectra of fibers aged for 120 h. Peaks at  $1686\text{ cm}^{-1}$ , which was



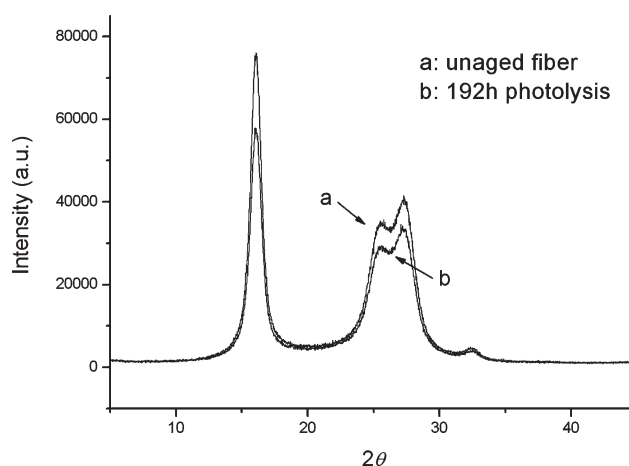
**Figure 6** ATR-FTIR spectra of PBO fibers exposed to UV-Vis light for different time.



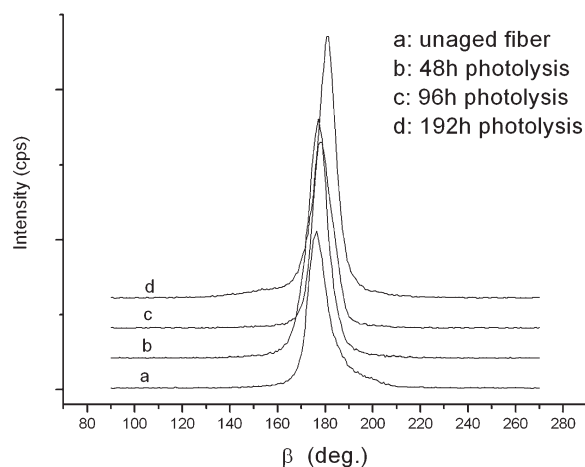
**Scheme 2** Proposed degradation reactions for PBO in Ref. 9.

assigned to the stretching vibrations of carbonyl groups,<sup>21</sup> increased in intensity after the fibers had been aged for 120 h. It means that at aging times longer than 96 h, chemical degradation of PBO, such as the opening of the benzoxazole ring and chain scission, may occur. The similar phenomenon is also observed by Chin J and the possible degradation mechanism was the ring opening of benzoxazole ring and formed carbonyl groups (Scheme 2).<sup>9</sup>

Combining the results of Figures 1, 5, and 6, it seems reasonable to divide the photoaging of PBO fibers into two development stages. The physical aging is the dominate factor at the first stage of photoaging relative to the second stage, in which the chemical aging is the dominate factor. In the first



**Figure 7** WAXD spectra of PBO fibers before and after photoaging.

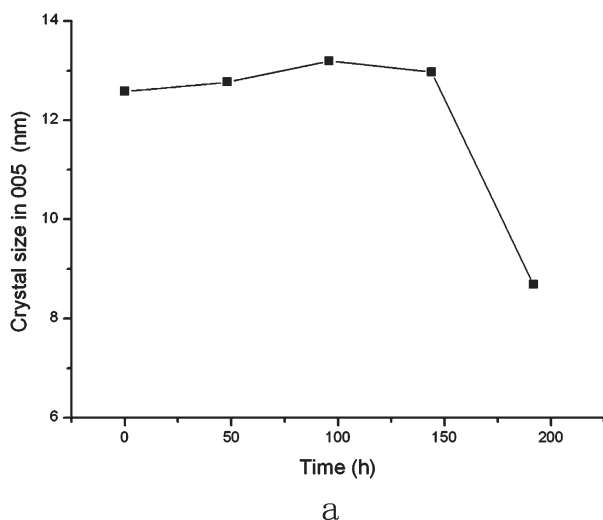


**Figure 8** X-ray diffraction of (200) Debye ring for PBO fibers exposed to UV-Vis light for different time.

degradation stage, the strength of the fibers slowly declines. The fact that the molecular weight of PBO shows almost no change means little chemical change occurs in this stage. The second degradation stage may be regarded as the chemical degradation stage, during which the chemical breakdown and chain scission of PBO molecules occurs, which result in the fast decline of fiber strength.

#### Crystal characteristics of PBO fibers during photoaging

Since the mechanical properties of polymer fibers partly depend on the crystallinity and orientation of the fibers, the crystallinity of PBO fibers before and after aging was investigated. Figure 7 shows the WAXD spectra of unaged PBO fibers and PBO fibers aged for 192 h. The calculated crystalline values are 90.3% for unaged fibers and 86.2% for aged fibers.



**TABLE I**  
Orientation Degrees of the Crystalline Region of the PBO Fibers

Aging time (h)	Orientation degree of crystalline region (%)
0	93.2
24	93.2
48	93.1
72	93.3
96	93.4
120	93.1
144	93.1
192	91.1

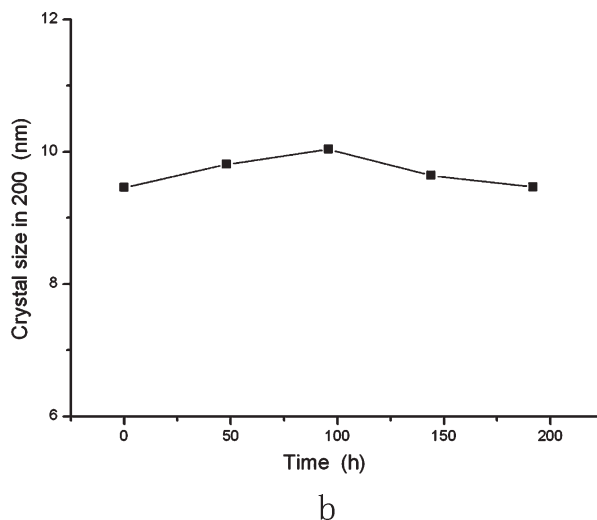
The degree of orientation of the crystalline region of the PBO fibers was determined by WAXD. X-ray scan along (200) Debye ring was done for PBO fibers aged for different time, as shown in Figure 8. By the experience formula of orientation as follow, the degree of orientation of the crystalline region of the PBO fibers aged for different time can be calculated.

$$f_x = \frac{180 - H}{180} \times 100\%$$

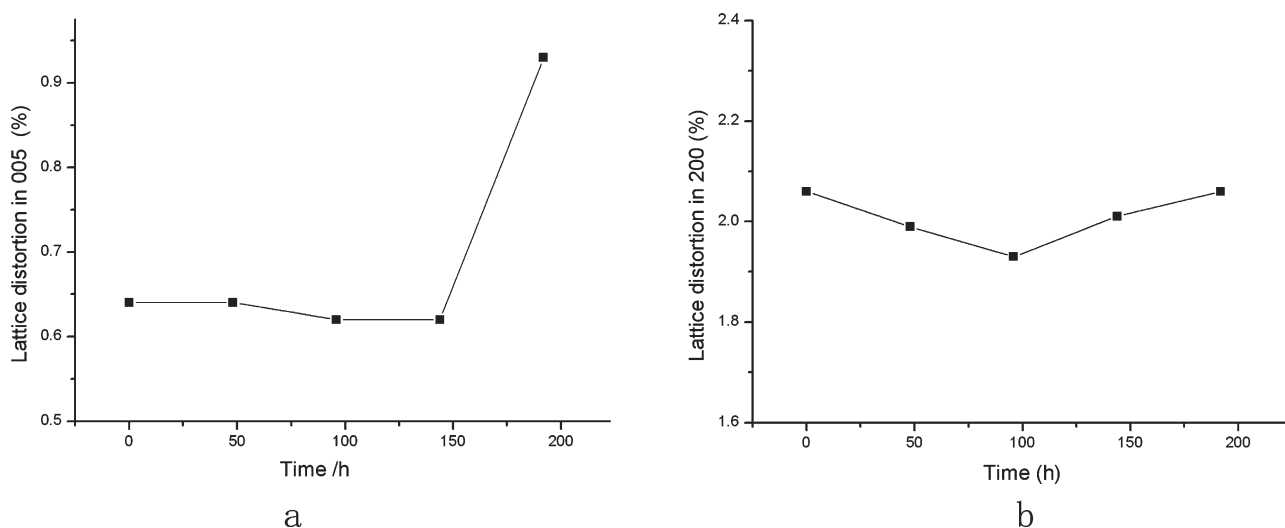
where  $H$  is FWHM of (200) diffraction peak along Debye ring scanning,  $f_x$  is the degree of orientation.

The results of orientation degrees of PBO fibers aged for different time list in Table I. It shows that the orientation degree of crystalline region of PBO fibers had almost no change until 192 h aging.

The meridional and equatorial XRD intensity profiles of the PBO fibers were also determined. Figure 9 shows the average crystal sizes of the fibers in both the axial and lateral directions calculated using Scherer's equation. Figure 10 shows the lattice distortions of the fibers in both the axial and lateral directions calculated using Stock's equation. The average crystal sizes and lattice distortions in the



**Figure 9** Apparent crystal sizes of PBO fibers during photoaging in the axial (005) and lateral (200) directions.



**Figure 10** Lattice distortion patterns of PBO fibers during photoaging in the axial (005) and lateral (200) directions.

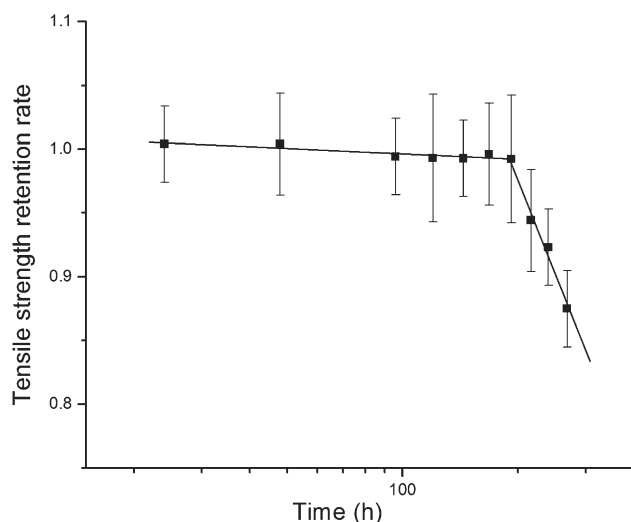
lateral direction were not significantly altered during photoaging. In the axial direction, however, significant changes were observed: the average crystal sizes decreased, whereas the lattice distortions increased after 150 h aging.

XRD patterns of PBO fibers show that crystal structure damages mainly occurred during the later stages of photoaging.

#### Effects of oxygen and moisture on the photoaging of PBO fibers

The effects of moisture and oxygen on the photoaging of PBO fibers were determined.

Figure 11 shows the tensile strength retention rate of fibers exposed to UV-Vis light without moisture and oxygen. Comparing Figures 1 and 11, the



**Figure 11** Tensile strength retention rate of PBO fibers exposed to UV-Vis light for different time after isolating moisture and oxygen.

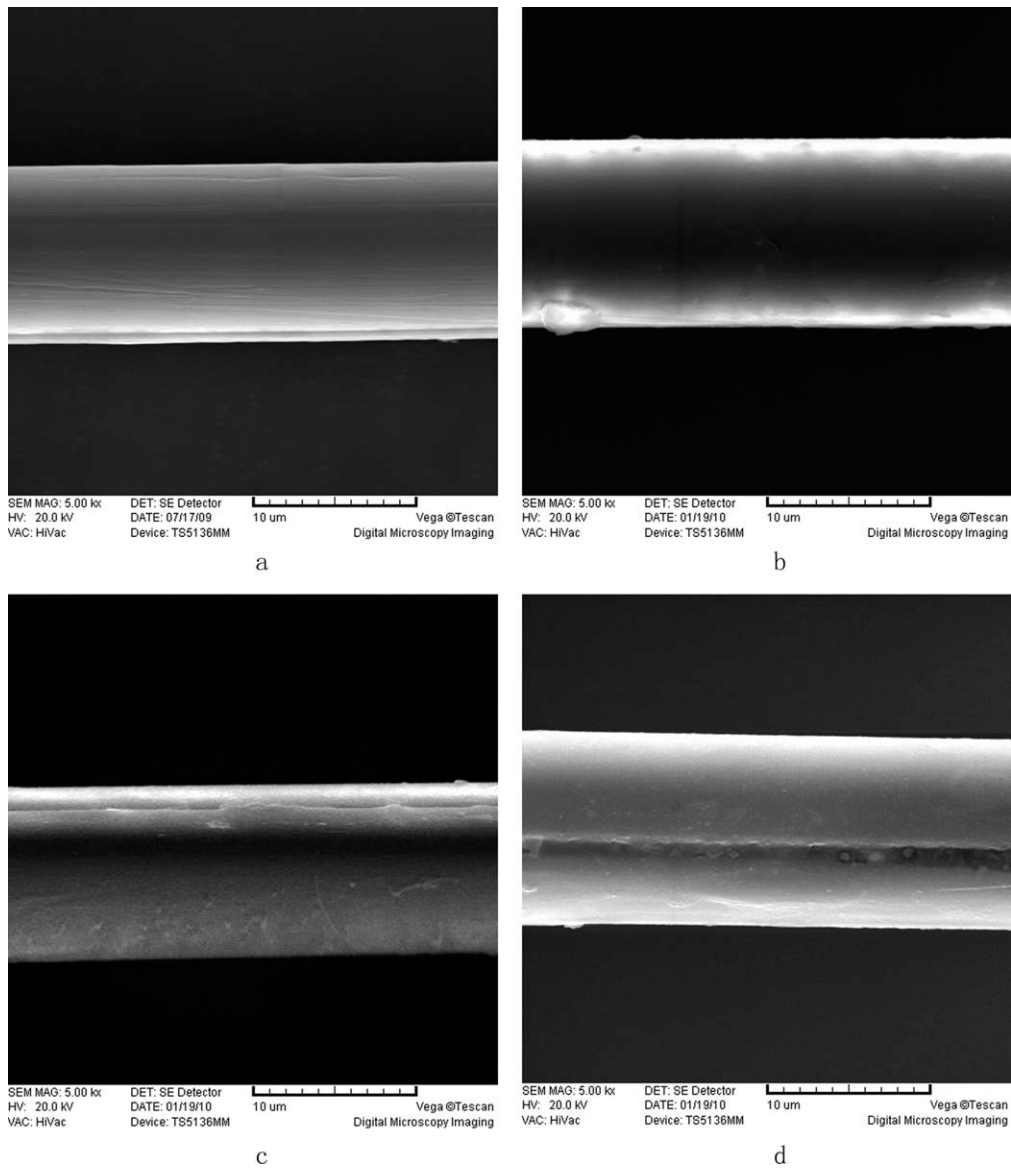
decrease in fiber mechanical strength was deferred when moisture and oxygen were eliminated from the reaction chamber. Under such conditions, the strength retention rate was 96% and the modulus showed no obvious change even after 192 h aging. In the early stage of photoaging, the effect of moisture is more obvious than that of oxygen. The possible reason is that moisture affects the physical degradation of the fibers, whereas oxygen mainly accelerates their chemical degradation.

Figure 12 shows SEM images of PBO fibers exposed to UV-Vis light after isolation of water and oxygen. Fiber surface damage mainly presented as long defects parallel to the fiber axis.

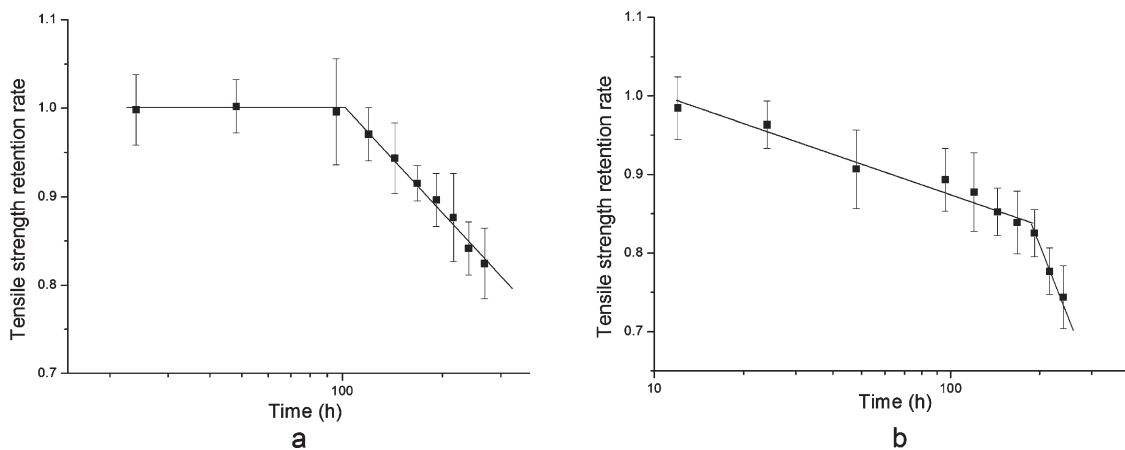
Photoaging experiments of PBO fibers after individual separation of moisture and oxygen are shown in Figure 13.

Comparing the results of Figures 11 and 13, the following were observed: (1) When PBO fibers were exposed to UV-Vis light without moisture and oxygen, the fibers remained stable for extended periods of time, and the fiber strength was not significantly decreased until after 192 h aging. (2) When PBO fibers were exposed to UV-Vis light with moisture but without oxygen, the fiber strength continuously decreased. The time during which fiber strength first slowly and then quickly decreased was 190 h. (3) When PBO fibers were exposed to UV-Vis light with oxygen but without moisture, the fiber strength first remained almost constant and then decreased quickly after 110 h.

Figures 11 and 13 also show that regardless of the presence or absence of oxygen and moisture, the photoaging of PBO fibers could be divided into two degradation stages. It is reasonable to assume that during photoaging, moisture mainly affects the physical degradation of the fibers, whereas oxygen mainly accelerates their chemical degradation. Water and its



**Figure 12** SEM photographs of PBO fiber exposed to UV-Vis light for different time after isolating moisture and oxygen: (a) unaged fibers, (b) 96 h, (c) 240 h, and (d) 310 h.



**Figure 13** Tensile strengths of PBO fibers exposed to UV-Vis light for different time after: (a) isolating moisture and (b) isolating oxygen.



plasticization effects may cause fiber swelling, thus increasing the numbers and sizes of fiber cortex defects. This in turn leads to a decrease in fiber strength.

### CONCLUSIONS

The properties of PBO fibers exposed to UV-Vis light were investigated in this study. The photoaging of PBO fibers was comprised of two degradation stages. The physical aging is the dominate factor at the first stage of photoaging relative to the second stage, in which the chemical aging is the dominate factor. In the first degradation stage, long defects appear and develop parallel to the fiber axis. Little chemical change occurs in this stage. Water accelerated the decrease in fiber strength at this stage. This may be due to the plasticization effect of the water molecules, which led to crystallite slippage and swelling of the fibers. These resulted in the loosening of the fiber morphology. IR spectra and molecular mass determination suggested that little or no chemical changes occurred during this stage. In the second degradation stage, the molecular mass of PBO decreases and chemical degradation occurs. This may have resulted from the opening of the benzoxazole ring and chain scission of PBO molecules. These led to fiber structure damage and quick decreases in fiber strength. Oxygen accelerated chemical degradation. Isolation of moisture and oxygen could cause the PBO fibers to become more stable during photoaging.

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