Mechanism of Degradation of Poly(*p*-phenylene benzobisoxazole) Under Hydrolytic Conditions

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ABSTRACT: Poly(*p*-phenylene benzobisoxazole) (PBO) fiber has received great interest because of its excellent mechanical properties and good thermal stability. The objective of this study was to expose degradation mechanism of PBO under neutral and acidic conditions by molecular mass and Fourier transform infrared (FTIR) spectroscopy. Results were not consistent with the classic degradation mechanism, which indicates that degradation should occur through the ring opening and chain scission of the benzoxazole ring. The FTIR absorption spectra of PBO suggested that the *o*-hydroxy amide linkage (the open ring structure) was present in the PBO molecule chain to some extent because of the incomplete polymerization. Further investigation showed that hydrolysis might occur in the open ring section during hydrolytic degradation. Based on the experimental data, a new degradation mechanism was proposed. It suggests that, in the early and middle stages, hydrolysis occurred primarily in the *o*-hydroxy amide linkage of the open ring. The concentration of the *o*-hydroxy amide structure determined the speed of degradation of PBO. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 121: 1734–1739, 2011

Key words: poly(*p*-phenylene benzobisoxazole); hydrolysis degradation; open ring; benzoxazole ring

INTRODUCTION

Poly(*p*-phenylene benzobisoxazole) (PBO) has received great interest because of its high performance such as excellent mechanical properties, good thermal stability, and environmental stability.[1–3] Typically, PBO fibers have been 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.[4] 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.[5]

The physical and chemical mechanisms of PBO degradation have been reported, including thermal degradation and photodegradation.[4–8] So et al. studied the stability of benzobisoxazole and benzobisthiazole compounds and polymers under hydrolytic conditions and found that benzobisoxazole underwent bond cleavage to generate carboxylic acid and *o*-aminophenol functional groups under very severe hydrolytic conditions, such as the dissolution of PBO in poly(phosphoric acid) (PPA) or methanesulfonic acid (MSA) with residual water followed by coagulation in water.[6] Kim et al. observed carboxylic acid peaks in the Fourier transform infrared (FTIR) spectra of PBO that have undergone acid-catalyzed hydrolysis. It also showed a concurrent decrease in the molecular mass measured by intrinsic viscosity. This phenomenon is consistent with the mechanism of chain scission.[7] Walsh et al. reported that exposure to moisture results in the loosening of the fiber morphology leading to an increase in the number and size of defects.[8] The presence of aqueous acid causes both loosening of the fiber structure and hydrolysis of the oxazole ring structure. FTIR spectroscopy and wide angle X-ray diffraction data indicate the occurrence of chemical degradation when the polymer was exposed to high concentrations of phosphoric acid. The hydrolysis of the oxazole ring, leading to formation of cyclic amines and amide linkages, is the most likely route of chemical reaction. Chin et al. studied the attenuated total reflection infrared (ATR-IR) spectra of benzoxazole fiber and 2-phenyl benzoxazole model compounds before
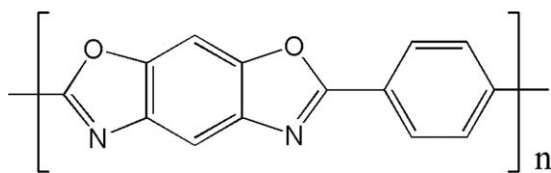
Scheme 1 The ideal chemical structure of PBO.

and after environmental aging for 157 days. A positive peak at 1650 cm^{-1} in the region associated with amide carbonyl or carboxylic acid grew progressively larger with time. Results indicated that the benzoxazole ring opening was formed through Scheme 2.[5]

Researchers have proposed hydrolytic degradation mechanisms but direct evidence has been insufficient. For example, the appearances of carboxylic acid peaks in the FTIR spectra of PBO have different explanations. The absorption of carboxylic acid is usually located at 1650 cm^{-1} in the FTIR spectra, but this region always contains a broad peak, which might include several overlapped peaks. Moreover, no direct evidence has been reported for the decrease in the amount of benzoxazole rings of PBO during hydrolytic degradation.

Because knowledge of the actual hydrolytic degradation mechanisms of PBO is important, we particularly investigated the characteristics of PBO before and after hydrolysis and explored the degradation mechanisms. In addition, unlike most investigations, the PBO film was chosen instead of the PBO fiber because the compact surface of the PBO fiber would hinder the water and acid molecule diffusion into the sample and disturb the degradation process.

EXPERIMENTAL

Materials

PPA, phosphorus pentoxide (P$_2$O$_5$), and terephthalic acid were purchased from Shanghai Lingfeng Chemical Co. H$_2$SO$_4$ was purchased from Shanghai Chemical Reagent Company. *N*-methyl-2-pyrrolidone (NMP), nitromethane, AlCl$_3$, and MSA were obtained from Aldrich. All materials were used as received.

PBO was synthesized in the laboratory by polycondensation in PPA following the procedure described in the reference.[2] Poly(*o*-hydroxyamide) was synthesized in NMP according to the Ref. 9.

Sample preparation and measurements

Thin polymer films were prepared using the method reported by Jenekhe,[10] i.e., spin coating of the polymer solution in nitromethane/AlCl$_3$ with a concentration of 3 wt % onto synthetic silica substrates.

Thin films were dipped in deionized water for 3 days to remove AlCl$_3$ completely. Then, thin films were dried at 80°C in a vacuum oven for 12 h.

The FTIR spectra were obtained using a Nicolet Magna-IR 550 FTIR spectrometer. Intrinsic viscosity was used to characterize the molecular weight of PBO. The intrinsic viscosities of all the samples were measured in MSA at 30°C using the Ubbelohde capillary viscometer by dissolving about 12 mg polymer in 25-mL MSA.

RESULT AND DISCUSSION

Hydrolytic degradation of PBO with and without acid

Because the primary aim is to achieve knowledge about chemical degradation, the principal measurement parameter used in this study was molecular mass, which is directly associated with chain scission, rather than the mechanical properties of PBO films.

PBO film samples were soaked in deionized water, 0.02N H$_2$SO$_4$, and 0.2N H$_2$SO$_4$ up to 25 days at room temperature. After an interval of time, one film was taken out, washed, and dried for characterization. The intrinsic viscosity values (I.V.) of PBO films during hydrolysis are plotted in Figure 1.

In Figure 1, the I.V. of the films are 16.4, 14.8, and 13.8 after soaking for 16 days. Then, the I.V. of PBO films seems stable. The existence of this flat stage is puzzling. According to the viewpoint that the mechanism of PBO hydrolytic degradation involves the ring opening and chain scission of the benzoxazole ring, the I.V. of the PBO film is expected to continually decrease until most of the benzoxazole rings are
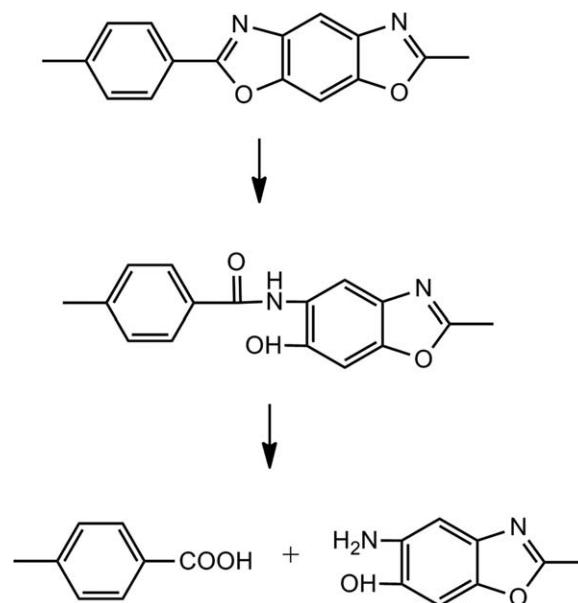

Scheme 2 Proposed reaction for PBO hydrolysis in Ref. 5.
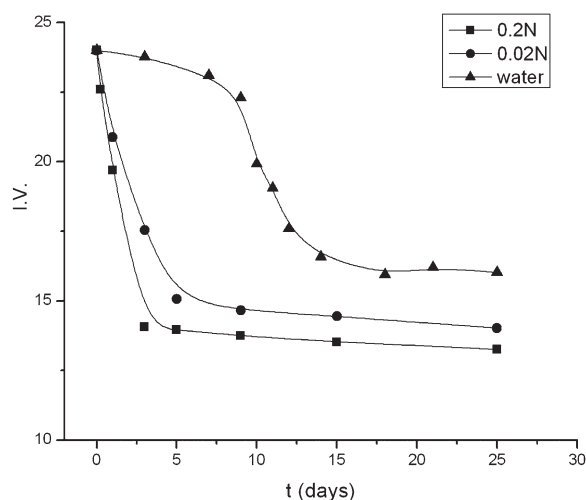
Figure 1 I.V. versus hydrolysis time for PBO films hydrolyzed in 0.02*N*, 0.2*N* H_2SO_4 solutions and deionized water.

opened and hydrolyzed. The flat I.V. stage of PBO in this study does not agree with the ring-opening mechanism. Thus, investigating the hydrolysis of PBO films becomes necessary.

Characterization of PBO films by FTIR

The FTIR spectra of PBO films before and after hydrolysis, which have been baseline corrected and normalized, are shown in Figure 2. The absorption bands of the two samples show distinct differences at 1600–1800 cm^{-1}. A similar phenomenon has been observed by Chin et al.[5] Chin found that in the ATR-IR analysis of PBO yarns extracted from vests before and after environmental aging for 157 days, a distinct peak intensity difference occurred at 900–1800 cm^{-1}.

However, according to the chemical structure of PBO (Scheme 1), the spectrum of the original PBO
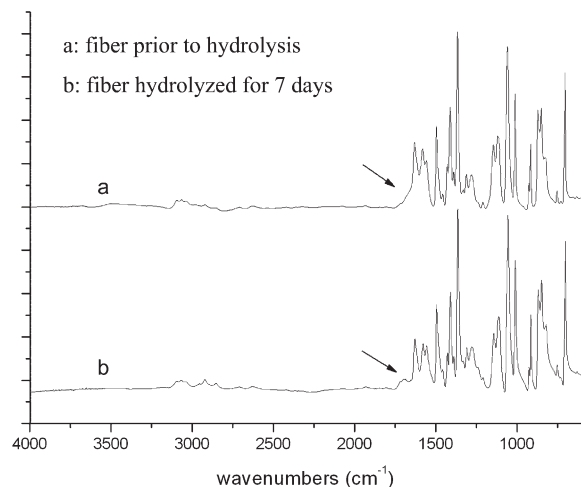
film is expected to show only two absorption peaks at 1600–1800 cm^{-1} (1625 cm^{-1}, C=N stretching of benzoxazole ring[11]; 1614 cm^{-1}, benzene ring). The broad peaks at 1600–1800 cm^{-1} in Figure 2 need to be explained.

Because this broad region might consist of some overlapping peaks, a curve-fit software was used for resolving the overlapping bands of the spectra. This technique is often helpful in extracting specific chemical changes and providing information on the formation and depletion of specific functional groups. The broad peak at 1600–1800 cm^{-1} for the original PBO film was analyzed. Results of the resolved spectral peaks are shown in Figure 3. As indicated by the resolved results, five overlapping absorption peaks are included. These are located at 1614, 1627, 1647, 1680, and 1717 cm^{-1}. Consequently, the absorption peak at 1627 cm^{-1} is assigned to vibrations associated with the benzoxazole ring, whereas the absorption peak at 1614 cm^{-1} is assigned to the aromatic rings.

To further investigate other absorption peaks in Figure 3, the FTIR spectra of PBO and poly (*o*-hydroxyamide) (PHA), the structure of which is very similar to PBO except for the benzoxazole ring (Scheme 3), were compared. The result is shown in Figure 4. The spectra show absorptions at 1614 and 1680 cm^{-1}. In addition, the FTIR spectrum of PHA shows absorption at 1647 cm^{-1}, whereas the FTIR spectrum of PBO shows absorption at 1627 and 1647 cm^{-1}.

According to the mechanism reported by So,[12] *o*-hydroxyamide was formed first during PBO polymerization. Then, this structure becomes dehydrated, and the benzoxazole ring is formed. This ring closure step is acid catalyzed. Because incomplete ring closure reactions may have occurred during polymerization, it is reasonable to qualify the absorption peak of 1647 cm^{-1} in Figure 3 as the absorption of the amide group in the *o*-hydroxyamide structure. These results suggest that the

Figure 2 FTIR spectra of PBO films prior to and after hydrolysis in 0.2*N* H_2SO_4.
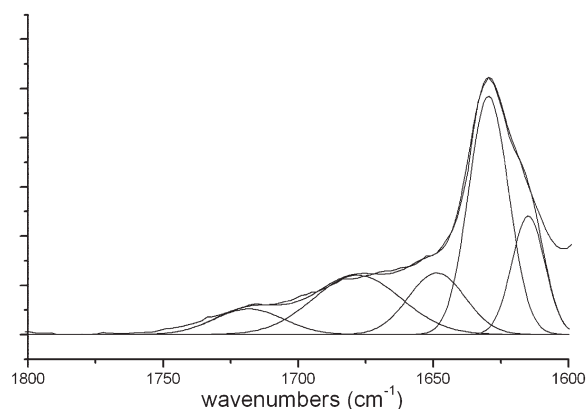
Figure 3 Resolved spectral results of original PBO film.
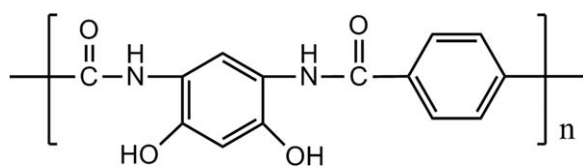
Scheme 3   Chemical structure of PHA.

o-hydroxy amide linkage exists in the PBO chain to some extent due to the incomplete reaction in the polymerization and the formation of an open ring structure in the PBO molecule.

Figure 5 was the ^{1}H-NMR spectrum of PBO. The resonances from 9.0 ppm to 8.4 ppm were assigned to hydrogen atoms of aromatic rings. It should be mentioned that weak resonance at 9.06 ppm was assigned to the hydrogen atoms of amide, which provided further evidence for the existence of hydroxyl amide linkages in the polymer.

Thus, the real chemical structure of PBO cannot be described by Scheme 1 but by Scheme 4, which includes the benzoxazole ring, *o*-hydroxy amide linkage (open ring structure), and terminal carboxyl group. The absorption peaks in the FTIR spectra at 1627, 1614, 1647, 1680 cm^{-1} are attributed to the (a), (b), (c), and (d) groups, respectively.

Degradation mechanism of PBO under hydrolytic conditions

Because the real chemical structure of PBO is described according to Scheme 4 instead of Scheme 1, the hydrolytic degradation mechanism of PBO previously reported has to be reconsidered and supplemented.
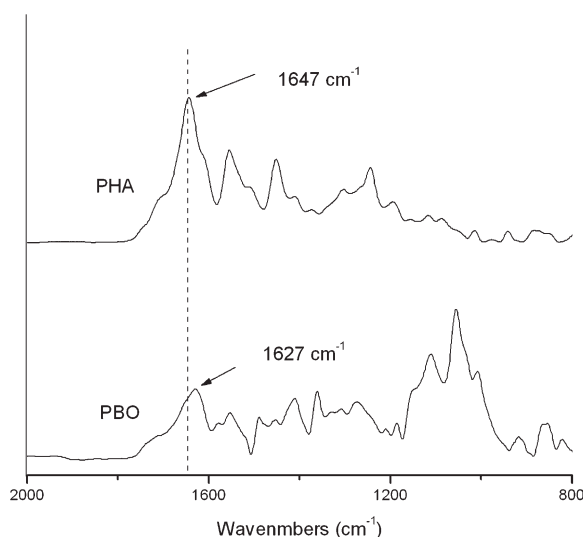

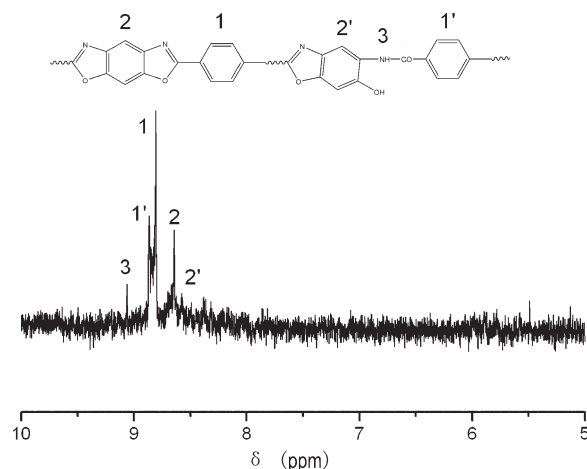Figure 4   FTIR spectra of PBO and poly(*o*-hydroxy amide).

Figure 5 ^{1}H-NMR spectrum of PBO.

To study the chemical changes that occurred during hydrolysis, all FTIR spectra of the PBO film hydrolyzed at different times were baseline corrected. The overlapping bands at 1600–1800 cm^{-1} were decomposed into several peaks using a mixed Gaussian/Lorentzian model. The integrated peak intensity of the benzoxazole ring absorption (*a*) was set as a ratio against the integrated peak intensity of the aromatic ring absorption (*b*). The latter peak served as an internal standard, because preliminary studies showed that the aromatic ring was stable and the integrated peak intensity of this band did not change significantly during hydrolytic degradation. Therefore, the peak ratios *a*/*b* can be directly related to the change of benzoxazole ring concentration as a function of time. Similarly, the peak ratios *c*/*b* can describe the change of the concentration of the *o*-hydroxy amide linkage group. The letters *a*, *b*, and *c* represent the benzoxazole ring, aromatic ring, and *o*-hydroxy amide, respectively. Integration of the area under selected bands in the FTIR data is accomplished using the integration option in Origin v8.0. A similar method has been used widely by researchers. For instance, Sommer characterized a thin-film negative resist via photo-FTIR and used this method.[13]

The relative amount of changes in the benzoxazole ring (*a*/*b*) and *o*-hydroxy amide group (*c*/*b*) during hydrolytic degradation of PBO films in 0.2*N* H$_2$SO$_4$ solution is shown in Figure 6. In addition, the relative amount of benzoxazole ring almost does not change, whereas the relative amount of *o*-hydroxy amide group decreases at first and then flattens at around the 15th day. The I.V. of films notably decreases and then flattens at around the 15th day (Fig. 1).

Comparing the relative amount of benzoxazole ring (*a*/*b*) with the corresponding I.V. of PBO, the relative amount of benzoxazole ring does not change
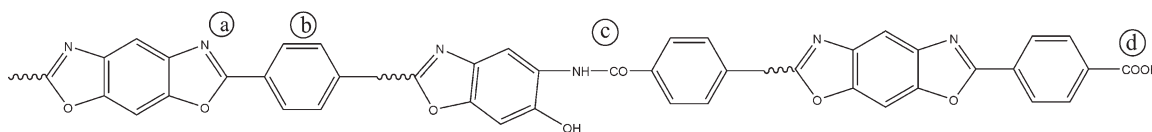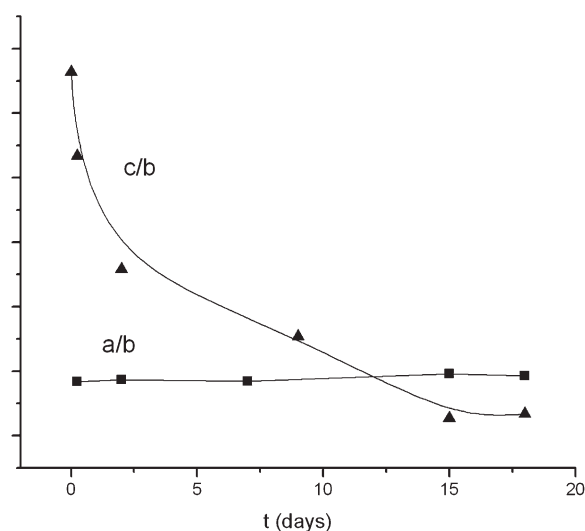
Scheme 4 The real chemical structure of PBO.

until almost the final stage, at which the value of I.V. was about 12 (Fig. 7). Clearly, these phenomena cannot be explained by the classical ring-opening mechanism described in the introduction because, according to this mechanism, both the relative amounts of benzoxazole ring and the I.V. of PBO should decrease continually until the ring-opening reaction stops.

The only possibility is that the opening of the benzoxazole ring does not occur, and the main degradation mechanism is a chain scission from the o-hydroxy amide linkage, at least in the early and middle stages of hydrolytic degradation. The concentration of o-hydroxy amide linkages determines the speed of degradation.

Figure 7 shows that, with the decrease of the relative amount of o-hydroxy amide, the I.V. of PBO decreases isochronously during hydrolysis. Considering that the relative amount of the benzoxazole ring almost does not change at the early stage of degradation, it is reasonable to think that, at the early and middle stages of degradation, the decrease of the I.V. of PBO is due to the hydrolysis and chain scission of the o-hydroxy amide linkage, which comes from incomplete reactions during polymerization.

Based on the aforementioned mechanism of hydrolysis, PBO films soaked in 0.2N H$_2$SO$_4$ are understood to degrade faster than PBO films soaked in 0.02N H$_2$SO$_4$ solution and deionized water (Fig. 1). This is because the o-hydroxy amide linkage is sensitive to an acidic environment.

Furthermore, PBO films are expected to be more stable under hydrolytic condition if the concentration of o-hydroxy amide linkage in the PBO molecular chain is lower. Heat treatment can promote the ring-closing reaction of PBO molecules and decrease the concentration of o-hydroxy amide linkage. Therefore, heat treatment of PBO films was done by placing films into the furnace at 400°C for 10 min under a N$_2$ atmosphere. The relative amounts of benzoxazole ring (a/b) before and after heat treatment are listed in Table I. The relative amount of benzoxazole ring (a/b) increases after heat treatment, indicating that the degree of ring closing of PBO improved after heat treatment.

The degradation results for soaked original PBO film without heat treatment and the PBO film heat treated at 400°C for 10 min in 0.2N H$_2$SO$_4$ are shown in Figure 8. The hydrolysis speed decreases for PBO film after heat treatment. This is consistent with the aforementioned mechanism.
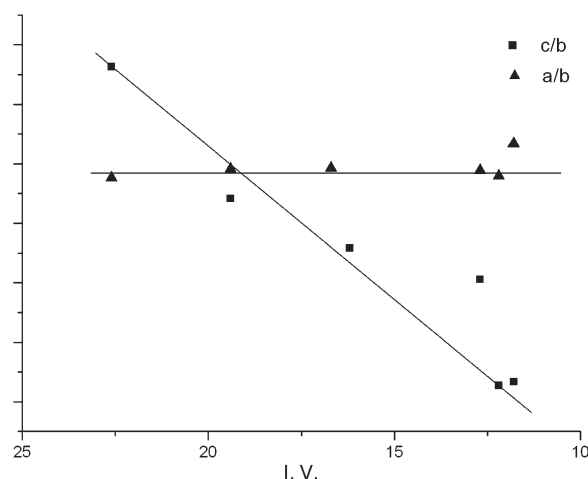
Figure 7 Changes in the concentration of benzoxazole ring versus the value of I.V. in 0.2N H$_2$SO$_4$.

Figure 6 Relative concentration changes of benzamide (c/b) and benzoxazole ring (a/b) in 0.2N H$_2$SO$_4$.

TABLE I
Relative Amount of Benzoxazole Ring (a/b) of PBO Heat Treated at Different Time

	original	2 min	5 min	10 min
a/b	3.52	3.67	4.36	4.53
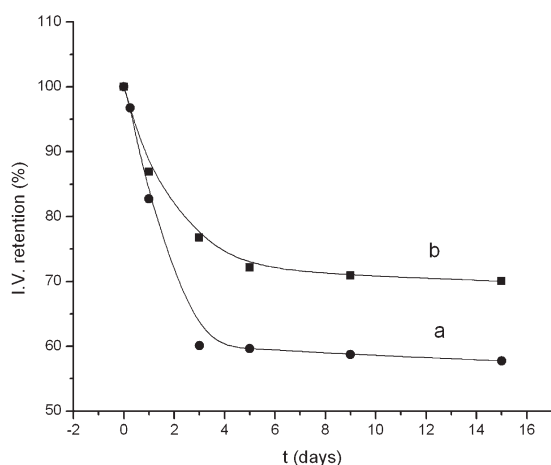
Figure 8 I.V. versus hydrolysis time for PBO films hydrolyzed in 0.2N H$_2$SO$_4$ solutions (a: original PBO; b: PBO after heat treatment).

CONCLUSIONS

In this article, the hydrolysis of PBO films was studied by soaking PBO film in deionized water, 0.02N H$_2$SO$_4$, and 0.2N H$_2$SO$_4$ for up to 25 days. The I.V. values of the PBO films during hydrolysis decreased and then stabilized. The FTIR absorption spectra of PBO showed that the o-hydroxy amide linkage existed in the PBO molecule chain to some extent because of the incomplete polymerization that resulted in the formation of open ring structures in the PBO molecule. Further investigation showed that during hydrolytic degradation, the relative amount of benzoxazole ring almost did not change in the early and middle stages, whereas the relative amount of o-hydroxy amide group decreased at first and then stabilized. In the early and middle stages of hydrolytic degradation, the main degradation mechanism was the chain scission of the o-hydroxy amide linkage section. This is a reasonable explanation for the result. The concentration of o-hydroxy amide linkages determined the speed of hydrolytic degradation of PBO.

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