

Enhanced Degradation Stability of Poly(*p*-dioxanone) Under Different Temperature and Humidity with Bis-(2,6-diisopropylphenyl) Carbodiimide

Yin-Qiao Zhao, Song-Dong Ding, You Yuan, Yu-Zhong Wang

Center for Degradable and Flame-Retardant Polymeric Materials (SC Key Laboratory), National Engineering Laboratory of Eco-Friendly Polymeric Materials (Sichuan), College of Chemistry, State Key Laboratory of Polymer Materials Engineering, Sichuan University, Chengdu 610064, China

Correspondence to: S.-D. Ding (E-mail: dsd68@163.com) or Y.-Z. Wang (E-mail: polymers@126.com).

ABSTRACT: The influences on the degradation of poly(*p*-dioxanone) (PPDO) under different temperature and relative humidity is initially investigated by adding bis-(2,6-diisopropylphenyl) carbodiimide (commercial name: stabaxol[®]-1). The changes of intrinsic viscosity, mechanical properties, crystallinity, surface morphologies, and microstructure of PPDO and PPDO containing stabaxol[®]-1 for 6 weeks are monitored. With increasing the degradation time, the intrinsic viscosity and mechanical properties of PPDO decrease much faster than those of PPDO containing 0.6 wt % stabaxol[®]-1. During the degradation, PPDO containing 0.6 wt % stabaxol[®]-1 shows a better physical integrity than PPDO. It has been shown that stabaxol[®]-1 can retard the hydrolysis degradation of PPDO and enhance its hydrolytic stability. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40026.

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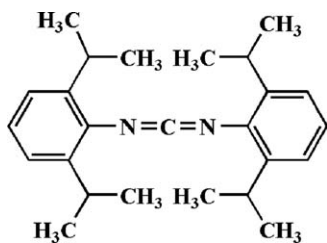
INTRODUCTION

Poly(*p*-dioxanone) (PPDO), a semicrystalline aliphatic polyester, has not only good mechanical properties with a strength at break close to 46 MPa and an ultimate elongation ranging from 500% to 600%, but also excellent biodegradability, biocompatibility and bioabsorbability.^{1–5} Now, it has been used as a biomaterial for suture, bone repair device and drug delivery systems.^{6,7} During recent years, owing to the great progress on the catalytic synthesis technology of 1,4-dioxan-2-one (PDO) monomer from diethylene glycol, the cost of PDO decreased significantly.⁸ It makes possible for PPDO to be a candidate for general applications such as films, molded product, laminates, foams, non-woven materials, adhesives, and coatings.⁷ However, PPDO is prone to degradation in the ambient circumstance, which leads to the great limitation for the availability of PPDO as general material. Therefore, it is very important to improve its stability for widespread applications.

Up to now, some studies on the hydrolytic degradation of PPDO have been reported. Bai *et al.* investigated the degradation of PPDO in the phosphate buffer solution of pH 7.44 at 37°C. Only after 4 weeks, PPDO with intrinsic viscosity of 2.4 dL g⁻¹ lost 73% of its initial tensile strength and 95% of its initial maximum breaking elongation.⁹ Sabino *et al.* studied the

hydrolytic degradation of PPDO on the surface morphology under the same conditions. Some small cracks were observed on the surface of PPDO sutures by scanning electronic microscopy at the 4th week of degradation.¹⁰ Sabino *et al.* also found PPDO lost almost 50% of its weight after 10 weeks degradation at 37°C in distilled water in their later study.¹¹ Lin *et al.* presented a mechanism for PPDO suture degradation in phosphate buffer solution of pH 7.4 at 37°C.¹² The random hydrolysis process of PPDO via two distinct stages: random scission of chain segments located in the amorphous regions of microfibrils and intermicrofibrillar space, followed by stepwise scission of chain segments located in the crystalline regions of microfibrils. This scission of chain segments is ascribed to the break of unstable ester bonds. The produced low molecular weight acid species can further catalyze the scission of ester bonds, suggesting the acceleration for PPDO hydrolysis.¹¹ Conversely, if the catalytic activity of acid species is suppressed, the hydrolytic stability of PPDO can be enhanced.

To improve the hydrolytic stability of PPDO, some efforts have been made. Liu investigated the hydrolytic degradation of PPDO containing polycarbodiimide (PCD) in the phosphate buffer solution of pH 7.44 at 37°C.¹³ During the degradation, PPDO containing 1 wt % PCD of 10th week was not as fragile as neat PPDO of 7th week from the scanning electron microscopy



Scheme 1. Chemical structures of stabaxol[®]-1.

(SEM) graphs. It can also be observed that the elongation of PPDO ranged from 270% at origin to 14% at first week, whereas that of PPDO containing 1 wt % PCD changed from 245% to about 100% in the same time span. These results indicated that PCD could dramatically enhance the hydrolytic stability of PPDO. The reason for enhancement is that PCD can react with terminal carboxyl groups to generate stable *N*-acylurea and reduce the autocatalytic activity of acid species originated from the break of ester bonds.¹⁴ However, PCD is a multigroup carbodiimide and may give rise to the crosslinking of PPDO, which is to the disadvantage of further processing of PPDO. Therefore, it is not a good choice for the enhancement of hydrolytic stability of PPDO by adding PCD. To avoid the disadvantage of PCD, it is necessary to investigate further the influences of the hydrolytic stability of PPDO by adding the monogroup carbodiimide. In recent years, a kind of monogroup aromatic carbodiimide compound, bis-(2,6-diisopropylphenyl) carbodiimide (commercial name: stabaxol[®]-1) with high stability and suitable melting point of 40–45°C, was paid more and more attention. It has also been employed to improve the hydrolysis resistance for some aliphatic polyesters. The chemical structure of stabaxol[®]-1 is shown in Scheme 1. Adding stabaxol[®]-1 can satisfy durability, impact resistance, and moldability of the molded article made of the polylactic acid resin composition.¹⁵ Kim *et al.* found polybutylene succinate added stabaxol[®]-1 exhibited increased resistance to hydrolysis on tensile strength of ~30% under 90% relative humidity and 50°C condition for 30 days.¹⁶ On the basis of these good effectiveness obtained, it may be expected that stabaxol[®]-1 can also improve the hydrolytic stability of PPDO.

In this article, the influences on hydrolytic degradation of PPDO under different temperature and relative humidity are investigated by adding stabaxol[®]-1. The changes of intrinsic viscosity, mechanical properties, crystallinity, and surface morphologies of PPDO and PPDO containing stabaxol[®]-1 are monitored by Ubbelohde viscosimeter, electro mechanical universal testing machine, differential scanning calorimetry (DSC), and SEM, respectively. As far as the authors know, no available data have been reported on hydrolysis resistance for PPDO by using stabaxol[®]-1 as a stabilizer. In addition, the degradation behaviors of PPDO under the different temperature and relative humidity conditions are still investigated for the first time, while the degradation conditions for all of the early studies are almost in phosphate buffer solution.^{11,13,17,18}

EXPERIMENTAL

Sample Preparation

PDO monomer was provided by the Pilot Plant of the Center for Degradable and Flame-Retardant Polymeric Materials

(Chengdu, China) and purified two times by vacuum distillation from CaH₂. By reference to literature,¹⁹ the bulk polymerization of PPDO was carried out in previously dried 3L reaction kettle (Weihai Automatic Control Reaction Kettle, China). The reaction kettle was evacuated and purged with argon three times prior to addition of PDO and stannous octoate catalyst solution with a syringe. The polymerization was performed at 120°C for 6 h, and then vacuum was applied for 2 h to remove unreacted monomers. PPDO containing stabaxol[®]-1 (abbreviated to PPDO/stabaxol[®]-1) was prepared in the same way except for adding desired amount of stabaxol[®]-1 into the reaction kettle at the time of polymerization for 5 h at 120°C. The reasons for adding stabaxol[®]-1 in the polymerization process rather than blending after polymerization are that PPDO has poor thermal melt stability above 140°C^{5,20} and stabaxol[®]-1 can be distributed better. Here, stabaxol[®]-1 was provided by Rhein Chemie, Germany.

Degradation Conditions

PPDO and PPDO/stabaxol[®]-1 bars with the dimension of 25 × 4 × 0.5 mm³ were prepared by compression molding using vulcanizing press at the processing temperature of 130°C and the processing pressure of 10 MPa for 3 min. Five glass chambers were used to provide controlled environments for the hydrolytic degradation of sample bars. The chambers were placed in an oven at different temperature (25, 37, and 45°C). A saturated solution of potassium acetate, magnesium nitrate, or potassium chloride was used to maintain about 25, 50, or 85% relative humidity within each chamber, respectively (ASTM 104-85).^{21,22} The degraded samples were taken out of the chamber in a given time period for measurement.

Intrinsic Viscosity

PPDO with high intrinsic viscosity cannot be measured by gel permeation chromatography (GPC) due to its poor solubility in the solvents commonly employed to perform GPC. Thus, the intrinsic viscosity of both PPDO and PPDO/stabaxol[®]-1 were tested in phenol/1,1,2,2-tetrachloroethane (1 : 1 w : w) solution using an Ubbelohde viscosimeter thermostated at 30°C.

Tensile Test

An electro mechanical universal testing machine (Sans Testing Machine, China) was employed to perform the tensile tests. The samples were tested at room temperature at a drawing speed of 50 mm min⁻¹. The values presented were the mean of five replicate samples.

Differential Scanning Calorimetry

DSC analysis was carried out using an instrument DSC Q200 (TA Corporation, Delaware) with 3–5 mg of the specimens before and after hydrolysis at the designated time points. After the retreatment, each sample was subjected to a heat-cool-heat cycle from -50 to 140°C at a heating rate of 10°C min⁻¹ under a nitrogen atmosphere. The apparatus was calibrated with indium standards. The crystallinity was calculated from the reported enthalpy of fusion 14.4 kJ mol⁻¹ for 100% crystalline PPDO.²³

Scanning Electron Microscopy

SEM evaluation was carried out to examining the surface morphology of the samples. An instrument SEM JSM-5900LV

Table I. Influence of Stabaxol[®]-1 Addition Content on the Intrinsic Viscosity and Tensile Properties of the Prepared PPDO

Content (wt %)	$[\eta]$ (dL g ⁻¹)	δ (MPa)	ε (%)
0	1.77 ± 0.23	47.9 ± 2.6	504 ± 43
0.3	1.72 ± 0.29	56.2 ± 3.2	544 ± 32
0.6	1.80 ± 0.28	57.3 ± 2.9	582 ± 54
0.9	1.68 ± 0.33	53.6 ± 1.9	562 ± 38
1.2	1.54 ± 0.30	52.7 ± 2.5	516 ± 47

(JEOL Corporation, Japan) was used to observe the surfaces of the gold sputter-coated samples.

Fourier Transform Infrared (FTIR) Spectroscopy

FTIR-ATR (attenuated total reflectance) spectra of PPDO samples were obtained using a Nicolet 6700 FTIR spectrophotometer (Thermo Fisher Scientific, MA). The infrared absorption spectra of Stabaxol[®]-1 were performed using KBr pellet. The range of wave numbers is from 400 to 4000 cm⁻¹.

Nuclear Magnetic Resonance

Hydrogen nuclear magnetic resonance (¹H NMR) spectra were recorded on a Varian Inova 400 spectrometer (Varian, CA) with dimethyl sulfoxide-d₆ as a solvent.

RESULTS AND DISCUSSION

Influence of Stabaxol[®]-1 Addition Content on the Intrinsic Viscosity and Tensile Properties of the Prepared PPDO

Influence of stabaxol[®]-1 addition content on the intrinsic viscosity ($[\eta]$), tensile breaking strength (δ), and elongation at

break (ε) of the prepared PPDO are listed in Table I. Each polymerization described in Table I attained equilibrium. The values of $[\eta]$, δ , and ε increased with increasing of stabaxol[®]-1 content until 0.6 wt % and then decreased. Added to the polymerization system at 120°C, stabaxol[®]-1 can react with terminal carboxyl and terminal hydroxyl groups of PPDO,²⁴ leading to the reduction of the amounts of these groups. This is good for the molecular chain growth of PPDO. Thus, with the increase of stabaxol[®]-1 addition content, the intrinsic viscosity and tensile properties increase. However, further increase of stabaxol[®]-1 content gives rise to the complete end-capping of the active chain end of PPDO, which is bad for the growth of PPDO molecular chain. Therefore, the intrinsic viscosity and tensile properties decrease. To obtain high molecular weight PPDO and good mechanical properties, 0.6 wt % stabaxol[®]-1 addition content was used in the following degradation experiments.

Influence of Stabaxol[®]-1 on the Intrinsic Viscosity of PPDO

The changes of intrinsic viscosity of PPDO/0.6 wt % stabaxol[®]-1 and PPDO at different temperature and humidity are shown in Figure 1. The intrinsic viscosity of both PPDO/0.6 wt % stabaxol[®]-1 and PPDO declined as a function of the degradation time under all of the investigated conditions, but the intrinsic viscosity of the former reduced much slower than that of the latter. After 5 weeks degradation at 25°C, the intrinsic viscosity of PPDO under 25, 50, and 85% RH decreased 57, 74, and 86%, respectively, while PPDO/0.6 wt % stabaxol[®]-1 under the corresponding condition lost only 23, 36, and 47%. At the same time, after 5 weeks degradation at 37 and 45°C under 50% RH, the intrinsic viscosity decreased 82 and 86% for

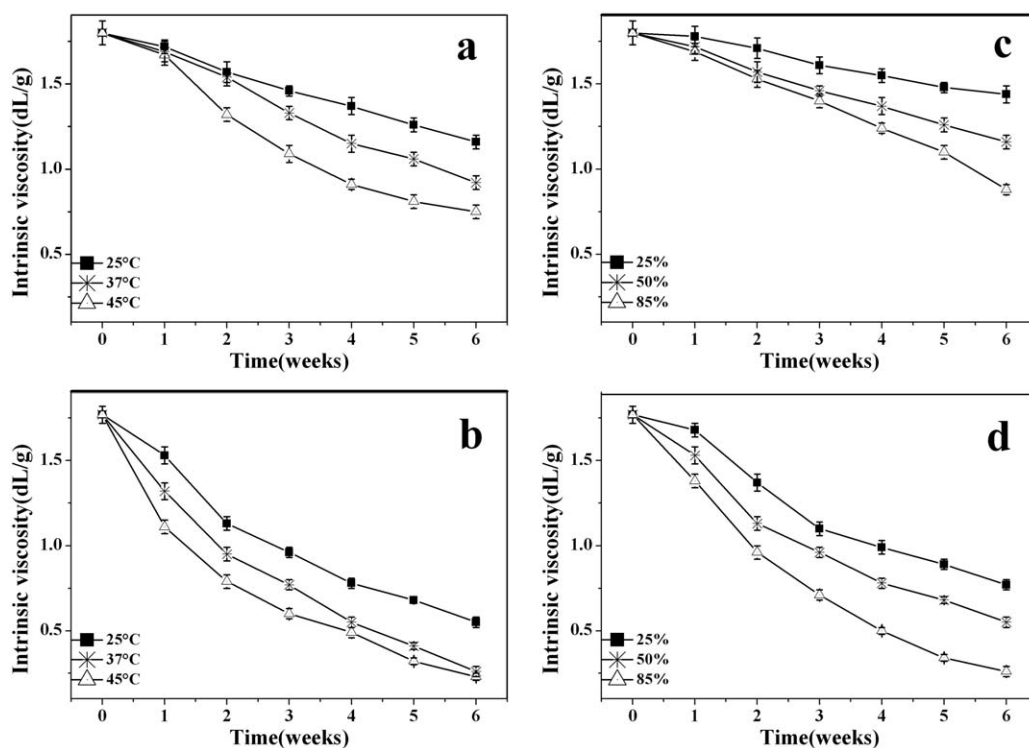


Figure 1. Influence of stabaxol[®]-1 on the intrinsic viscosity at 50% RH and different temperature for (a) PPDO/0.6 wt % stabaxol[®]-1 and (b) PPDO; at 25°C and different relatively humidity for (c) PPDO/0.6 wt % stabaxol[®]-1 and (d) PPDO.

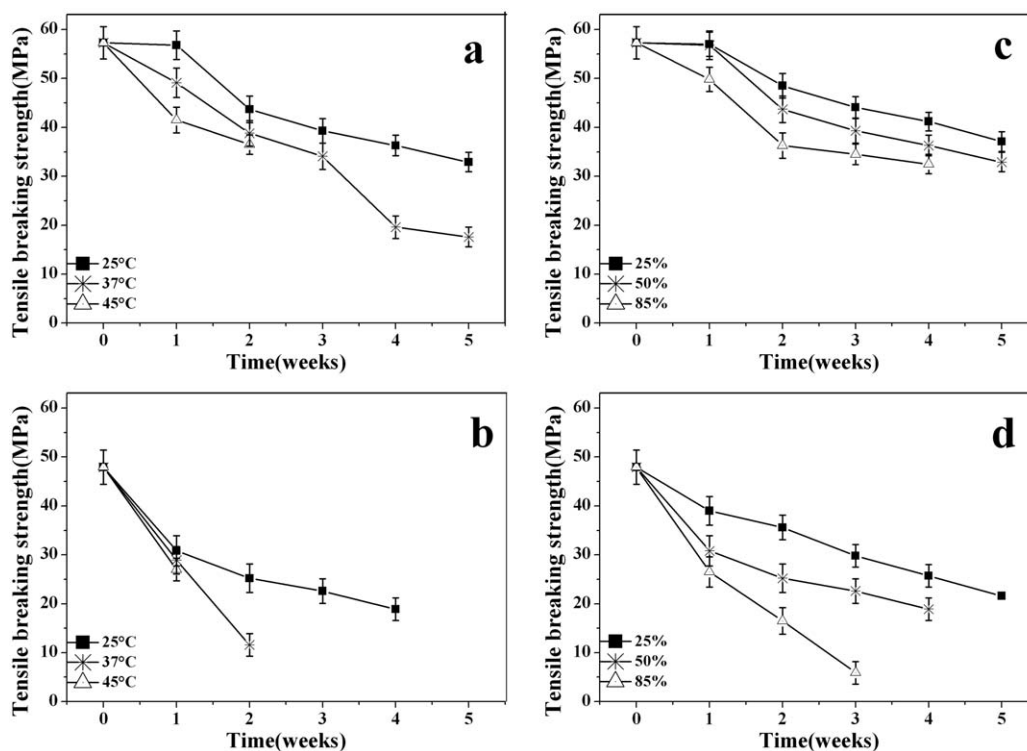


Figure 2. Influence of stabaxol[®]-1 on the tensile breaking strength of PPDO at 50% RH and different temperature for (a) PPDO/0.6 wt % stabaxol[®]-1 and (b) PPDO; at 25°C and different relative humidity for (c) PPDO/0.6 wt % stabaxol[®]-1, and (d) PPDO.

PPDO; 49 and 66% for PPDO/0.6 wt % stabaxol[®]-1, respectively. The changes at intrinsic viscosity are similar to those reported by Sabino *et al.* and Liu *et al.* in the case of the degradation in phosphate buffer solution.^{11,13} Lower relative humidity and temperature are good for the hydrolysis stability of PPDO. The influences of temperature on the degradation of PPDO are more obvious than those of relative humidity.

Influence of Stabaxol[®]-1 on the Tensile Properties of PPDO

The changes of tensile properties of PPDO/0.6 wt % stabaxol[®]-1 and PPDO at different temperature and humidity are shown in Figures 2 and 3. The tensile properties of PPDO/0.6 wt % stabaxol[®]-1 and PPDO decreased with the degradation time under all of the investigated conditions, but the former reduced much slower than the latter. With the increase of temperature under 50% RH, the tensile breaking strength and the elongation of both PPDO/0.6 wt % stabaxol[®]-1 and PPDO decreased with the degradation time except for PPDO/0.6 wt % stabaxol[®]-1 at 25°C which tensile breaking strength and the elongation kept a nearly constant during the first week degradation and then had a same change tendency as the other samples [Figures 2(a,b) and 3(a,b)]. In addition, the influence of relative humidity on the tensile properties [Figures 2(c,d) and 3(c,d)] follows the same trends as that of temperature. Temperature plays more significant roles than relative humidity does during the degradation.

Influence of Stabaxol[®]-1 on the Crystallinity of PPDO

Influence of stabaxol[®]-1 on the crystallinity of PPDO in the degradation process is listed in Tables II and III. Clearly, the introduction of stabaxol[®]-1 was able to induce the changes of

crystallization behaviors for PPDO. In the same degradation time period, the crystallinity of both PPDO/0.6 wt % stabaxol[®]-1 and PPDO increased with the degradation time under different relative humidity at 25°C. However, after 2 weeks degradation, the crystallinity values of PPDO under 50% RH and 37°C, 45°C; and PPDO/0.6 wt % stabaxol[®]-1 under 50% RH and 45°C became obviously larger than before degradation. Subsequently, the crystallinity decreased. In addition, the crystallinity of PPDO/0.6 wt % stabaxol[®]-1 changed much slower than that of PPDO.

With the increase of relative humidity at 25°C, the crystallinity of both PPDO/0.6 wt % stabaxol[®]-1 and PPDO decreased with the degradation time (Table II). Under 25% RH, the crystallinity of PPDO/0.6 wt % stabaxol[®]-1 was not obviously changed, while that of PPDO increased slightly. Under the higher relative humidity, the crystallinity of PPDO increased at a faster rate than PPDO/0.6 wt % stabaxol[®]-1. For example, under 25% RH and 25°C after 6 weeks degradation, the crystallinity of PPDO and PPDO/0.6 wt % stabaxol[®]-1 increased from 36.6%, 35.1% to 47.5%, 39.2%, respectively. Correspondingly, under 50% RH and 25°C after 6 weeks, the crystallinity of PPDO and PPDO/0.6 wt % stabaxol[®]-1 increased from 36.6%, 35.1% to 51.4%, 45.3%, respectively. Under the given relative humidity, the crystallinity of PPDO and PPDO/0.6 wt % stabaxol[®]-1 decreased with the increase of temperature (-Table III). Moreover, the influence of temperature on the crystallinity follows the similar trends as that of relative humidity.

The above results indicate that stabaxol[®]-1 played a role of restraining the hydrolysis of PPDO. When water in the ambient

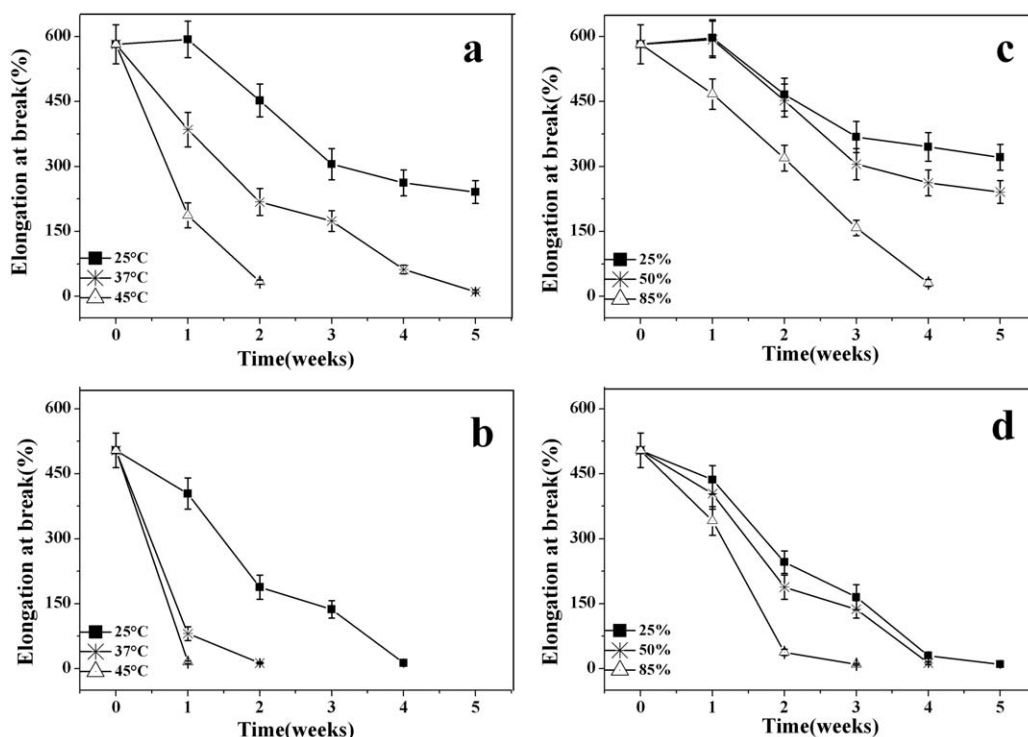


Figure 3. Influence of Stabaxol®-1 on the elongation at break of PPDO at 50% RH and different temperature for (a) PPDO/0.6 wt % Stabaxol®-1 and (b) PPDO; at 25°C and different relative humidity for (c) PPDO/0.6 wt % Stabaxol®-1 and (d) PPDO.

circumstance diffuses into PPDO, the attack happens on both amorphous and crystalline areas, but preferentially on the amorphous areas because of their low density. Afterwards, chain scission occurs and subsequently results in short chain segments. These short segments can organize themselves to the crystal, which causes an increase in crystallinity.^{25–27} PPDO/0.6 wt % Stabaxol®-1 had a slower rate of crystallinity than PPDO during the degradation, perhaps because of the restriction of mobility for PPDO chains with the rigid aromatic ends originated from the reaction with Stabaxol®-1. In addition, temperature increase can promote the chain segmental motion. The chain mobility increased allowing some of the amorphous segments to order themselves into a more crystalline structure.²⁸ Therefore, as the degradation proceeded at 45°C, the crystallinity increased at first. However, with degradation time further increasing, scis-

sion of chain segments located in the crystalline regions occurs.²⁹ Thus, the crystallinity then decreased.

Influence of Stabaxol®-1 on the Surface Morphology of PPDO

Surface micrographs of PPDO/0.6 wt % Stabaxol®-1 and PPDO before and after hydrolysis with different degradation time are shown in Figures 4 and 5, respectively. Among them, Figures 4(a) and 5(a) give the pictures before hydrolysis. Both of PPDO/0.6 wt % Stabaxol®-1 and PPDO presented a relative smooth and clear surface. Under 25°C and 50% RH after 6 weeks, some small cracks exhibited on the surface of PPDO, while no cracks were observed on the surface of PPDO/0.6 wt % Stabaxol®-1. With further increasing temperature and relative humidity, there were some cracks on the surface of both PPDO and PPDO/0.6 wt % Stabaxol®-1. In addition, PPDO/0.6 wt %

Table II. Influence of Stabaxol®-1 on the Crystallinity of PPDO at 25°C and Different Relative Humidity for 6 Weeks

Time (week)	PPDO/0.6 wt % Stabaxol®-1						PPDO					
	25%		50%		85%		25%		50%		85%	
	ΔH_m (J/g)	D_c (%)	ΔH_m (J/g)	D_c (%)	ΔH_m (J/g)	D_c (%)	ΔH_m (J/g)	D_c (%)	ΔH_m (J/g)	D_c (%)	ΔH_m (J/g)	D_c (%)
0	49.5	35.1	49.5	35.1	49.5	35.1	51.6	36.6	51.6	36.6	51.6	36.6
2	49.5	35.1	50.2	35.6	58.8	41.7	59.8	42.4	63.9	45.3	64.1	45.4
4	54.6	38.7	59.3	42.0	61.4	43.5	63.9	45.3	67.2	47.6	69.0	48.9
6	55.3	39.2	63.9	45.3	72.7	51.5	67.1	47.5	72.6	51.4	73.7	52.2

ΔH_m : The enthalpy obtained by integrating the melting peak from DSC curves.

D_c : The crystallinity that was calculated from the reported enthalpy of fusion 14.4 kJ mol⁻¹ for 100% crystalline PPDO.

Table III. Influence of Stabaxol[®]-1 on the Crystallinity of PPDO at 50% RH and Different Temperature for 6 Weeks

Time (week)	PPDO/0.6 wt % stabaxol [®] -1						PPDO					
	25°C		37°C		45°C		25°C		37°C		45°C	
	ΔH_m (J/g)	D_c (%)	ΔH_m (J/g)	D_c (%)	ΔH_m (J/g)	D_c (%)	ΔH_m (J/g)	D_c (%)	ΔH_m (J/g)	D_c (%)	ΔH_m (J/g)	D_c (%)
0	49.5	35.1	49.5	35.1	49.5	35.1	51.6	36.6	51.6	36.6	51.6	36.6
2	50.2	35.6	58.6	41.5	66.2	46.9	63.9	45.3	77.3	54.8	80.4	56.9
4	59.3	42.0	63.3	44.8	64.4	45.6	67.2	47.6	68.7	48.7	64.9	46.0
6	63.9	45.3	64.7	45.8	57.2	40.5	72.6	51.4	59.0	41.8	57.3	40.6

ΔH_m : The enthalpy obtained by integrating the melting peak from DSC curves.

D_c : The crystallinity which was calculated from the reported enthalpy of fusion 14.4 kJ mol^{-1} for 100% crystalline PPDO.

stabaxol[®]-1 under 25°C and 85% RH was not as fragile as PPDO under 25°C and 50% RH. The changes of surface morphologies show that PPDO/0.6 wt % stabaxol[®]-1 had better physical integrity than PPDO in the degradation process, suggesting that stabaxol[®]-1 can inhibit the hydrolytic degradation of PPDO.

Influence of Stabaxol[®]-1 on the Microstructure of PPDO

To research the microstructure changes in the degradation process, the FTIR and ¹H NMR spectra of degraded samples were analysed. Figure 6(b) shows the FTIR spectra of stabaxol[®]-1. The absorption bands at 1584, 1516 and 1460 cm^{-1} are attributed to the vibrations of phenyl group and the peak at 2164 cm^{-1} is the characteristic absorption of carbodiimide group. In Figure 6(a,c,d), the absorption bands of O—H, C=O, and

H—O—C(O)—C groups are located at 3429, 1742 and 1203 cm^{-1} , respectively. The peaks at 1633 and 1563 cm^{-1} are the characteristic absorption of phenyl group introduced by the addition of stabaxol[®]-1. After degradation for 6 weeks under 37°C and 50% RH, the disappearance of absorption band of carbodiimide group at 2164 cm^{-1} was clearly observed, which indicated that stabaxol[®]-1 has been exhausted during the degradation.

Figure 7(a,c) shows the ¹H NMR spectra of PPDO/0.6 wt % stabaxol[®]-1 and PPDO before degradation. Resonances located at δ H 4.35 ppm, δ H 4.18 ppm, and δ H 3.80 ppm were assigned to the three methylene hydrogen atoms of PPDO, respectively. Meanwhile, there was no obvious miscellaneous peak in the spectra. Figure 7(b,d) shows the ¹H NMR spectra of

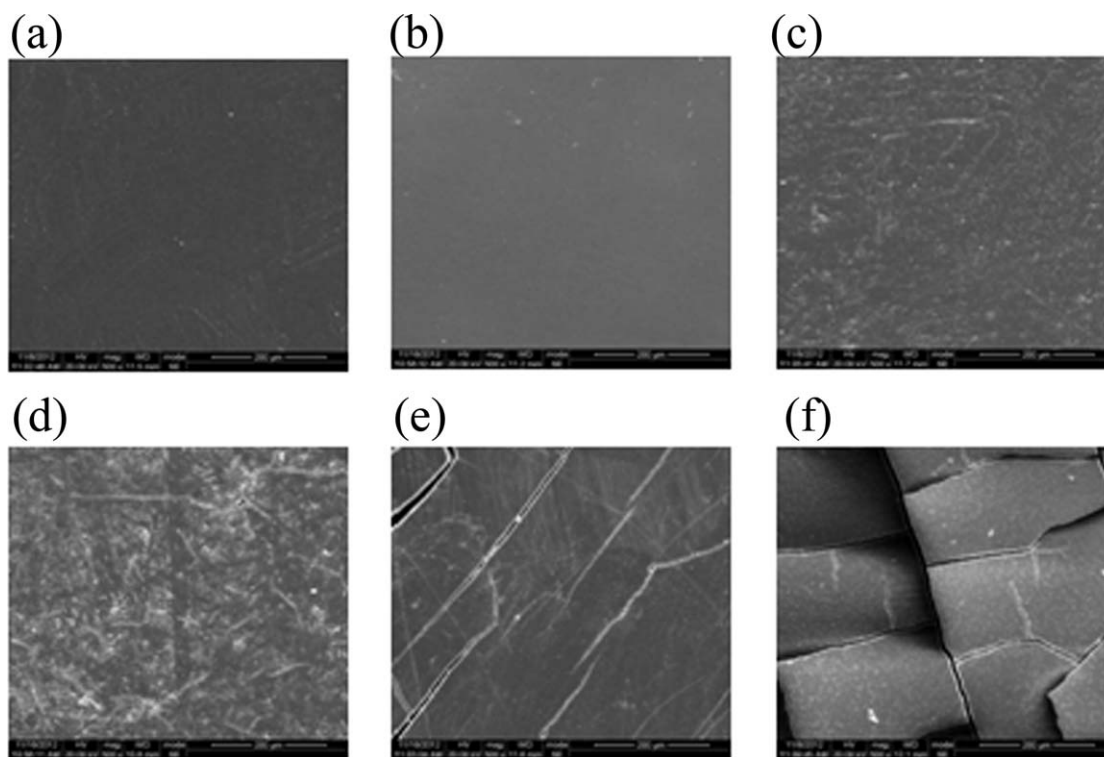


Figure 4. Surface morphology of PPDO/0.6 wt % stabaxol[®]-1 from SEM micrographs ($\times 500$) for (a) before degradation; (b) 25°C and 25% RH, (c) 25°C and 50% RH; (d) 25°C and 85% RH; (e) 37°C and 50% RH; and (f) 45°C and 50% RH after degradation for 6 weeks.

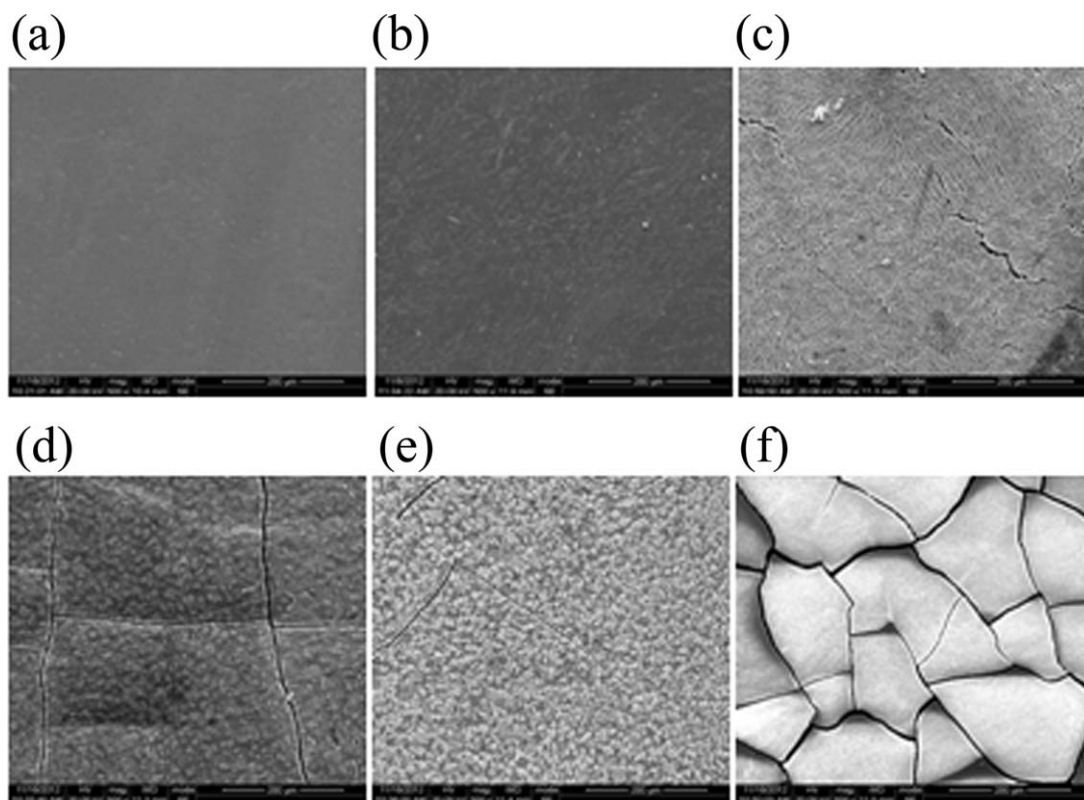


Figure 5. Surface morphology of PPDO from SEM micrographs ($\times 500$) for (a) before degradation; (b) 25°C and 25% RH; (c) 25°C and 50% RH; (d) 25°C and 85% RH; (e) 37°C and 50% RH; and (f) 45°C and 50% RH after degradation for 6 weeks.

PPDO/0.6 wt % stabaxol[®]-1 and PPDO after degradation for 6 weeks under 37°C and 50% RH. There are few differences between Figure 7(a,b), whereas obvious differences occur between Figure 7(c,d). Several new peaks located at δ H 4.51 ppm, δ H 4.38 ppm, δ H 4.21 ppm, δ H 4.15 ppm, δ H 3.88 ppm, and δ H 3.72 ppm appeared in Figure 7(d), owing to the

signals of hydrogen atom in aliphatic hydroxyl group originated from the cleavage of ester bonds. The ¹H NMR analyses confirm the faster degradation process of PPDO as compared with PPDO/0.6 wt % stabaxol[®]-1.

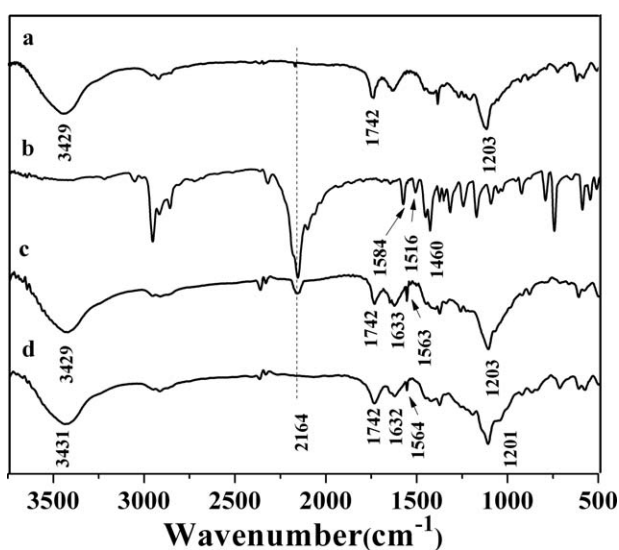


Figure 6. FTIR spectra of (a) PPDO before degradation; (b) stabaxol[®]-1; (c) PPDO/0.6 wt % stabaxol[®]-1 before degradation; and (d) PPDO/0.6 wt % stabaxol[®]-1 after degradation for 6 weeks at 37°C and 50% RH.

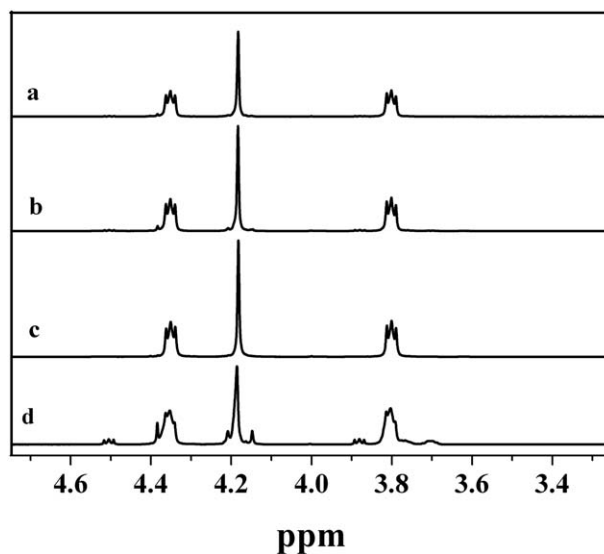
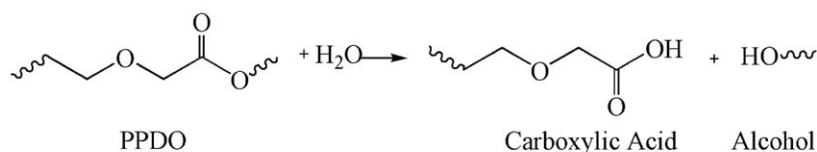
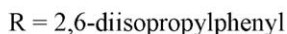
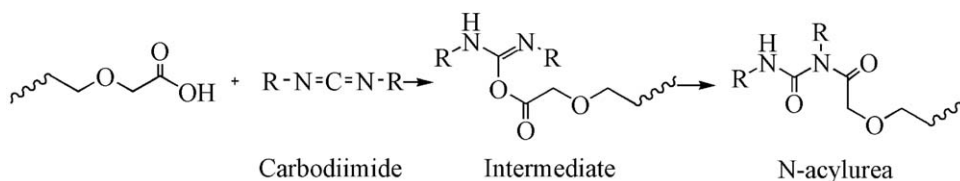


Figure 7. ¹H NMR spectra of (a) PPDO/0.6 wt % stabaxol[®]-1 before degradation; (b) PPDO/0.6 wt % stabaxol[®]-1 after degradation for 6 weeks at 37°C and 50% RH; (c) PPDO before degradation; and (d) PPDO after degradation for 6 weeks at 37°C and 50% RH.

Hydrolysis mechanism:



Removal of acidic degradation fragments:



Scheme 2. Chemical reaction schemes of (a) hydrolysis process of PPDO and (b) reaction of carboxylic acid with carbodiimide.

A presumable degradation mechanism was given in Scheme 2. The first degradation step of PPDO concerned the ester hydrolysis, during which carboxylic acid was formed as degradation product. When not removed, the carboxylic acid further promotes ester hydrolysis because of its autocatalytic nature.³⁰ In the presence of stabaxol[®]-1, the free acid was consumed via the reaction between the carbodiimide groups and carboxyl groups, and thus assuring that carboxylic acid is no longer available to promote degradation.

CONCLUSIONS

It has been shown that the hydrolytic degradation stability of PPDO can be enhanced significantly by adding stabaxol[®]-1. With the increase of temperature or relative humidity, the intrinsic viscosity, mechanical properties of both PPDO and PPDO/0.6 wt % stabaxol[®]-1 decreased in the degradation process, but the latter reduced much slower than that of the former. At the same time, the crystallinity increased at first and then decreased. PPDO/0.6 wt % stabaxol[®]-1 showed a better physical integrity than PPDO. The influences of temperature on the degradation are more significant than that of relative humidity. The analyses of FTIR and ¹H NMR spectroscopy confirmed that the ester bands in PPDO were easily breakdown and carboxylic acid was formed as degradation product. In the presence of stabaxol[®]-1, the free acid was consumed via the reaction between the carbodiimide groups and carboxyl groups, thus assuring that carboxylic acid is no longer available to promote degradation. Stabaxol[®]-1 can be used as a stabilizer for inhibiting the hydrolysis degradation of PPDO.

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