

Hydrolytic Degradation Behaviors of Poly(*p*-dioxanone) in Ambient Environments*

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Abstract The effects of temperature and relative humidity on the hydrolytic degradation of poly(*p*-dioxanone) (PPDO) were investigated. The hydrolytic degradation behaviors were monitored by tracing the changes of water absorption, mechanical and crystalline properties, molecular weight and its distribution, surface morphologies, as well as infrared absorption peaks and hydrogen chemical shifts during the degradation. It is found that the water absorption increases whilst the intrinsic viscosity, tensile strength and elongation at break decrease as the temperature or relative humidity increases. With degradation time growing, the molecular weight drops and its distribution broadens. The crystallinity of PPDO has a tendency to increase at first and then to decrease, while the crystalline structure is not significantly changed. At the same time, some cracks are observed on the surface and keep growing and deepening. All results show that temperature plays more significant roles than relative humidity during the degradation. The analyses of Fourier transform infrared spectroscopy and hydrogen nuclear magnetic resonance spectroscopy reveal that the degradation of PPDO is a predominant hydrolysis of ester linkages.

Keywords: Poly(*p*-dioxanone); Hydrolytic degradation; Temperature; Relative humidity.

INTRODUCTION

Poly(*p*-dioxanone) (PPDO) has good biocompatibility, bioresorbability, degradability and excellent mechanical properties^[1–3]. In 1970s, it was manufactured as absorbable monofilament suture PDS[®] by Ethicon Inc, and now PDS[®] is still commonly used in surgery^[4]. Recently, due to the successful use of a highly active dehydrogenation catalyst for the preparation of *p*-dioxanone (PDO) monomer from diethylene glycol, the cost of PDO decreased significantly^[5–7]. Furthermore, PPDO is also a feedstock recyclable polymer, which can be decomposed into PDO with a high yield of more than 90% by means of pyrolysis^[8, 9]. This can give rise to the further cost reduction of PPDO. Therefore, it becomes possible for the extensive applications of PPDO, such as films, molded products, unwoven materials and shape memory devices^[10–12].

The hydrolytic degradation of PPDO has played a key role in biomedical materials applications and has been investigated in previous reports^[13–15]. Most of the researches were only conducted in the phosphate buffer solution (PBS) of pH 7.4 at 37 °C in order to simulate the degradation of PPDO *in vivo*^[13, 15]. Generally, with the process of the hydrolytic degradation, the retention weight decreases; the molecular weight reduces; and the

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mechanical properties deteriorate. The degradation of PPDO proceeds in a two-stage process: the chain segments located in the amorphous regions are broken down randomly at first, and then those located in the crystalline regions are attacked gradually^[16]. These aforementioned research results have an important guiding significance for the applications of PPDO *in vivo*.

With the great progress in the research and development, PPDO can also be widely used as general materials in ambient environments^[11, 12, 17]. In fact, the hydrolytic degradation of PPDO not only occurs *in vivo*, but also takes place in ambient environments. It is well known that the degradation behaviors of materials are seriously dependent on the degradation medium^[18]. For example, the degradation behaviors of polylactic acid (PLA) in ambient environments with different temperatures and relative humidities (RH) showed that both of the temperature and relative humidity had significant effects on the degradation of PLA^[19, 20]. Moreover, the degradation behaviors in ambient environments are quite different from those in PBS, such as mechanical properties changes, surface morphologies changes^[21–23]. The degradation behaviors of materials in ambient environments are more close to the actual situation for processing and application environment of polymers^[20]. However, there have been few reports on the hydrolytic degradation of PPDO in ambient environments up to now. This is not in favor of PPDO material development, extending its applications, predicting its life time and so on. In the meantime, the research concerning the degradation in ambient environments also has a vital guiding significance for the transportation and storage of PPDO. Therefore, a detailed description of the degradation behaviors occurring in ambient environments with different temperatures and relative humidities is very necessary.

In the present paper, the hydrolytic degradation behaviors of PPDO were investigated in ambient environments with different temperatures and relative humidities. The changes of water absorption, mechanical and crystalline properties, molecular weight and its distribution, surface morphologies of PPDO were monitored by weight loss measurement, tensile test, differential scanning calorimetry, wide-angle X-ray diffraction, Ubbelohde viscosimeter, gel permeation chromatography, and scanning electron microscopy. The process of degradation was traced by the Fourier transform infrared spectroscopy and hydrogen nuclear magnetic resonance.

EXPERIMENTAL

Materials

p-Dioxanone, provided by the Pilot Plant of the Center for Degradable and Flame-Retardant Polymeric Materials (Chengdu, CHN), was dried over CaH₂ for 48 h and distilled twice under reduced pressure of 30 Pa at 80 °C before use. Stannous octoate (AR grade) was purchased from Sigma (USA) and used as received. After diluted with anhydrous toluene, stannous octoate solution was stored in the glass ampoules under nitrogen. Phenol, 1,1,2,2-tetrachloroethane, acetone and other chemicals with AR grade were procured from Kelong Chemical Corporation (Chengdu, CHN) and used without further purification.

Preparation of PPDO

PPDO was synthesized by ring-opening polymerization of PDO with stannous octoate as catalyst. Predetermined amount of PDO and stannous octoate with a molar ratio of 10000:1 were charged into a pre-dried 3 L reaction kettle (Weihai Automatic Control Reaction Kettle Co. Ltd., CHN) under nitrogen atmosphere. The reaction was performed at 120 °C for 6 h, and then the unreacted monomer was removed by vacuum distillation at 30 Pa and 120 °C for 1 h. The obtained crude polymer was milled into powder and then further purified by removing the unreacted monomers in Soxhlet extractor with acetone for 8 h. The purified PPDO was dried to constant weight under vacuum at 40 °C and stored in a desiccator over silica gel.

Sample Preparation

PPDO bars with the slice of 25 mm × 4 mm × 0.5 mm were prepared by platen vulcanizing press (Qingdao Ya Dong Rubber Machinery Group Co., Ltd., CHN) at a pressure of 10 MPa and 130 °C for 3 min, and then cooled at room temperature.

Degradation Conditions

Five glass chambers were used to provide controlled environments for the hydrolytic degradation of PPDO bars. The chambers were placed in ovens at different temperatures (25, 37 and 45 °C). Saturated salt solutions were used to maintain specific relative humidity within each chamber (ASTM 104-85)^[24, 25]. At 25 °C, the chamber was maintained at 23%, 52% and 86% RH by using a saturated solution of potassium acetate, magnesium nitrate and potassium chloride, respectively. At 37 °C and 45 °C, due to the slight influence of temperature on the relative humidity, only ~50% RH (not accurate) was obtained through magnesium nitrate saturated solution. The degraded samples were taken out of the chamber in a given time period for measurements^[24, 26].

Measurements

Measurements of water absorption and retention weight

Before being placed in the chamber, each sample was weighed on an analytical balance (AL204, Mettler Toledo Co., SUI). Each week, samples were removed from the chamber and weighed by the analytical balance, and then dried for 2 days to a constant weight under reduced pressure of -0.09 MPa at 30 °C in a vacuum oven (DZF-6050, Keelrein instrument Ltd., CHN). After drying, the samples were weighed. Based on the changes of weight, the retention weight and the water absorption were calculated from the following relationships: retention weight (%) = W_r/W_i , water absorption (%) = $(W_w - W_r)/W_r$, with W_i and W_r representing the initial and remaining weights of the dried samples, and W_w representing the wet weight of the samples after degradation.

Measurements of mechanical properties

The mechanical properties of PPDO samples were measured with a tensile tester (Sans Testing Machine Co. Ltd., CHN). The samples were tested at a drawing speed of 50 mm/min and at 25 °C. The values presented were the mean of five replicate samples.

Measurements of intrinsic viscosity

PPDO with high molecular weight cannot be measured by gel permeation chromatography (GPC) due to its poor solubility in solvents commonly employed to perform GPC. Thus, the viscosity-average molecular weights were determined by capillary viscosity measurements using an Ubbelohde viscosimeter with capillary of inside diameter 0.7 mm. The tests were measured at 25 °C with phenol/1,1,2,2-tetrachloroethane (2:3 W/W) as solvent.

Measurements of gel permeation chromatography

The molecular weight and molecular weight distribution of degraded PPDO was determined by GPC (Waters 1515, Waters Inc., USA). Chloroform (HPLC grade) was used as the eluant at a flowing rate of 1.0 mL/min, and a sample concentration of 2.5 mg/mL was used. The number and weight average molecular weights were calculated by using a calibration curve which was obtained by monodisperse polystyrene standards.

Measurements of differential scanning calorimetry

Differential scanning calorimetry (DSC) analysis was performed with a TA instrument (DSC Q200, TA Co., Delaware). Tests were carried out under nitrogen atmosphere. All samples (3–5 mg) were placed in aluminum pans and a study of the thermal history (based on the first heating scan) from 40 °C to 140 °C at a scanning rate of 10 K/min was conducted. The crystallinity was calculated from the reported enthalpy of fusion 14.4 kJ/mol for 100% crystalline PPDO^[15].

Measurements of wide-angle X-ray diffraction

Wide-angle X-ray diffraction (WXR) measurements were carried out using an X-ray diffractometer (Bruker D8 Advance, Bruker AXS Handheld Inc., GER). The radiation used was Cu-K α radiation at room temperature and the scan range was between 5° and 40° with a scan rate of 2 (°)/min.

Measurements of scanning electron microscopy

Surface morphology was observed with a scanning electron microscope (SEM) (JSM-5900LV, Jeol Co., JP) after the sample surface was coated with a thin layer of gold by vacuum deposition.

Measurements of Fourier transformed infrared spectroscopy

The Fourier transform infrared spectroscopy (FTIR) was performed using a Fourier transform infrared spectrometer (Nicolet 6700, Thermo Fisher Scientific Inc., USA). The range of wave numbers was from 4000 cm^{-1} to 400 cm^{-1} for a total of 32 scans. The specimens doped with KBr were pressed into slices for the testing.

Measurements of nuclear magnetic resonance

Hydrogen nuclear magnetic resonance (^1H -NMR) spectra were recorded with a nuclear magnetic resonance spectrometer (NMR AV II-400 MHz, Bruker AXS Handheld Inc., GER) and performed at ambient temperature with dimethyl sulfoxide- d_6 as a solvent.

RESULTS AND DISCUSSION

Water Absorption and Retention Weight

The changes of the water absorption were measured, and the results are shown in Fig. 1. It shows that the phenomenon of water absorption still appears when PPDO degraded in ambient environments. With the increase of temperature or relative humidity, the water absorption increases. Especially at $25\text{ }^\circ\text{C}$ and 86% RH, 9% of water absorption has been attained after 12 weeks of degradation. The occurrence of this phenomenon may be ascribed to the water absorption of the hydrophilic oligomers which are produced by degradation and migrate from the interior to the surface of the sample^[20]. Once the oligomers diffuse away from the surface, a weight loss of the sample can be measured. The weight loss is a simple evaluation for the degradation process of PPDO^[13]. Figure 2 shows the changes of the retention weight during degradation. The retention weight decreases with the increase of the temperature or relative humidity. It is indicated that both the temperature and relative humidity have significant effects on the degradation of PPDO.

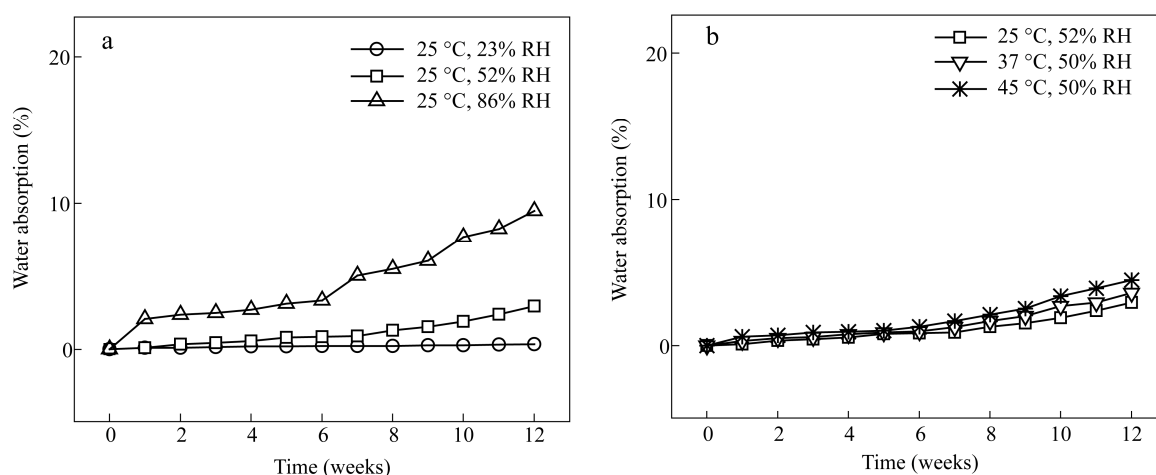


Fig. 1 Changes of the water absorption of PPDO during degradation: (a) $25\text{ }^\circ\text{C}$ and different relative humidities (23%, 52%, 86%), (b) $\sim 50\%$ RH and different temperatures ($25\text{ }^\circ\text{C}$, $37\text{ }^\circ\text{C}$, $45\text{ }^\circ\text{C}$)

Molecular Weight

Generally, the important indication of hydrolysis is the change of molecular weight. Due to the poor solubility in common solvents, PPDO with high molecular weight cannot be measured by GPC. Thus, the changes of molecular weight were measured by Ubbelohde viscosimeter^[15]. The changes of the intrinsic viscosity with degradation time are plotted in Fig. 3. With the increase of temperature or relative humidity, the intrinsic viscosity decreases. After 1 week at $\sim 50\%$ RH, the intrinsic viscosity of PPDO at $25\text{ }^\circ\text{C}$, $37\text{ }^\circ\text{C}$ and $45\text{ }^\circ\text{C}$ decreased by 11%, 34% and 44%, respectively. In the meantime, after 1 week at $25\text{ }^\circ\text{C}$, the intrinsic viscosity of samples at 23%, 52% and 86% RH decreased by 7%, 11% and 19%, respectively. It is shown that the effect of temperature on the degradation of PPDO is more significant than that of relative humidity.

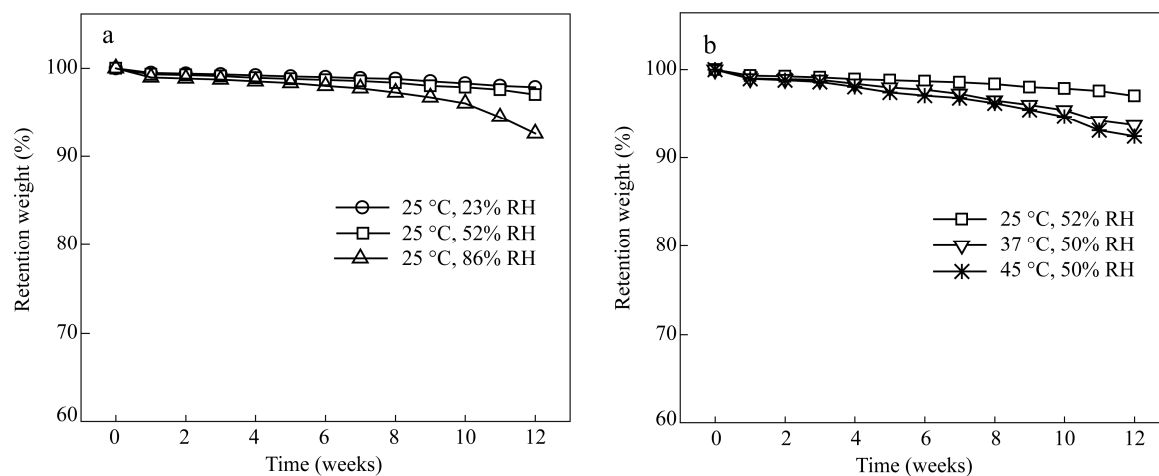


Fig. 2 Changes of the retention weight of PPDO during degradation: (a) 25 °C and different relative humidities (23%, 52%, 86%), (b) ~50% RH and different temperatures (25 °C, 37 °C, 45 °C)

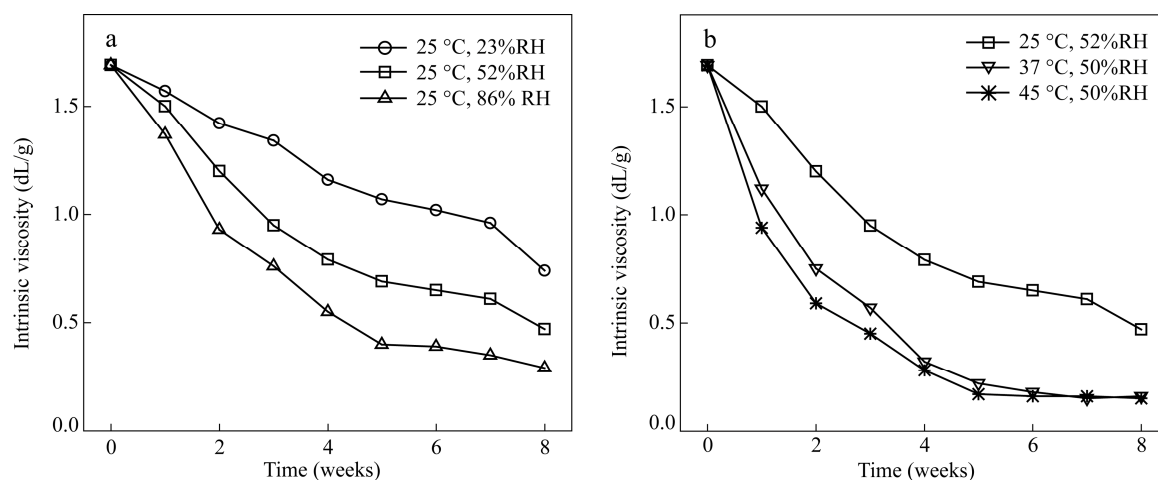


Fig. 3 Changes of the intrinsic viscosity of PPDO during degradation: (a) 25 °C and different relative humidities (23%, 52%, 86%), (b) ~50% RH and the different temperatures (25 °C, 37 °C, 45 °C)

With the process of degradation, the molecular weight of PPDO become lower until PPDO can dissolve in chloroform, and then the molecular weight and its distribution of the sample can be measured by GPC, giving insight into the process of degradation. The weight-average molecular weights (M_w), the number-average molecular weight (M_n), as well as polydispersity (M_w/M_n) of PPDO degraded at 45 °C and 50% RH are listed in Table 1. It shows that the molecular weight of samples is gradually reduced. At the same time, molecular weight distribution has no obvious change during the period from 4 to 12 weeks, but it remarkably broadens after 20 weeks. This indicates that the long polymer chain has been cut short and small molecular fragments are produced during the degradation^[22].

Table 1. Changes of the molecular weight and its distribution of PPDO degraded at 45 °C and 50% RH

Time (weeks)	$M_w \times 10^{-3}$ (g/mol)	$M_n \times 10^{-3}$ (g/mol)	Polydispersity
4	5.18	3.85	1.35
8	4.65	3.79	1.23
12	4.54	3.62	1.25
20	2.74	1.51	1.81

Mechanical Properties

The break of the long polymer chain provokes an inhomogeneous decrease in the molecular weight and results in an accelerated loss of the mechanical properties. The changes of the mechanical properties at different temperatures and relative humidities are shown in Figs. 4 and 5. With the increase of temperature, both the tensile strength and elongation at break of PPDO rapidly decrease, but the former reduces more slowly than the latter. For example, after 1 week at ~50% RH, the tensile strength of PPDO at 25, 37 and 45 °C decreased by 15%, 24% and 34%, respectively. However, under the same degradation conditions, the elongation at break of these samples decreased by 42%, 89% and 98%, respectively. The rapid decrease of the elongation at break may be due to that the increased crystallinity and decreased molecular weight can cause the increase in the fragility of PPDO bars greatly^[4]. With the process of degradation, the rupture mode of PPDO gradually transforms from ductile fracture to brittle fracture. In addition, the effect of relative humidity on the mechanical properties follows the same trends as that of temperature. The temperature plays more significant roles than the relative humidity does during degradation, which is in good agreement with the results of intrinsic viscosity measurements.

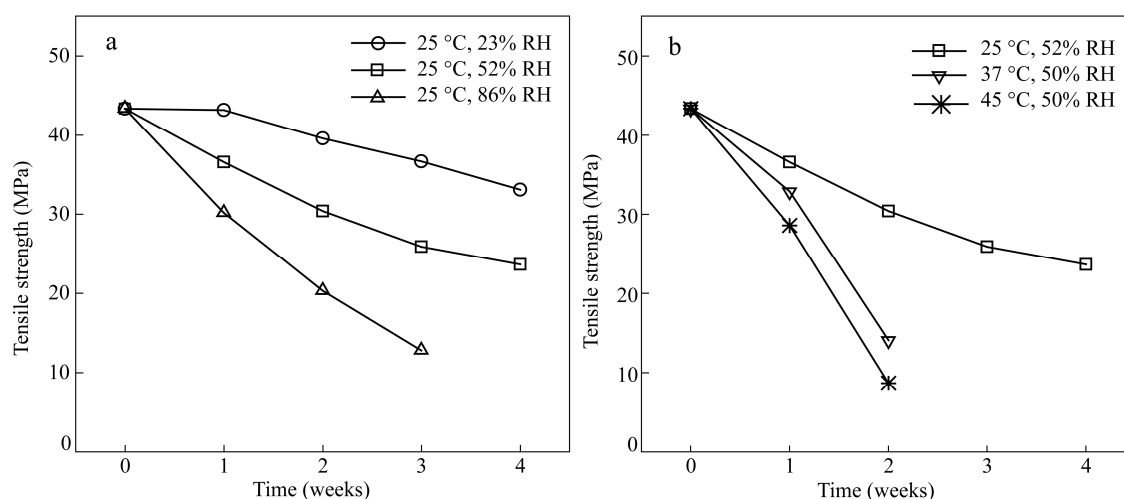


Fig. 4 Changes of tensile strength of PPDO during degradation: (a) 25 °C and different relative humidities (23%, 52%, 86%), (b) ~50% RH and different temperatures (25 °C, 37 °C, 45 °C)

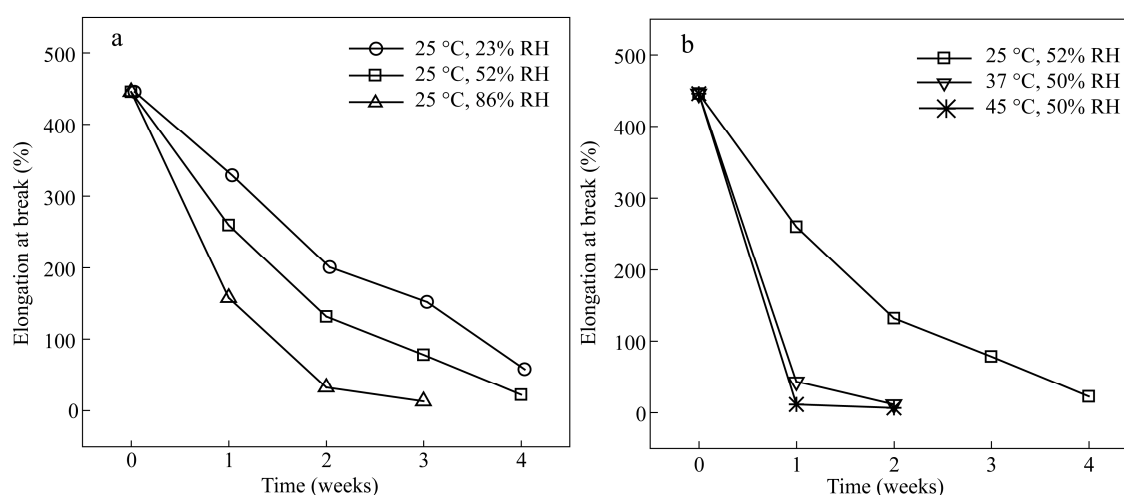


Fig. 5 Changes of elongation at break of PPDO during degradation: (a) 25 °C and different relative humidities (23%, 52%, 86%), (b) ~50% RH and different temperatures (25 °C, 37 °C, 45 °C)

Crystallinity

The crystallinity changes of samples determined by DSC measurements are displayed in Table 2. The crystallinity of PPDO gradually increases with the degradation time under different relative humidities at 25 °C. However, at 37 and 45 °C under 50% RH, the crystallinity of PPDO increases with increasing of degradation time until 12 weeks and then decreases. This phenomenon can be explained by the “cleavage-induced crystallization” mechanism^[27]. When samples absorb water, the attack of water molecules happens on both crystalline and amorphous areas, but preferentially on the more accessible amorphous areas because of their less density. Then chain scission occurs and subsequently leads to a decrease in molecular entanglement and an increase in chain mobility. These short segments can organize themselves to the crystal, which causes an increase in the crystallinity at the initial stage of degradation. An increase in the crystallinity of the material can cause an increase in the fragility of the material, and thus a reduction in the mechanical properties. After longer degradation periods, a greater degradation breaking activity occurs in the crystal regions and gradually destroys these regions, consequently the crystallinity of PPDO decreases at last.

Table 2. Changes of the crystallinity (D_c) of PPDO as a function of degradation time

Time (weeks)	25 °C						37 °C		45 °C	
	23% RH		52% RH		86% RH		50% RH		50% RH	
	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	54.6	38.7	54.6	38.7	54.6	38.7	54.6	38.7	54.6	38.7
4	67.3	47.7	68.4	48.4	74.6	52.8	92.6	65.6	94.3	66.8
8	68.2	48.3	77.8	55.1	78.8	55.9	95.9	67.9	100.9	71.5
12	71.2	50.4	78.5	55.6	81.4	57.7	116.0	82.2	115.2	81.6
16	78.6	55.7	84.8	60.1	88.5	62.3	110.6	78.3	108.3	76.7
20	88.3	62.6	85.3	60.4	92.0	65.2	103.7	73.5	101.3	71.8

For further investigation of the changes of crystallinity, WXR D measurements were carried out. The WXR D patterns in the range of 2θ 10°–40° for PPDO degraded at 45 °C and 50% RH are shown in Fig. 6. Virgin PPDO has the diffraction peaks at 2θ of 22.2°, 24.0° and 29.2°, corresponding d spacings calculated from the Bragg equation are 0.400 (d_{210}), 0.371 (d_{020}) and 0.306 (d_{310}) nm, respectively. With the process of degradation, the intensity of diffraction peaks increases at the first 12 weeks and then decreases. It is implied that the crystallinity of PPDO increases with the increase of degradation time until achieving a maximum value after degradation for 12 weeks, and then decreases as the further increasing of degradation time. The WAXD results agree well with those obtained from DSC measurements. In addition, both virgin and degraded samples give nearly identical diffraction peak positions during the degradation, suggesting the crystalline structure is not significantly changed.

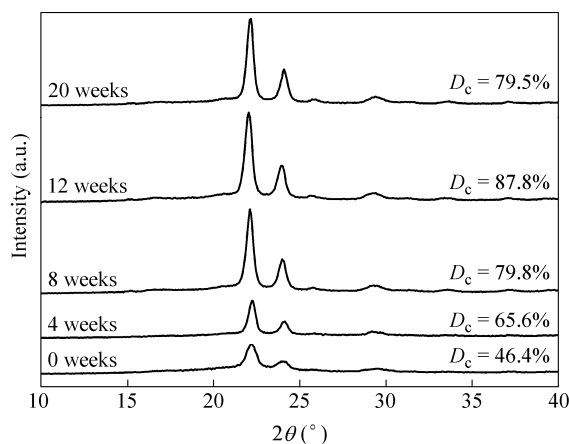


Fig. 6 Changes of the degree of crystallinity (D_c) and the crystalline structure of PPDO degraded at 45 °C and 50% RH

Morphology

While the hydrolysis progresses, the fragments of chains involved in this hydrolysis can diffuse away from the polymer or incorporate into the crystal, leaving empty spaces on the surface of the sample^[13]. The cracks on the surface could be observed by SEM. Micrographs of PPDO surface with different degradation durations (4 and 8 weeks) are shown in Figs. 7 and 8, respectively. Obviously, virgin PPDO exhibits a relatively smooth and clear surface. After 4 weeks of degradation, although no cracks are observed on the surface of the sample degraded at 25 °C and 25% RH, some cracks are gradually observed with the increase of temperature or relative humidity. The morphological defects lead to the decrease of the mechanical properties, particularly of the tensile strength and the elongation at break^[13]. When the degradation time increases to 8 weeks, there are some cracks on the surface of all samples. The cracks grow much larger and the surface becomes coarser. Especially at 45 °C and 50% RH, the surface of the sample becomes very uneven and loses almost physical integrity. The effect of temperature on the surface morphologies of PPDO is more obvious than that of relative humidity.

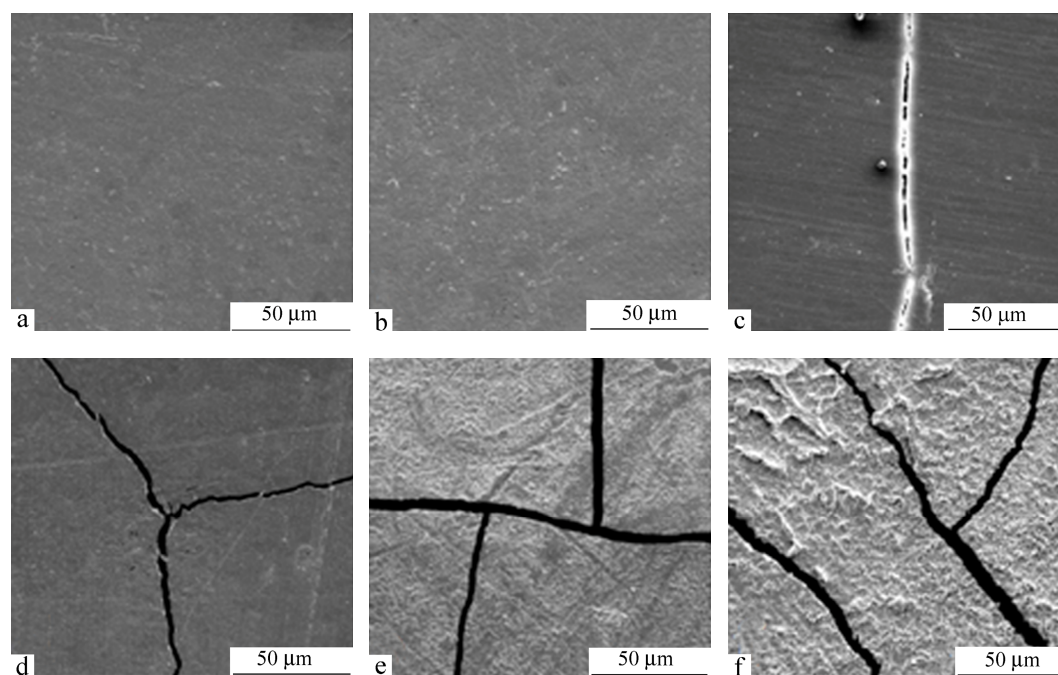


Fig. 7 Surface morphology of PPDO from SEM micrographs after degradation 4 weeks: (a) Virgin PPDO, (b) 25 °C and 23% RH, (c) 25 °C and 52% RH, (d) 25 °C and 86% RH, (e) 37 °C and 50% RH and (f) 45 °C and 50% RH

Degradation Mechanism of PPDO

For the random break of the long polymer chain during degradation, the degradation products become very complex, making it hard to be analyzed clearly. Generally, the process of degradation can be traced by the FTIR and ¹H-NMR testing^[28–31]. The FTIR spectra changes of PPDO with different degradation time lengths are shown in Fig. 9. The characteristic bands of virgin PPDO are observed as follows. The absorption bands at 1049, 1129 and 1206 cm⁻¹ are attributed to the —C—O— stretching vibration and the peak at 1431 cm⁻¹ is the characteristic absorption of —CH— deformation vibration. The stretching vibration absorption bands of —C=O, —CH— and O—H groups are located at 1744, 2920 and 3457 cm⁻¹, respectively. With the process of degradation, the O—H stretching vibration peak increases relative to other peaks, implying the increasing number in hydroxyl group at the end of PPDO chains after degradation^[29, 30]. These hydroxyl groups are from alcohol and carboxylic groups. After 20 weeks of degradation, the band at 1744 cm⁻¹ corresponding to —C=O stretching vibration of ester band decreases by a shift to lower wave 1735 cm⁻¹. The new band is attributed to

—C=O stretching vibration of carboxyl acid generated during degradation^[20, 31]. Meanwhile, a new band appears at about 1631 cm^{-1} , which may correspond to C—O stretching asymmetric vibration in the carboxyl ion^[31, 32]. These results are in good concordance with those reported about the hydrolytic degradation of other aliphatic polyesters, such as PLA and PGA, suggesting that carboxylic acid is formed as degradation product and the degradation is a predominant hydrolysis of ester linkage^[20, 29].

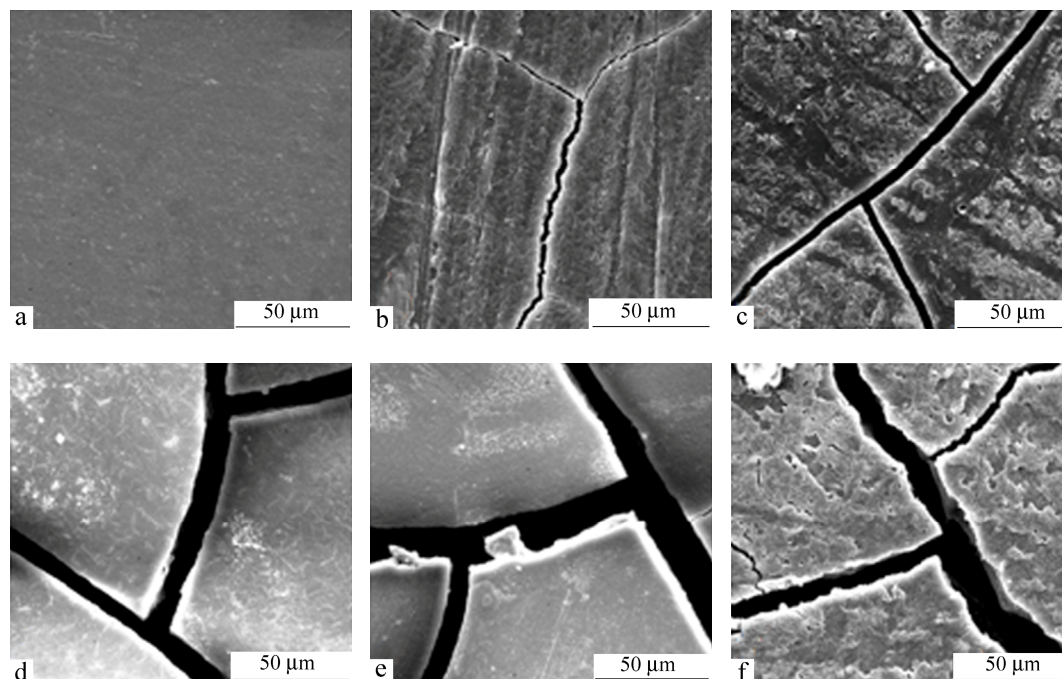


Fig. 8 Surface morphology of PPDO from SEM micrographs after degradation 8 weeks: (a) Virgin PPDO, (b) 25 °C and 23% RH, (c) 25 °C and 52% RH, (d) 25 °C and 86% RH, (e) 37 °C and 50% RH and (f) 45 °C and 50% RH

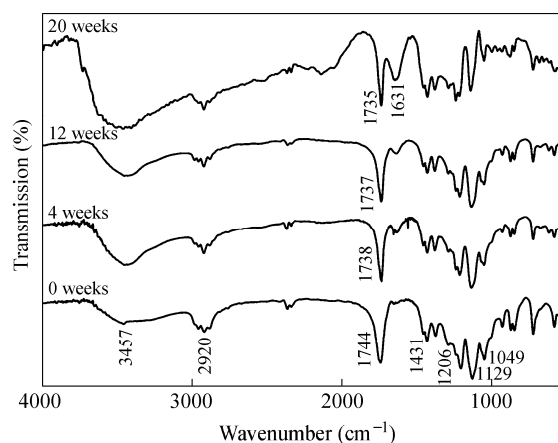


Fig. 9 Changes of the FTIR spectra of PPDO degraded at 45 °C and 50% RH

Figure 10 shows the changes of ^1H -NMR spectra of PPDO degraded at 45 °C and 50% RH as a function of degradation time. In the ^1H -NMR spectrum of virgin PPDO, the resonance signals belonging to the three kinds of methylene protons in the repeating PPDO units are observed at $\delta = 4.16$ (δH^a), 3.70 (δH^b) and 4.21 (δH^c). After degradation, some new peaks at $\delta = 4.14$, 4.04, 4.02, 3.50 appears, ascribing to the signals of hydrogen

atom in aliphatic hydroxyl group^[28]. These results confirm that the products of degradation contain aliphatic hydroxyl groups, which are in perfect accordance with those obtained from FTIR. For the sake of detecting the number changes of hydrogen atoms in the polymer chain during degradation, the integral area of peak “c” is defined as 1 to compare with that of the other peaks. The changes of integral area ratio of peaks as a function of degradation time are listed in Table 3. With the increase of degradation time, the relative ratio of integral area of peak “a” gradually decreases, implying the decrease of the hydrogen atoms of methylene between ether and carbonyl group. While the hydrogen atom between the ether groups of PPDO remains unchanged with the extension time of degradation. This may be due to the fact that the property of ether group is stable and it is especially difficult to be broken. The ¹H-NMR experimental results can support the degradation course mentioned above in the analysis of FTIR spectra. It is further confirmed that the probable reaction site is located at the carbonyl group of the molecular chain.

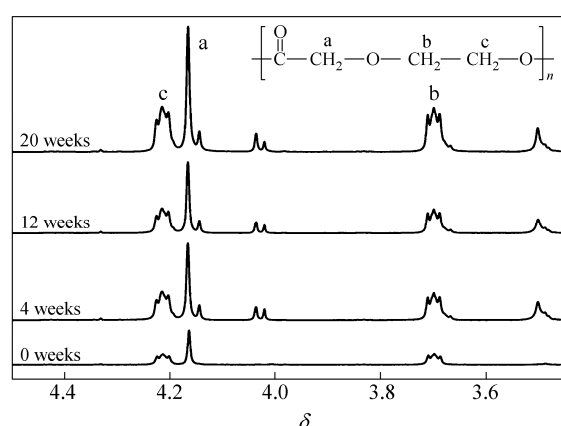
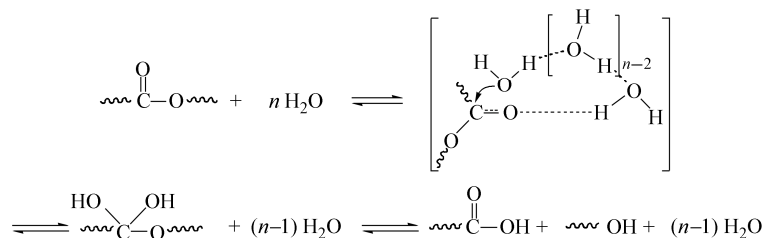


Fig. 10 Changes of the ^1H -NMR spectra of PPDO degraded at 45 °C and 50% RH

Table 3. Changes of integral area ratio of peaks as a function of degradation time

Time (weeks)	Integral area ratio (a:b:c)
0	1:1:1
4	0.91:1:1
12	0.84:1:1
20	0.82:1:1

According to the analyses of FTIR and $^1\text{H-NMR}$, a presumable degradation mechanism of PPDO is given in Scheme 1. The ester groups are active sites of degradation in the polymer chain. These groups are randomly attacked by water molecules, then the long polymer chain is broken down and some carboxylic species are generated as degradation products. With the increase of temperature and relative humidity, water molecules can easily access and attack these ester bonds. Thus, the rate of degradation increases with the increasing of the temperature and relative humidity.



Scheme 1 Degradation process of PPDO in ambient environments

CONCLUSIONS

It has been shown that PPDO is still a kind of material with excellent degradability in ambient environments. The temperature and relative humidity play an important role in the degradation of PPDO. With the increase of temperature or relative humidity, the water absorption increases and the retention weight decreases. The mechanical properties and intrinsic viscosity drop rapidly and molecular weight distribution broadens. The crystallinity of PPDO has a tendency to increase at first and then to decrease, while the crystalline structure is not significantly changed. During degradation, some cracks are observed gradually on the surface and keep growing and deepening. The surface becomes coarser and then loses their physical integrity. The effect of temperature on degradation is more significant than that of relative humidity. The degradation of PPDO is a predominant hydrolysis of ester linkages which is accelerated by increasing temperature or relative humidity. These results have a vital guiding significance for the transportation, storage, processing as well as application of PPDO. In the meantime, it also provides useful and meaningful reference information about the environments where the waste material of PPDO is dealt with for the purpose of environment-friendly treatment.

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