

Long-Term Investigation on Hydrolytic Degradation and Morphology of Poly(ethylene glycol terephthalate)-*b*-Poly(butylene terephthalate) Copolymer Films

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ABSTRACT: Poly(ethylene glycol terephthalate)-*b*-Poly(butylene terephthalate) copolymer (PEGT-*b*-PBT) films with different copolymer compositions were incubated in phosphate buffered saline under pH 7.4 at 37°C to study hydrolytic degradation and morphology up to 300 days. With the fall of intrinsic viscosity and mass of degraded films, SEM micrographs show that a set of particular and highly interconnected porous morphologies closely related to the content of PBT hard segments in copolymer is developed. Moreover, the variation in PBT crystallinity for copolymer films with weight ratio of 70/30 fluctuates with the development of degradation profiles, and PEGT content for copolymer films with weight ratio of 80/20 and

70/30 gradually decreases. The hydrolytic experiments demonstrate that the degradation of PEGT-*b*-PBT copolymer results from the cleavage of ester bonds between hydrophilic PEG and terephthalate. At the beginning period of degradation, PEGT-*b*-PBT copolymer films follow a typical mechanism of bulk degradation, and then undergo both bulk degradation and surface erosion, all of which finally generate the particular porous morphologies for copolymer films. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 111: 1462–1470, 2009

Key words: PEGT-*b*-PBT copolymer; porous interconnected morphology; long-term degradation

INTRODUCTION

Poly(ethylene glycol terephthalate)-*b*-poly(butylene terephthalate) copolymer(PEGT-*b*-PBT), as a kind of thermoplastic elastomer, nowadays is extensively used under biomedical investigation due to its unique physical properties, good compatibility, and degradability.^{1–6} Several studies show that PEGT-*b*-PBT copolymer could be used as antiadhesive barrier,⁷ artificial skin,^{8–10} controlled drug delivery,^{11,12} bone replacement.^{13–17}

As the biomedical application of PEGT-*b*-PBT is closely related to the pattern and rate of copolymer degradation in bioactive environment, an increasing interest in degradation has drawn much attention. Some reports^{1,3,18,19} have confirmed that the degradable rate of PEGT-*b*-PBT is relatively slow, even for those copolymers containing high amounts of PEG. Although it has been suggested that *in vitro* degradation mechanism for PEGT-*b*-PBT might undergo

hydrolysis and oxidation reactions,¹ the long-term and detailed profiles of *in vitro* degradation of PEGT-*b*-PBT is not well-known yet, only limited *in vitro* degradable profiles during a shorter degradation time have been acquired, but there still exists some confusing results in the literature. Feijen and coworkers¹ reported that PEOT content of solution cast films for PEOT/PBT copolymer with starting PEO molecular weight at 1000 decreased from 69 to 60 wt % after 12 weeks in PBS and 52 wt % remained after 24 weeks. However, for hot-pressed films of PEOT/PBT (70/30 weight ratio) copolymer with starting PEO molecular weight at 1000, while the molecular weight of copolymer films rapidly decreased, until 26 weeks the PEOT proportion almost remained constant accompanying only by topographical formation on the surfaces, thereafter the drop of PEOT proportion was faster and reached 54.6 wt % at 52weeks.¹⁸ Bezemer¹⁹ also observed that the composition of solution cast films for PEG/PBT copolymer with PEG block length of 1000 g/mol had no change after 54 days degradation at 37°C in phosphate buffered saline (PBS). In addition, while PEO/PET copolymer, another kind of thermoplastic elastomer, was incubated in citrate-phosphate buffered solution of pH7.0 at 37°C, PEO/PET film underwent no change in average composition over the 1–8 weeks degradation period, and only a 65%

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fall in M_w and a 20% mass loss over 8 weeks period.^{20,21} As a matter of fact, degradation is a complex process that depends on many factors such as chemical composition, size and shape, configuration of sample and degradable time etc., so knowledge of the degradation for PEGT-*b*-PBT copolymer might be considered incomplete until now.

This research aims to detail the degradation induced variation in morphologies, thermal properties and composition as well as hydrolytic degradation mechanism of PEGT-*b*-PBT copolymer at 37°C in PBS. PEGT-*b*-PBT copolymer was cast into film, from which sample was cut. Incubation in PBS at pH 7.4 and 37°C for predetermined periods of time up to 300 days was investigated. Besides, particular morphologies of copolymer films under different periods of degradation time were first presented in this article.

MATERIALS AND METHODS

Materials

Commercially available dimethyl terephthalate (DMT), 1,4-butanediol (BDO), poly(ethylene glycol) (PEG, $M_n = 1000$), titanium tetrabutoxide ($\text{Ti}(\text{OBu})_4$), and magnesium acetate (MgAc_2) are all of analytical grade and used as received. Irganox-1010 and AT-168, the stabilizers used with equal mass dosage, are generously provided by Beijing Chemical Industry Research Institute. All other chemicals are of A.R. grade and used without further treatment.

Polymerizations

Take sample 70/30 as example. Comonomers DMT (30.0 g), BDO (12.5 g) and PEG1000 (48.3 g) as well as antioxidant 0.18 g (0.2 wt % of total comonomer mass) were charged into a well-dried-three-neck flask equipped with a condenser, a stirrer and a gas inlet. The flask was immersed into a silicone oil bath at 160°C under nitrogen atmosphere for 20 min, then the catalyst 0.45 g (0.5 wt % of total comonomer mass), methanol solution of the mixture of $\text{Ti}(\text{OBu})_4$ and MgAc_2 with mole ratio at 3 : 1, was transferred into the reactor at 160°C with gentle agitation. Then, the temperature slowly went up to 210°C at rate of 25°C/h in 2 h and stayed at 210°C for another 2 h, gradually decreasing the pressure to 1330 Pa in 30 min, to reach the endpoint of the transesterification. The molten polycondensation was also performed in the same vessel as the temperature reached and stayed at $240 \pm 5^\circ\text{C}$ with the pressure below 60–70 Pa for about 3 h until the appearance of serious Weissenberg effect. Finally, the resulting copolymer was taken out from the flask under dry nitrogen atmosphere, cooled to room temperature,

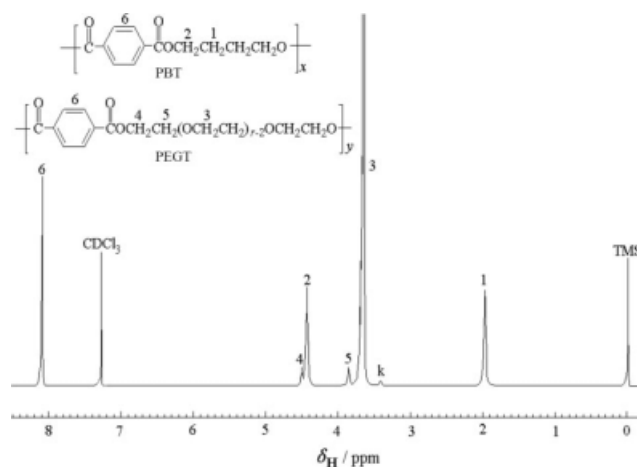


Figure 1 The chemical structure and ^1H -NMR spectra of PEGT-*b*-PBT copolymer.

dissolved in chloroform, filtrated and precipitated by pouring the filtrate into the excess petroleum ether, washed with methanol, then dried in vacuum at 50°C for 2 days. So a series of PEGT-*b*-PBT copolymers based on starting PEG 1000 synthesized over the composition range 80–50 wt % PEGT by above melt polycondensation reaction were built up of hard segments (PBT) and soft segments (PEGT) (Fig. 1).²²

The block copolymer sample was described as *a/b*, in which *a* was the weight percentage of PEGT soft segments and *b* the weight percentage of PBT hard segments as shown in Table I. Phosphate-buffered saline (PBS) pH 7.4 was adjusted according to the Ref. 23 Chloroform and CDCl_3 , obtained from the ATOZ fine chemical company, and hexafluoroisopropanol, obtained from Aldrich, were of analytical grade.

Preparation of PEGT-*b*-PBT films

PEGT-*b*-PBT copolymer (about 1 g) was dissolved in 10 mL of chloroform and cast on PTFE plate. Copolymer having 50 wt % PBT was dissolved in 10 mL of a mixture of chloroform and hexafluoroisopropanol (6 : 1, v/v). The solvent was slowly evaporated at 25°C and then the films were dried in vacuum oven at 30°C for 3 days before measurement. The ultimate sample had a thickness of 100–150 μm . The mass of sample before and after degradation was weighed accurately using an electronic balance with a resolution of 0.1 mg. Three of the samples were considered as a group.

Swelling and degradation in PBS

Sample with dimension of $15 \times 15 \times 0.1 \text{ mm}^3$ and weighted as m_0 was incubated in 20 mL PBS at 37°C in a shaking bath. PBS was refreshed every week. To

TABLE I
The Characteristics of PEGT-*b*-PBT Copolymer Films

Sample	Composition of PEGT/PBT (in molar ratio)		<i>S</i>	<i>W_{c,s}</i> (%)	<i>W_{c,h}</i> (%)	<i>T_{g,h}</i> (°C)
	Theoretical	Experimental				
80/20	44/56	44/56	1.16	15.0	5.7	55.4
70/30	31/69	31/69	0.77	7.7	3.3	45.8
60/40	23/77	22/78	0.58	1.1	10.8	50.7
50/50	16/84	17/83	0.51	- ^a	16.2	35.5

W_{c,s} and *W_{c,h}* are noted as crystallinity of soft segment and hard segment in copolymer respectively.

T_{g,h} is noted as the glass transition temperature of hard segment in copolymer.

^a not observed.

determine the equilibrium swelling ratio (*S*) [eq. (1)], sample was removed and weighted (*m_t*) after rinsing thoroughly in distilled water and blotting surplus surface water with a wet tissue. After a certain time of degradation, the sample was dried in a vacuum oven at 30°C for 7 days and weighted as *m_d*. The mass remaining was calculated as eq. (2). When a sample fragments at extension time periods, the sample was put in a weighed glass plate, rinsed with distilled water, dried, and weighed on the glass plate.

$$S = (m_t - m_o)/m_o \quad (1)$$

$$\text{Mass remaining } \% = m_d/m_o \times 100 \quad (2)$$

Characterizations

The intrinsic viscosity of PEGT-*b*-PBT sample dissolved in phenol/tetrachloroethane mixing solution (1 : 1, v/v) was measured by single point measurements using an Ubbelohde viscometer (Type 0c) at 25°C. Polymer solutions with a concentration of ~ 0.1 g dL⁻¹ were used. In the present work, the variation of intrinsic viscosity was used to describe the extent of bond scission. A parameter *X_η* [eq. (3)] was defined as the intrinsic viscosity exponent, where $[\eta]_o$ was the initial intrinsic viscosity of sample, and $[\eta]_d$ was the intrinsic viscosity of sample at a certain time of degradation.

$$X_\eta = 1 + \ln([\eta]_d/[\eta]_o) \quad (3)$$

Morphologies of PEGT-*b*-PBT samples were observed under a JSM-35C-Jeol scanning electron microscope (SEM) after gold coating. Cross specimen was fractured in liquid nitrogen followed by gold coating.

Thermal behaviors of copolymer sample were performed using a Perkin-Elmer TA-2901M DSC calorimeter with a heating rate of 10°C min⁻¹ under

nitrogen atmosphere. About 10 mg sample was first heated up to 250°C for 10 min and then reheated after quenching to -100°C in liquid nitrogen. The glass temperature (*T_g*) was taken as the midpoint of the heat capacity change. The melting enthalpy (ΔH_m) was referred to as the corresponding energies (J g⁻¹) (the peak areas above the baseline) during the melting range. The crystallinity (*W_c*) of PEGT-*b*-PBT sample was calculated by ratioing the melting enthalpy of PEGT to 262 J g⁻¹ and PBT to 144.5 J g⁻¹ respectively, the melting enthalpy of 100% crystalline PEGT and PBT suggested in Refs. 24 and 25.

The copolymer composition was determined by proton nuclear magnetic resonance spectroscopy (¹H-NMR). 300 MHz ¹H-NMR (Varian Unity) spectra were recorded using polymer solutions in deuterated chloroform and TMS as internal standard. In the case of copolymers insoluble in deuterated chloroform, small amounts of trifluoroacetic acid were added. The effect of degradation on composition of copolymer sample was evaluated using ¹H-NMR. The experimental polymerization degree of PEG (*n_{exp}*) was determined according to eq. (4), where *I_n* denoted the integration of the H_{*n*} resonance.

$$n_{\text{exp}} = I_3/I_5 + 2 \quad (4)$$

RESULTS AND DISCUSSION

Degradation behaviors

For the evaluation of copolymer hydrolytic degradation, the characterization of water swollen matrices was of primary interest. It could be measured that swelling ratio of samples increased rapidly during the first hour, then went up slowly and after 3 days almost unchanged, which was named the equilibrium swelling ratio (*S*). Table I summarizes the swelling characteristics of samples. The results showed that *S* increased with the increasing in PEGT content. Feijen¹ and Fakirov²⁴ as well as their coworkers investigated the structure of PEOT/PBT copolymer

by DSC and SAXS. As was the case in their work, PEGT-*b*-PBT copolymer studied here was also semi-crystalline at room temperature,²² which suggested that PEGT-*b*-PBT copolymer exhibited particular microphase-separated morphology due to “hard” PBT domains as physical crosslinking dispersed in the “soft” amorphous phase consisting of both hydrophilic PEG segments and hydrophobic PBT segments.¹ As shown in Table I, DSC experiments showed that the increase in PEGT content of copolymer could lead to the decrease in crystallinity of hard segments ($W_{c,h}$) because of the interaction between PEGT and PBT segments. Hence, the increase in PEGT content not only favored hydrophilicity, but accelerated the diffusion of water molecules into matrices as well, which was attributed to the tendency of microphase-separated weakening and the copolymer structure loosing. Therefore, it could be elucidated that *S* was deeply related to the hydrophilicity and the crosslinking network of copolymer.

Table II shows the significant changes in intrinsic viscosity exponent (X_η) of PEGT-*b*-PBT samples during degradation. The results indicate that PEGT-*b*-PBT copolymer could degrade by hydrolysis, and the cleavage of chains would lead to the decrease in intrinsic viscosity. It was noted that at the beginning of degradation X_η dropped sharply for the first two samples with higher PEGT content, but slowly for another. This phenomenon was also previously observed for PEGT-*b*-PBT discs²⁵ and roll¹⁸ in PBS at 37°C.

The mass remaining of PEGT-*b*-PBT samples was measured throughout the beginning period of degradation as shown in Figure 2. PEGT-*b*-PBT samples in PBS at 37°C exhibited little mass loss in the first 7 days of degradation. Thereafter, samples with higher PEGT content, especially sample 80/20 showed a much faster mass loss within the tested time, and just after 35 days the mass loss of sample 70/30 became notably faster. It was elucidated that when the cleavage of copolymer chains had occurred, the

TABLE II
The Changes of Intrinsic Viscosity Exponent (X_η) of PEGT-*b*-PBT Copolymer Films Under pH 7.4 in PBS at 37°C

t_{deg} (days)	X_η			
	80/20	70/30	60/40	50/50
0	1	1	1	1
7	0.71	0.99	0.78	0.71
16	0.55	0.80	0.75	0.73
25	0.42	0.70	0.73	0.68
35	0.26	0.44	0.54	0.52
45	0.21	0.45	0.47	0.40
55	0.04	0.21	0.46	0.37

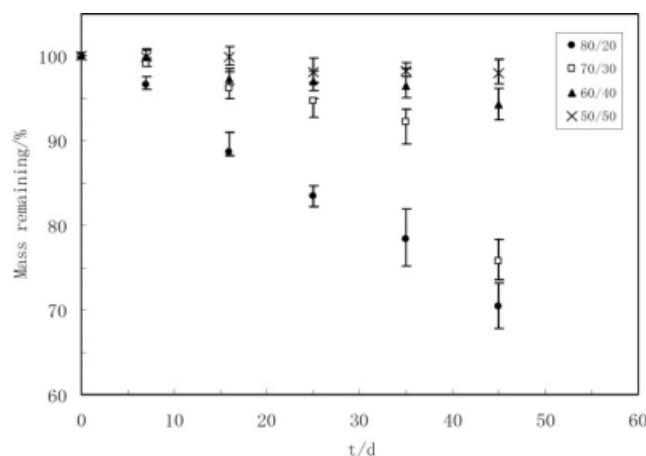


Figure 2 Mass remaining of PEGT-*b*-PBT copolymer films as a function of degradation time under pH 7.4 in PBS at 37°C.

erosion of some short segments led to a rapid degradation. The mass loss of another two samples dropped a little during 45 days of degradation because of higher content of PBT and lower *S*. As the degradation extending, it was difficult for sample 80/20 to be collected and accurately weighed due to break into several little fragments, so the subsequent measurement of mass loss was impossible.

Although both changes of intrinsic viscosity and mass loss of PEGT-*b*-PBT sample showed the similar decreasing tendency with degradation, the fall in intrinsic viscosity took place earlier for all samples in contrast to that of mass loss. Hence, PEGT-*b*-PBT underwent bulk degradation in the beginning period of degradation.

Morphology

The morphologies of samples after 200 days degradation, except for sample 50/50, changed a lot, as shown in Figure 3. These samples became yellowish. Macroscopically, more and more microcracks appeared on the surfaces of sample 80/20 at 21 days, and after 35 days the sample broke into several fragments. Although the degradable rate of sample 70/30 and 60/40 was relatively slow, they also followed the similar trend to sample 80/20. The reason for variation in morphologies could be subjected to the following two factors. First, water molecules would more easily diffuse into hydrophilic phase and make soft segments swell due to the higher PEGT content for the first three samples, and at the moment the hydrophobic phase basically kept invariable. So the internal stress formed among copolymer matrix would induce to generate microcracks. Second, the swollen PEGT segments would increase the possibility to hydrolyze the ester bonds in these PEGT domains,²⁶ and then parts of ester bonds came to crack. Because of the higher PBT content and the

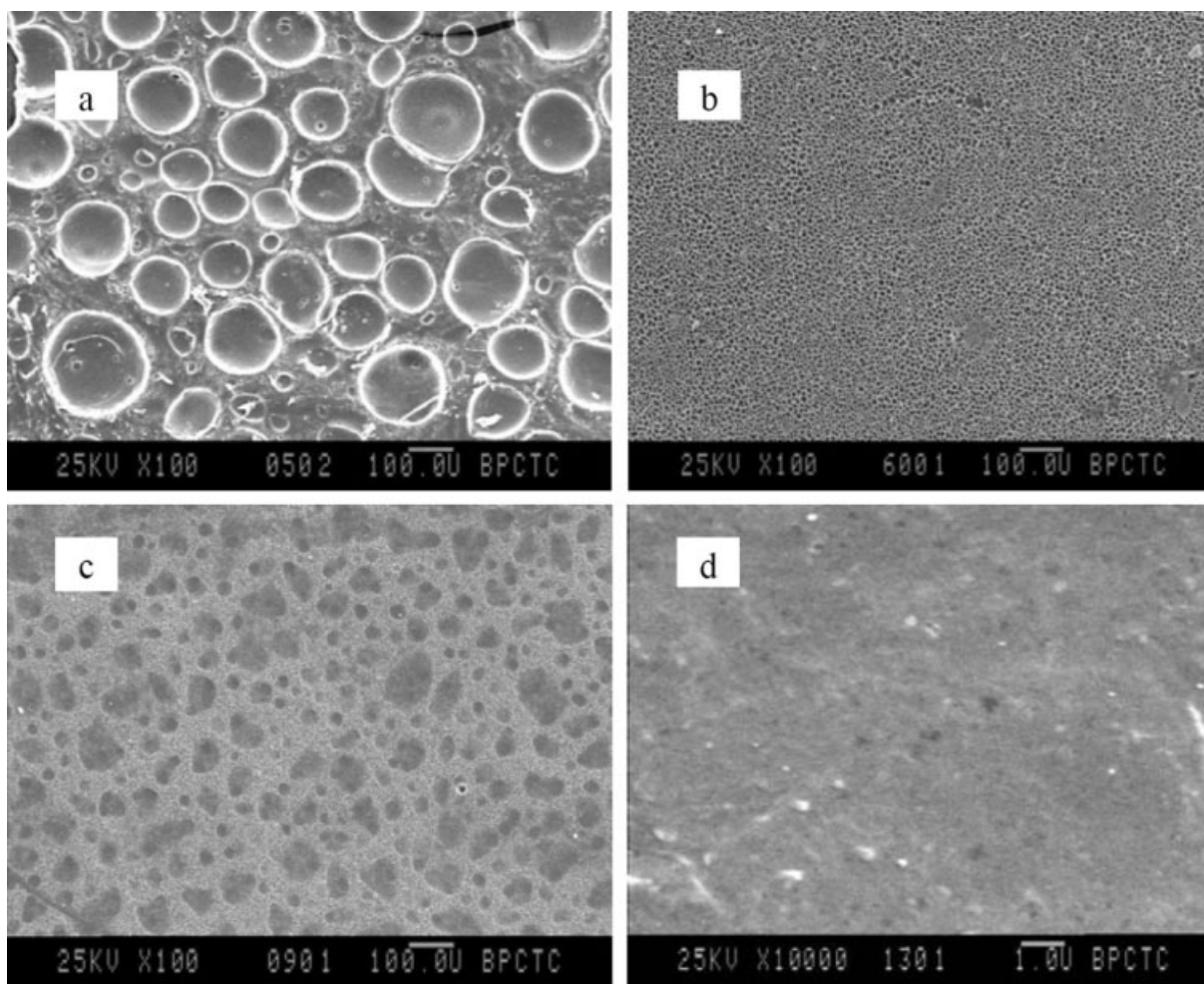


Figure 3 SEM micrographs of PEGT-*b*-PBT copolymer films including (a) Sample 80/20 (b) Sample 70/30, (c) sample 60/40 and (d) sample 50/50 after 200 days degradation.

closely physical crosslinking the image of sample 50/50 even with 10,000 magnification showed unchangeable. As for these samples, yellowing might as well come from the thermal oxidation of aromatic groups.

To investigate on the morphological variation of copolymer films, the micrographs before and after different periods of degradation of sample 70/30 were tracked by SEM, as shown in Figure 4. Comparing with the nondegraded sample, the variety of morphologies strongly depended on degradation time. At 16 days, no significant change on the sample occurred, except for only few pores about 0.1 μm in diameter formed. After 35 days of degradation, these pores not only gradually expanded, but the number of pores rose as well. Furthermore, the shape of pores in different regions [in black box of Fig. 4(b)] was different. This variety could be attributed to the microphase separated structure of copolymer which induced the different degradable rate among different regions. Irregular small dots at 16 days degradation on the surface might be the

metal iron originated from the PBS.¹⁴ This vision would little by little disappear with the development of degradation. Lots of large piece residues produced [as shown in Fig. 4(b)] during the sequent degradation might be the low molecular weight substances which came from the breakage of segments. During a period of 55 days degradation, several various pores were generated on the surface, which accelerated the formation of unique topographies. Simultaneously X_n dropped dramatically and the mass loss was over 30%. All above results showed that copolymer chains broke down to a great extent so that low molecular weight substances would easily eroded and diffused into media due to the swelling characteristics of copolymer in PBS, and eventually porous structure which was interconnected and about 2–20 μm pores in diameter was developed over 100 days of degradation. Degradation of the polymer also acts as a type of etching making the crystalline PBT superstructures visible.¹⁸ Although the breakage tendency of copolymer chains with degradation would last until 150 days,

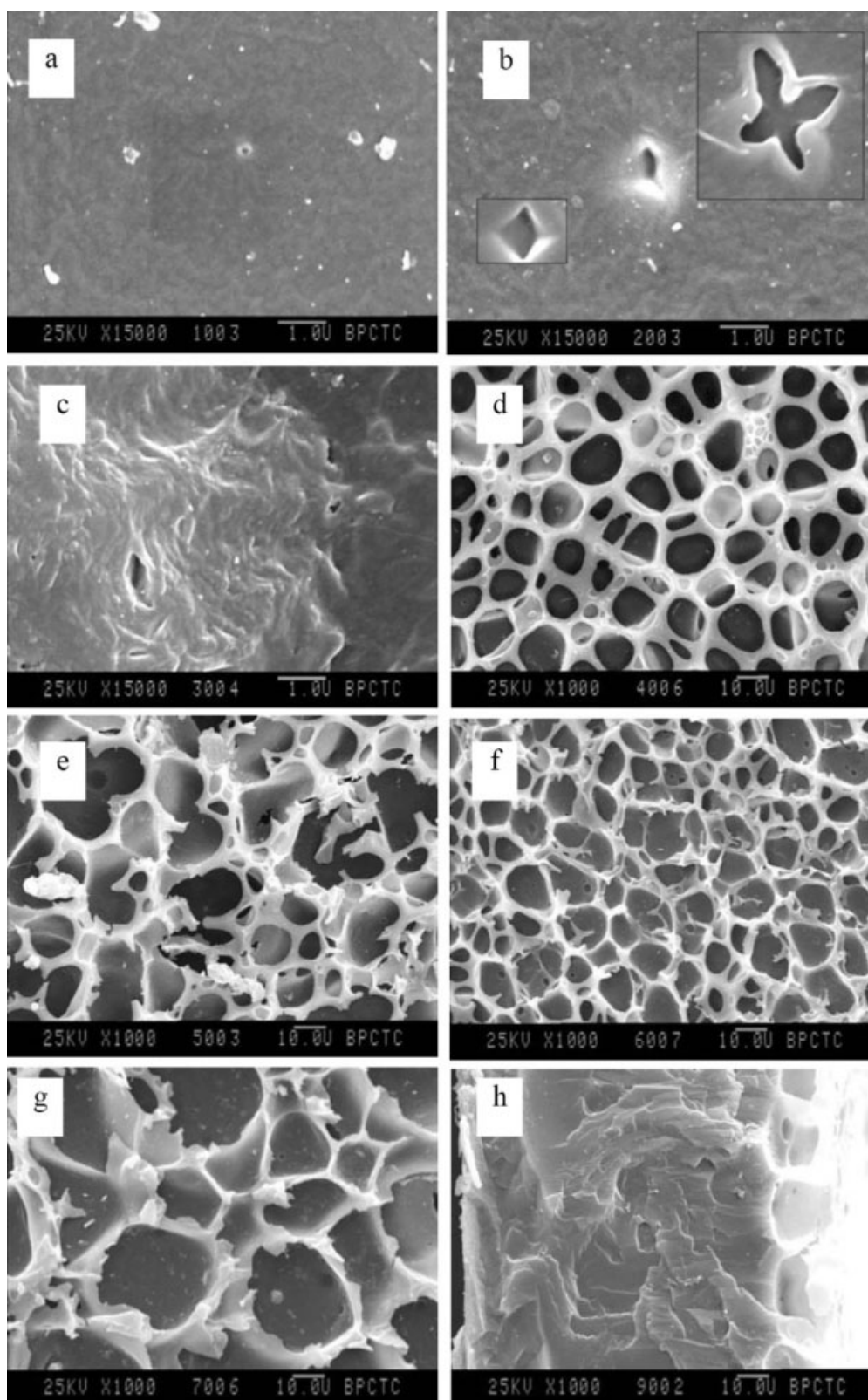


Figure 4 SEM micrographs of sample 70/30 as a function of degradation time, in which (h) is cross-section profile of 100 days, and others are surface morphologies (a) 16 days, (b) 35 days, (c) 55 days, (d) 100 days, (e) 150 days, (f) 200 days, and (g) 300 days.

TABLE III
The Thermal Properties of PEGT-*b*-PBT Copolymer Films Hydrolyzed Under pH 7.4 in PBS at 37°C

t_{deg} (days)	80/20			70/30			50/50		
	$W_{c,s}$ (%)	$T_{m,h}$ (°C)	$W_{c,h}$ (%)	$W_{c,s}$ (%)	$T_{m,h}$ (°C)	$W_{c,h}$ (%)	$W_{c,s}$ (%)	$T_{m,h}$ (°C)	$W_{c,h}$ (%)
0	15.0	102.2	5.7	7.7	145.9	3.3	–	180.8	16.2
16	9.6	106.8	9.7	5.2	102.0	3.2	–	187.2	18.1
35	10.8	78.5	9.5	5.8	146.2	3.6	0.8	186.0	25.0
55	14.3	– ^a	–	8.3	146.6	20.8	–	188.8	23.7
100	10.0	–	–	5.4	–	–	–	188.7	21.1
150	7.4	–	–	5.2	142.4	4.6	–	190.1	13.7
200	–	–	–	5.8	–	–	–	199.2	18.3
300	10.0	–	–	5.3	117.4	69.9	–	168.3	10.8

^a not observed.

the upper layer porous network came to collapse, and up to 200 days the expanded pore sizes were ascribed to the more serious collapse. Finally, at about 300 days the upper layer porous network was completely deteriorated, and a set of microporous network of about 40- μm pores in diameter was formed.

Therefore, once the interconnected porous structure was formed, the rate of surface erosion obviously increased with the expansion of surface areas. When the rate of erosion was faster than that of bulk degradation, the mechanism of surface erosion which led to the collapse of network would become the main role.

Thermal behaviors

The thermal properties of three PEGT-*b*-PBT samples before and after different periods of degradation were given in Table III. The change of soft segments crystallinity ($W_{c,s}$) for sample 80/20 and 70/30 fluctuated a little during degradation. The crystallinity of nondegraded sample was measured directly after synthesis. Although incubated in PBS, the conformation of PEGT segments easily varied with the relaxant extending of swollen molecular chains. After dried, the mobility of PEGT segments was fixed, and the segments existed in amorphous phase, so $W_{c,s}$ at 16 days dropped. Throughout 35 days of degradation the copolymer structure would be more loosely and easily hydrolyzed by water molecules, therefore the preferential cleavage of PEGT segments could take place at the borders connecting between the crystalline and amorphous regions, which might favor the remaining PEGT segments to rearrange themselves to lead to a slight increase in $W_{c,s}$ for sample 80/20 and sample 70/30. The same change of crystallinity was also observed during the degradation of PLLA fibers.^{27–29} Sample 50/50 did not show the same trend because of the lower PEGT content.

DSC thermograms illustrated the change in the melting temperatures ($T_{m,h}$) and crystallinity of hard segment ($W_{c,h}$) of PEGT-*b*-PBT samples as a function

of their degradation, as already shown in Table III. Over the degradation of 35 days, an increase in $W_{c,h}$ of three samples took place, for sample 80/20 from 5.7% to 9.5%, for sample 70/30 from 3.3% to 3.6% and for sample 50/50 from 16.2% to 25.0% respectively. The preferential breakage of PEGT segments in amorphous regions would decrease the molecular entanglement and increased the mobility of remaining molecular chains. Moreover, the preferential degradation of ester bonds could result in the appearance of residues with high PBT contents.¹ Hence, active PBT segments could organize themselves more orderly to form the PBT crystallites encouraging the rise in crystallinity.

Afterwards, sample 70/30 was indicated by a significantly increase in enthalpy of melting at 55 days and 300 days, which gave $W_{c,h}$ as 20.8 and 69.9, respectively, along with the shift of the melting peak 146.6°C to 117.4°C. In addition to the earlier discussed reasons, the increase in crystallinity could be considerably enhanced by the long-term degradation under pH 7.4 in PBS at 37°C similar to the annealing of samples at 37°C. Therefore, different size and irregularity of the PBT crystallites will finally be formed at degradation processing¹⁸ and crystallinities of PBT segments might change a lot.

Generally, the melting temperature depends strongly on the perfection of the crystallites and the mobility of the macromolecular chains. Long-term degradation could probably deteriorate the perfection of PBT crystallites and encourage the mobility of the debris PBT segments. Hence, the melting temperature decreased notably. In the case of the experiment on the accelerated degradation of poly(L-lactic acid) fibers in phosphate buffered saline, Yuan also observed the decrease in melting temperatures of the degraded PLLA fibers.²⁷ Comparing with sample 70/30, the change in $W_{c,h}$ and melting temperature for sample 50/50 was slighter throughout 300 days period, which was probably due to the higher PBT contents in copolymer leading to the slower degradation.

TABLE IV
Changes of Molar Composition and Experimental Polymerization Degree of PEG (n_{exp}) of PEGT-*b*-PBT Copolymer Films by Degradation Under pH 7.4 in PBS at 37°C

t_{deg} (days)	80/20		70/30		50/50	
	PEGT/PBT Mol (%)	n_{exp}	PEGT/PBT Mol (%)	n_{exp}	PEGT/PBT Mol (%)	n_{exp}
0	44/56	20.1	31/69	20.0	17/83	19.6
16	46/54	19.1	34/66	19.6	20/80	17.3
35	44/56	19.7	35/65	18.6	18/82	19.7
55	38/62	19.0	35/65	19.2	19/81	19.4
100	24/76	20.7	34/66	20.5	21/79	18.3
150	33/67	20.8	20/80	19.5	15/85	18.0
200	37/63	20.9	21/79	20.7	19/81	17.3
300	29/71	23.1	30/70	20.4	21/79	17.0

¹H-NMR studies

Table IV summarized the changes in molar composition of three samples during the tested time. Like what Feijen had reported,¹ there also existed a fall in PEGT content in our experiment. Moreover, the obvious variety of molar composition for samples with higher PEGT content occurred at earlier stage of degradation. Considering the slight increase in soft segment content at 16 days degradation, the reason might result from the diffusion of PBT oligomer due to swelling. In addition, by comparing the ¹H-NMR spectra (not given here) of degraded sample for 300 days with that of nondegraded sample, the peak position of each spectrum had no change and the polymerization degree of PEG (n_{exp}) almost kept the same, as shown in Table IV. Therefore, it suggested that PEG itself did not degrade and was oxidized and the degradation of copolymer came from the cleavage of the ester bonds between PEG and terephthalate.

When the cleavage happened to the ester bonds attached to PEG, PEG segments would break off from the copolymer backbones, the swollen microphase-separated structure favored diffusion of the broken PEG segments. As a result, the soft segment content for sample 80/20 and 70/30 decreased with time. For sample 80/20, the soft segment content rapidly fell 13.6% at 55 days. The soft segment content of sample 70/30, however, almost remained constant until 100 days, then showed a decrease of 32.2% at 200 days, and at 300 days went up close to the initial molar component. This further revealed that not only PEG segments largely broke and extricated, which led to the decrease in the molar content of PEGT, but also indicated that degradation occurred in the "hard segments" of the copolymer to some extent.²⁶ With the development of degradation, the further cleavage of PEGT segments could give rise to the collapse of PBT segments as crosslinking network, leading to the breakage of PBT segments, especially located on the surface from the main chain.

Considering the mechanism of degradation for PEGT/PBT copolymer involving the combination of bulk degradation and surface erosion, it might be concluded that the degraded products could be taken away from the matrix layer by layer against the degradation time leading to the collapse of the first network during the 300 days period, which was also apparent from SEM studies discussed before (shown in Fig. 4). Hence in the case of 300 days degradation the breakage of parts of PBT segments from the backbone encouraged the increase in the PEGT molar ratio of sample 70/30. The molar composition for sample 50/50 had no apparent change during the periods of 300 days degradation.

Comparing Feijen's experiment¹ and our experiment with Kellomäki's,¹⁸ the molecular structure of copolymers studied in the three experiments is the same. In Feijen's and our experiment, the thickness of film is around 100 μm and the film is processed by solution cast, while the thickness of film in Kellomäki's experiment is three times higher, up to 400 μm and the film is hot-pressed. The different processing method could mean different internal structure of sample due to several lamellar growing and internal reorganization of the initially lamellar structure by annealing.³⁰ Furthermore, based on earlier analyzes the mechanism of degradation for PEGT-*b*-PBT copolymer involves the bulk degradation and the surface erosion. Hence, the thickness and processing method for sample could get a pronounced effect on degradation. So, when the cleavage of ester bonds occurs, the broken segments are difficult to diffuse from the matrices because of thicker dimension and dense structure in Kellomäki's experiment.

CONCLUSIONS

During a period of 300 days, hydrolytic degradation profiles of PEGT-*b*-PBT copolymer films at 37°C in PBS strongly count on copolymer composition and degradable time. Films with higher PEGT content exhibit a faster decrease in intrinsic viscosity and

mass loss. And with the development of degradation, highly interconnected porous morphologies for PEGT-*b*-PBT films with weight ratio of 70/30 are gradually formed, afterwards collapsed and emerged. Moreover, the changing tendency of hard segment crystallinity fluctuates with the formation and sequent collapse of porous network. The molar content of PEGT for sample 80/20 and 70/30 gradually decreases and for sample 50/50 almost keeps no change during the tested time. The degradation behavior for PEGT-*b*-PBT copolymer films first follows a bulk degradation mechanism, and then proceeds by both bulk degradation and surface erosion, which finally lead to the interconnected porous morphologies.

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