

Characterization of the Mechanical Properties, Crystallization, and Enzymatic Degradation Behavior of Poly(butylene succinate-co-ethyleneoxide-co-DL-lactide) Copolyesters

Licheng Tan,^{1,2} Yiwang Chen,^{1,2} Weihua Zhou,² Huarong Nie,² Suwen Ye²

¹Department of Chemistry, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

²Institute of Polymers, Nanchang University, 999 Xuefu Avenue, Nanchang 330031, China

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ABSTRACT: A series of aliphatic biodegradable poly(butylene succinate-co-ethyleneoxide-co-DL-lactide) copolyesters were synthesized by the polycondensation in the presence of dimethyl succinate, 1,4-butanediol, poly(ethylene glycol), and DL-oligo(lactic acid) (OLA). The composition, as well as the sequential structure of the copolyesters, was carefully investigated by ¹H-NMR. The crystallization behaviors, crystal structure, and spherulite morphology of the copolyesters were analyzed by differential scanning calorimetry, wide angle X-ray diffraction, and polarizing optical microscopy, respectively. The results indicate that the sequence length of butylene succinate (BS) decreased as the OLA feed molar ratio increasing. The crystallization behavior of the copolyesters was influenced by the compo-

sition and sequence length of BS, which further tuned the mechanical properties of the copolyesters. The copolyesters formed the crystal structures and spherulites similar to those of PBS. The incorporation of more content of ethylene oxide (EO) units into the copolyesters led to the enhanced hydrophilicity. The more content of lactide units in the copolyesters facilitated the degradation in the presence of enzymes. The morphology of the copolyester films after degradation was also studied by the scanning electron microscopy. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2272–2282, 2012

Key words: poly(butylene succinate); poly(ethylene glycol); DL-oligo(lactic acid); crystallization; enzymatic degradation

INTRODUCTION

In the past few decades, biodegradable polymers, especially aliphatic polyesters and their copolymers, have drawn growing attentions from both academic and industrial workers due to their potential applications in both biomedical materials^{1,2} and general environmentally friendly materials.^{3,4} As one of the most representative and generally acknowledged biodegradable aliphatic polyester, poly(butylene succinate) (PBS), which has good degradability and excellent melt processability, has been used extensively.^{5,6} Therefore, many studies have been performed to investigate the mechanical properties and biodegradability,^{7,8} as well as the crystal structure, crystallization, and melting behavior.^{9–15} However, PBS exhibits a slow biodegradation rate as a result of its high degree of crystallinity.¹⁶ One way of pro-

moting the biodegradability properties of PBS, is to prepare polyesters copolymerized with different diacids or diols. Till now, more attention has been paid on the numerous copolyesters such as poly(butylene succinate-co-ethylene succinate), poly(butylene succinate-co-propylene succinate), and poly(butylene succinate-co-butylene adipate).^{17–23}

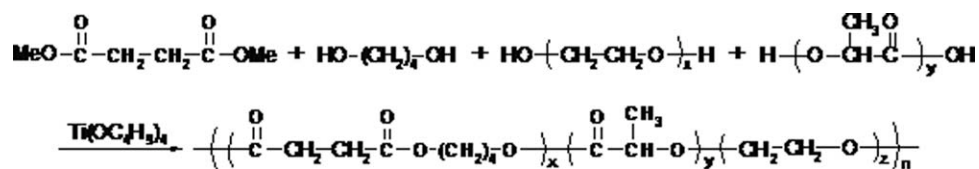
In addition, the introduction of poly(lactic acid) (PLA) into the PBS molecular chains might also be useful to improve the degradation rate of PBS. It is well known that PLA possesses many desirable properties, such as nontoxicity, low immunogenicity, and good biocompatibility, so as to be used in biomedical and pharmaceutical fields.^{24,25} PLA oligomers with average molecular weights less than several tens of thousands can be synthesized by polycondensation of lactic acid. The research works based on copolymerization of PLA with PBS have been reported in recent years.^{26–30}

In general, the biodegradability of polyesters is influenced not only by the chemical structure, especially the presence of functional groups and a hydrophilicity/hydrophobicity balance, but also by a highly ordered structure, such as crystallization, orientation, and other morphologies.³¹ The biodegradability properties of polyesters can be improved by increasing the hydrophilicity, such as polyethers,

Correspondence to: Y. Chen (ywchen@ncu.edu.cn) or W. Zhou (dramzwh@126.com).

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Scheme 1 Synthesis of PBSGLA copolyesters.

into the backbone of the polymer chains.³² PBS and its copolyesters are hydrophobic polymers while poly(ethylene glycol) (PEG) is a hydrophilic polymer. Furthermore, PEG is nontoxic, nonantigenic, and nonimmunogenic,³³ which often used as the component to impart good hydrophilicity as well as biocompatibility of biomaterials. Hence, much attention has been paid to modify the hydrophilicity of PBS as well as its copolyesters by copolymerization with PEG to improve the biodegradation rate of PBS. Nagata et al.³⁴ synthesized poly(butylene succinate) copolymers containing PEG with molecular weights in the range from 200 to 2000 and reported that with increasing content of PEG, the hydrolytic degradation rate of the copolymers was increased. Zhang et al.³⁵ synthesized three series of poly(butylene terephthalate-co-succinate)-b-poly(ethylene glycol) segmented random copolymers and proved that the number-average molecular weight of PEG had a predominant role on the improvement of elasticity and degradation rate of the copolymers.

Therefore, the article is aimed to prepare a series of poly(butylene succinate-co-ethyleneoxide-co-DL-lactide) (PBSGLA) copolyesters with relatively higher degradation rates by the direct polycondensation method. The effect of PEG on the morphology, crystallization kinetics, hydrophilicity, and biodegradability improvement of biodegradable PBSGLA copolyesters was investigated.

EXPERIMENTAL

Materials

A 90% aqueous solution of racemic DL-lactic acid and dimethyl succinate (DMS) were purchased from Fluka and Alfa Aesar Co. (Tianjin, China), respectively. The 1,4-butanediol (BDO) was purchased from Sinopharm Chemical Reagent Co. (Shanghai, China). The reagents were used as received without further purification. Hydroxyl end-capped PEG 1000 (PEG, $M_n = 1000$) was purchased from Lancaster and dried by vacuum at 40°C prior to use. The Titanium (IV) butoxide catalyst ($\text{Ti}(\text{OBu})_4$) was purchased from Acros and the lipase of *Pseudomonas cepacia* was purchased from Fluka. All the other chemicals and solvents of analytical grade were used as received without further purification.

Synthesis of copolyesters

DL-lactic acid was heated stepwise to 200°C and kept at this temperature in a vacuum for 4 h. This procedure yielded α -hydroxy- ω -carboxyoligo (lactic acid) (OLA, $\overline{M}_w = 4500$ g/mol, $\overline{M}_n = 1700$ g/mol, $\overline{M}_w/\overline{M}_n = 2.60$).

The aliphatic copolyesters PBSGLA were synthesized by the two-stage melt polycondensation method composing of esterification and polycondensation in the presence of DMS, BDO, PEG, and DL-oligo(lactic acid) (OLA) as shown in Scheme 1. The molar ratio of BDO to DMS was 1.2 to 1. In the first stage, the reaction mixture was charged into a 250 mL glass reactor under nitrogen, followed by the addition of $\text{Ti}(\text{OBu})_4$ (0.025 mol % of the total chemicals). The mixture was heated to 180°C and reacted for 2 h under nitrogen protection and vigorous stirring. The esterification was complete when the theoretical amount of byproduct was yielded; a second portion of catalyst $\text{Ti}(\text{OBu})_4$ (0.025 mol % of the total chemicals) was then added. In the second step of polycondensation, a vacuum (50 Pa) was applied slowly over a period of time of about 30 min, to avoid excessive foaming and to minimize oligomer sublimation, which is a potential problem during the melt polycondensation. The temperature was slowly increased to 230°C and continued for 3 h for all prepared polyesters. After the polycondensation reaction was completed, the polymer was allowed to cool to room temperature, dissolved in 50 mL of chloroform, isolated by precipitation in 800 mL of methanol, and collected on a filter. The white polymer was then dried at 40°C for 24 h under vacuum.

Measurements

The proton nuclear magnetic resonance ($^1\text{H-NMR}$) spectra were recorded in CDCl_3 solution with tetramethylsilane ($\delta = 0$) as the reference standard using a Bruker ARX 400 NMR spectrometer.

Differential scanning calorimetry (DSC) measurements of copolyesters were carried out on a Shimadzu DSC-60 under a nitrogen flow at a rate 20 mL/min. The calibration of the temperature was performed using indium as the standard before the measurement. About 5 mg of samples encapsulated in the DSC aluminium pan, were heated quickly to

150°C and held for 3 min to erase thermal history. Then, the samples were cooled to -50°C and subsequently heated to 150°C at 10°C/min. The corresponding glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), melting enthalpy (ΔH_m), and crystallization enthalpy (ΔH_c) were recorded, respectively.

The wide angle X-ray diffraction (WAXD) study was adopted to analyze crystalline structure of the samples by a Bruker D8 Focus X-ray diffractometer, operating at 30 kV and 20 mA with a copper target ($\lambda = 0.154$ nm) and in the 2θ angle range of 5–40° at a scanning rate of 0.5°/min.

The crystal morphology of the copolyesters was analyzed by a Nikon E600POL polarizing optical microscope (POM) equipped with an Instec HS 400 heating and cooling stage.

Mechanical properties of the copolyesters were determined by a SANS WDW universal test system with electronic data evaluation on specimen of 70 × 25 mm with a thickness in the range of 0.04 to 0.06 mm determined by a vernier caliper. The specimens were cut from melt-pressed films by a mold equipped with knives. The values of tensile strength, elongation at break and modulus were measured under a speed 10 mm/min. Data was taken as the average value of at least five measurements.

A contact angle measurement JC2000A was used to measure static water contact angles of the polymer films at 25°C and 60% relative humidity using a sessile drop method. For each angle reported, at least five sample readings from different surface locations were averaged. The angles reported were reliable to $\pm 1^\circ$.

The surfaces of degraded samples after the enzymatic degradation were observed with Quanta 200F scanning electron microscopy (SEM) after gold vapor deposition onto the samples in an Edwards Auto 306.

Water uptake

The film of 70 × 25 mm with a thickness of about 0.06 mm is weighed as m_0 , and incubated into distilled water at 37°C in shaking bath for 2 days. After the equilibrium adsorption of water, the film was wiped with filter paper and weighed as m_1 . The water uptake was calculated as follows:

$$\text{Water uptake (\%)} = (m_1 - m_0)/m_0 \times 100\% \quad (1)$$

Enzymatic degradation

The copolyesters films (50 × 20 × 0.06 mm) prepared by melt-pressed were placed in vials containing 20 mL of phosphate buffer solution (pH 7.4 at

25°C) with 0.20 mg/mL *P. cepacia* lipase at constant temperature of 37°C. At predetermined degradation time intervals, the specimens were removed from the medium, rinsed with distilled water, dried under vacuum at room temperature for 1 week, and weighed. Weight loss percentages of the copolyesters were obtained according to the relationship:

$$\text{Weight loss (\%)} = (W_0 - W_r)/W_0 \times 100\% \quad (2)$$

where W_0 is the initial weight, and W_r is the dry weight of the specimens after degradation.

RESULTS AND DISCUSSION

Structure of copolyesters

The PBSGLA copolyesters were synthesized via the two-stage polycondensation process as shown in Scheme 1. Both of the ethyleneoxide (EO) and lactide (LA) units were built into the PBS molecular chains by the transesterification. In the copolyesters, the "BS" in the sample code represents for the butylene succinate unit, and "G" represents for ethyleneoxide unit, and "LA" represents for lactide unit. The subscript numbers at the end of each unit indicate the molar ratio of BS, EO, and LA units in the copolyesters.

The chemical structure is one of the key points determining the properties of the copolyesters. A clear outlook on chain structure is indispensable to understand the thermal properties, crystallization behavior, degradation profiles as well as mechanical properties.³⁶ Figure 1 shows the ¹H-NMR spectra of the copolyesters, and the peaks corresponding to the BS, EO, and LA units are observed. The peak at 2.62 ppm (proton a) is assigned to protons from the CH₂ of succinate. The peaks at 4.13 ppm (proton b) and 1.70 ppm (proton c) are attributed to the side and central CH₂ protons of the butylene, respectively. The peak at 3.65 ppm (proton f) is ascribed to the OCH₂ of ethyleneoxide. Furthermore, the peaks at 1.50 ppm (proton d) and 5.08 ppm (proton e) correspond to the CH₃ and CH protons of lactide. Besides the traditional resonance peaks of BS, EO, and LA units mentioned above, several new peaks are discerned, showing the formation of new segmental units due to the transesterification. The peak at 2.74 ppm (proton g) is attributed to the CH₂ protons of the succinate linking to lactide. The peak at 4.20 ppm (proton h) is assigned to the OCH₂ protons of the butyleneoxide linking to lactide. The peak at 4.25 ppm (proton j) corresponds to the OCH₂ protons of the butyleneoxide linking to ethyleneoxide while the peak at 3.71 ppm (proton i) corresponds to the protons of OCH₂ in ethyleneoxide unit linking to butyleneoxide unit. It is noticed that the relative intensity

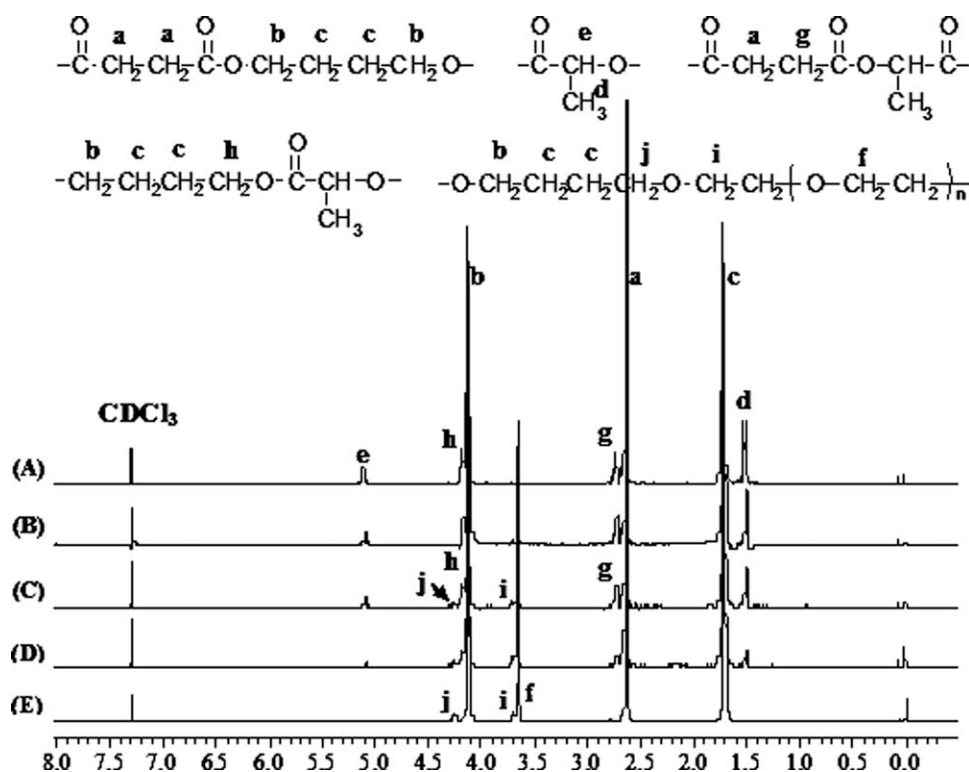


Figure 1 400 MHz $^1\text{H-NMR}$ spectrum of the copolyesters of (A) $\text{PBS}_{80}\text{G}_0\text{LA}_{20}$, (B) $\text{PBS}_{73}\text{G}_9\text{LA}_{18}$, (C) $\text{PBS}_{76}\text{G}_{11}\text{LA}_{13}$, (D) $\text{PBS}_{68}\text{G}_{28}\text{LA}_4$, and (E) $\text{PBS}_{65}\text{G}_{35}\text{LA}_0$, respectively.

of peaks of protons d, e, and g decrease as the lactide content decreasing, confirming the incorporation of less content of LA units. It is also observed that the relative intensity of peaks of protons f and i increases as the EO content increasing, indicating of the incorporation of more content of EO units. The above results suggest that the BS, EO, and LA units are built into the molecular chains of the copolyesters due to the transesterification.

In general, the properties of the copolyesters are not only influenced by the chemical compositions but also determined by the sequence length of the segments. The composition of the copolyesters is calculated on the basis of the corresponding resonance peak integrals of the protons of the butylene succinate (BS) units, ethyleneoxide (EO) units, and lactide (LA) units by the following equations:

$$x_{\text{BS}} = \frac{I_b/4}{I_b/4 + I_d/3 + I_f/4} \quad (3)$$

$$x_{\text{EO}} = \frac{I_f/4}{I_b/4 + I_d/3 + I_f/4} \quad (4)$$

$$x_{\text{LA}} = \frac{I_d/3}{I_b/4 + I_d/3 + I_f/4} \quad (5)$$

where x_{BS} , x_{EO} and x_{LA} are the molar fractions of BS, EO, and LA units, I_b , I_d , and I_f are the integrals of the corresponding peaks, respectively. The sequence

length of the BS units (N_{BS}) could be calculated by the following equation:

$$N_{\text{BS}} = \frac{I_b/4}{(I_g + I_h + I_j)/2} \quad (6)$$

where I_b is the peak integral of the protons in succinate units, I_g is the peak integral of protons in succinate units connecting to lactide, I_h is the peak integral of protons in butyleneoxide linking to lactide, and I_j is the peak integral of protons in butyleneoxide linking to ethyleneoxide, respectively.

The composition of copolyesters, as well as the calculated number-average sequence length of BS units is illustrated in Table I. It is found that the BS units content decrease as the EO units content increasing, in contrast to the decrease of LA units in the copolyesters, which is much lower than the feed ratios due to the inevitable loss of lactic acid during the condensation polymerization. It is also noticed that the sequence length of BS units increases as the PEG feed molar ratio increasing, which might be caused by the incorporation of less content of LA units.

Furthermore, the molecular weights of the copolyesters were determined by the use of GPC, and the results are listed in Table II. It is noticed that the number-averaged molecular weights (\overline{M}_n) of the copolyesters is ranging from 5.83×10^4 to $12.11 \times$

TABLE I
Chemical Composition and Sequence Length of BS Units of the Copolyesters

Sample	Feed molar ratio DMS/BDO/PEG/OLA	Feed composition BS/EO/LA	Composition ^a BS/EO/LA	N _{BS} ^b
PBS	1.0/1.2/0/0	100.0/0/0	100.0/0/0	–
PBS ₈₀ G ₀ LA ₂₀	1.0/1.2/0/0.5	66.6/0/33.4	80.0/0/20.0	1.9
PBS ₇₃ G ₉ LA ₁₈	1.0/1.2/0.1/0.4	66.6/6.7/26.7	73.4/8.8/17.8	2.0
PBS ₇₆ G ₁₁ LA ₁₃	1.0/1.2/0.25/0.25	66.6/16.7/16.7	75.8/11.4/12.8	3.6
PBS ₆₈ G ₂₈ LA ₄	1.0/1.2/0.4/0.1	66.6/26.7/6.7	68.3/27.7/4.0	5.8
PBS ₆₅ G ₃₅ LA ₀	1.0/1.2/0.5/0	66.6/33.4/0	65.4/34.6/0	14.2
PBS ₅₄ G ₄₀ LA ₆	1.0/1.2/0.8/0.2	50.0/40.0/10.0	53.5/40.4/6.1	3.7
PBS ₄₁ G ₅₀ LA ₉	1.0/1.2/1.2/0.3	40.0/48.0/12.0	41.4/49.6/9.0	2.6

^a The molar ratio of BS, LA and EO units in the copolyesters calculated from ¹H-NMR.

^b The average sequence length of BS units calculated from dyad peaks in NMR spectra.

10⁴ g/mol with the polydispersity between 1.34 and 1.76. The values obtained indicate that the copolyesters synthesized have high-molecular weights, and they are suitable to be used in fields where flexible materials are needed.

Thermal properties of copolyesters

The crystallization and melting behaviors of the copolyesters were investigated by the DSC analysis, and the heating and cooling curves are shown in Figure 2. The corresponding glass transition temperature (T_g), melting temperature (T_m), crystallization temperature (T_c), melting enthalpy (ΔH_m), as well as crystallization enthalpy (ΔH_c) are illustrated in Table III. It is noticed that all the copolyesters exhibit only one glass transition temperature, showing the formation of homogeneous phase without significant phase separation. Furthermore, the T_g values of the copolyesters decrease as the EO unit content increasing, suggesting that the molecular chains are more flexible. In Figure 2(a), the crystallization peaks shift to higher temperatures with the EO content increasing for the copolyesters with EO unit content lower than 40%. According to Vallance and Cooper,³⁷ the crystallization behavior of hard segments was controlled by hard segment block length and

TABLE II
Molecular Weights of the Copolyesters

Sample	$\bar{M}_n \times 10^{-4}$ (g/mol)	$\bar{M}_w \times 10^{-4}$ (g/mol)	Polydispersity
PBS	8.80	12.98	1.48
PBS ₈₀ G ₀ LA ₂₀	7.56	10.85	1.44
PBS ₇₃ G ₉ LA ₁₈	8.03	11.67	1.45
PBS ₇₆ G ₁₁ LA ₁₃	8.25	11.04	1.34
PBS ₆₈ G ₂₈ LA ₄	9.33	12.94	1.39
PBS ₆₅ G ₃₅ LA ₀	12.11	19.17	1.58
PBS ₅₄ G ₄₀ LA ₆	6.36	10.55	1.66
PBS ₄₁ G ₅₀ LA ₉	5.83	10.25	1.76

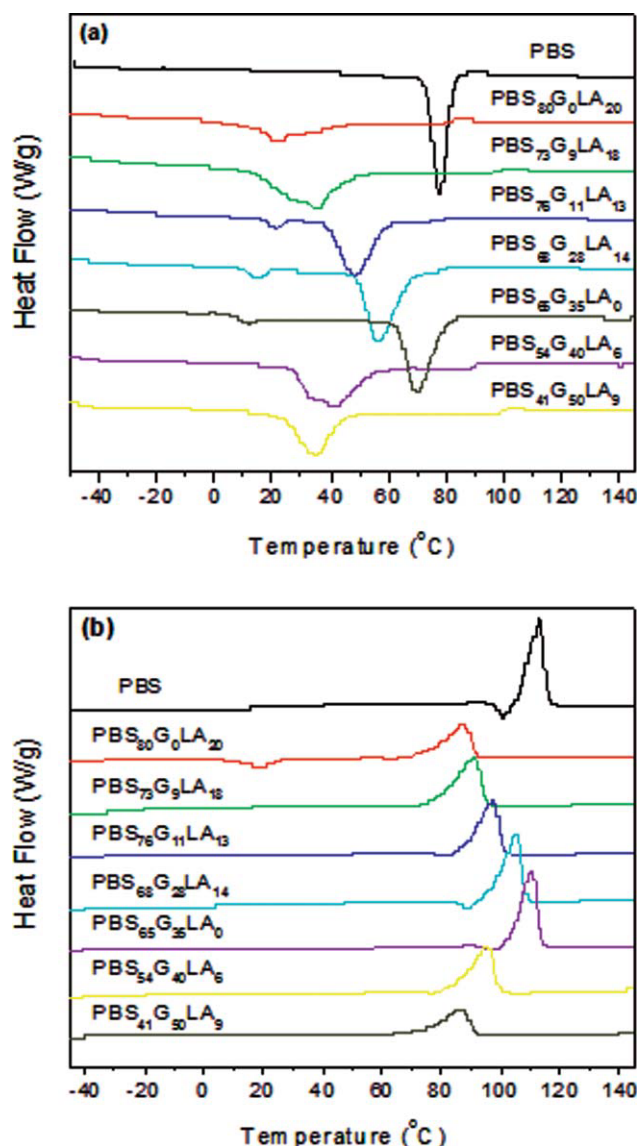


Figure 2 DSC (a) cooling and (b) second heating curves for the copolyesters. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
Thermal Properties and Degree of Crystallinity of the Copolyesters

Sample	T_g (°C)	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	X_{c-DSC} (%)
PBS	-26.7	112.9	73.6	77.9	68.4	66.6
PBS ₈₀ G ₀ LA ₂₀	-31.9	87.3	38.7	21.7	30.0	35.0
PBS ₇₃ G ₀ LA ₁₈	-30.2	90.8	46.8	35.4	44.3	42.4
PBS ₇₆ G ₁₁ LA ₁₃	-34.2	97.3	49.4	48.3	47.2	44.7
PBS ₆₈ G ₂₈ LA ₄	-38.4	105.1	54.3	56.9	50.6	49.2
PBS ₆₅ G ₃₅ LA ₀	-40.8	110.3	57.5	70.1	57.0	52.1
PBS ₅₄ G ₄₀ LA ₆	-43.9	95.4	41.6	41.2	48.8	37.7
PBS ₄₁ G ₅₀ LA ₉	-44.6	86.3	30.8	35.0	38.8	27.9

independent of the soft segment within certain composition. In this study, the existence of large amount of OLA leads to the formation of copolyesters with shorter sequence length of BS. Therefore, the T_c of the copolyesters increases with the increase of EO content due to the formation of longer sequence length of BS. However, the T_c of the copolyester decreases as the PEG molar fraction reaches 40%. The EO units restrict the crystallization of copolyesters, resulting in the crystallization at lower temperature.

It is further noticed that the copolyesters of PBS₇₃G₉LA₁₈ and PBS₅₄G₄₀LA₆ exhibit double crystallization peaks while the other copolyesters between them show an additional tiny crystallization peak besides of the major crystallization peak. The phenomenon is different from the crystallization behaviors of pristine PBS and PBSLA copolyesters. The tiny crystallization peak may originate from the crystallization of PEG segments. With respect to the composition of the copolyesters, it is discerned that the EO content increases with the increase of PEG feed molar ratio. Therefore, the tiny crystallization peak should shift to higher temperatures. However, the peak is observed to shift to lower temperatures with the increase of EO content. As reported by Inoue and coworkers,^{38,39} the PBS and PEG were compatible in the molecular level, and the PEG showed a crystallization peak of much lower temperature as the PEG content is less than 40% in the PBS/PEG blends. They ascribed the phenomenon to the confined crystallization. Therefore, in the PBSGLA copolyesters, the EO units may be confined in the lamellae of PBS crystals, resulting in the decrease of the crystallization temperature of tiny peak. This will be further discussed in the WAXD analysis.

In Figure 2(b), the melting temperatures of the copolyesters also depend on the molar ratio of EO content, and the copolyesters crystallize at higher crystallization temperatures lead to the formation of more perfect crystals which eventually melt at higher temperatures. The corresponding ΔH_c and ΔH_m values are also significantly influenced by the EO content due to the change of sequence length of

BS units. The degree of crystallinity of copolyesters could be calculated by the following equation:

$$X_{c-DSC} = \frac{\Delta H_m}{\Delta H_m^0} \quad (7)$$

where ΔH_m^0 is the theoretical value of the melting enthalpy of 100% crystallized PBS homopolymer, calculated on the basis of the group contribution method,⁴⁰ and the value was determined to be 110.5 J/g. It is noticed that the values increase as the EO content increases, which is the similar as those of the melting enthalpy.

Crystal structure and morphology of copolyesters

It is observed from DSC cooling curves that all the copolyesters are able to crystallize under certain cooling rate. Therefore, it is also important to determine the crystal structure of the copolyesters to illustrate the relationship between chemical composition and the crystallization behavior of the copolyesters. In this study, the crystalline structure of the copolyesters with different contents of EO segments was studied by WAXD and shown in Figure 3. As

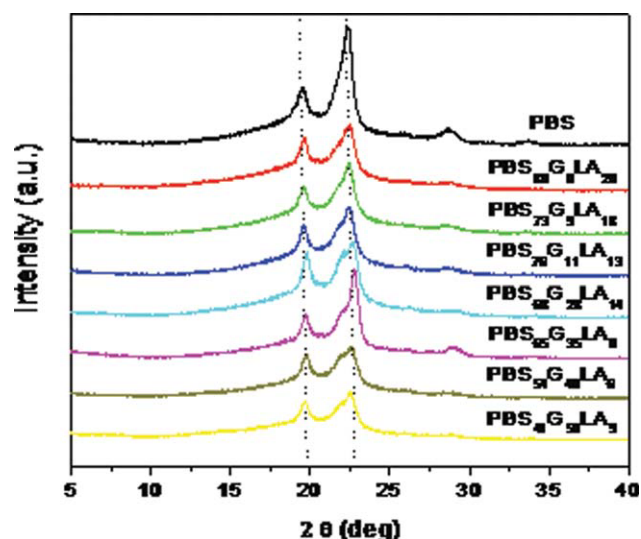


Figure 3 WAXD spectra of the copolyesters. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

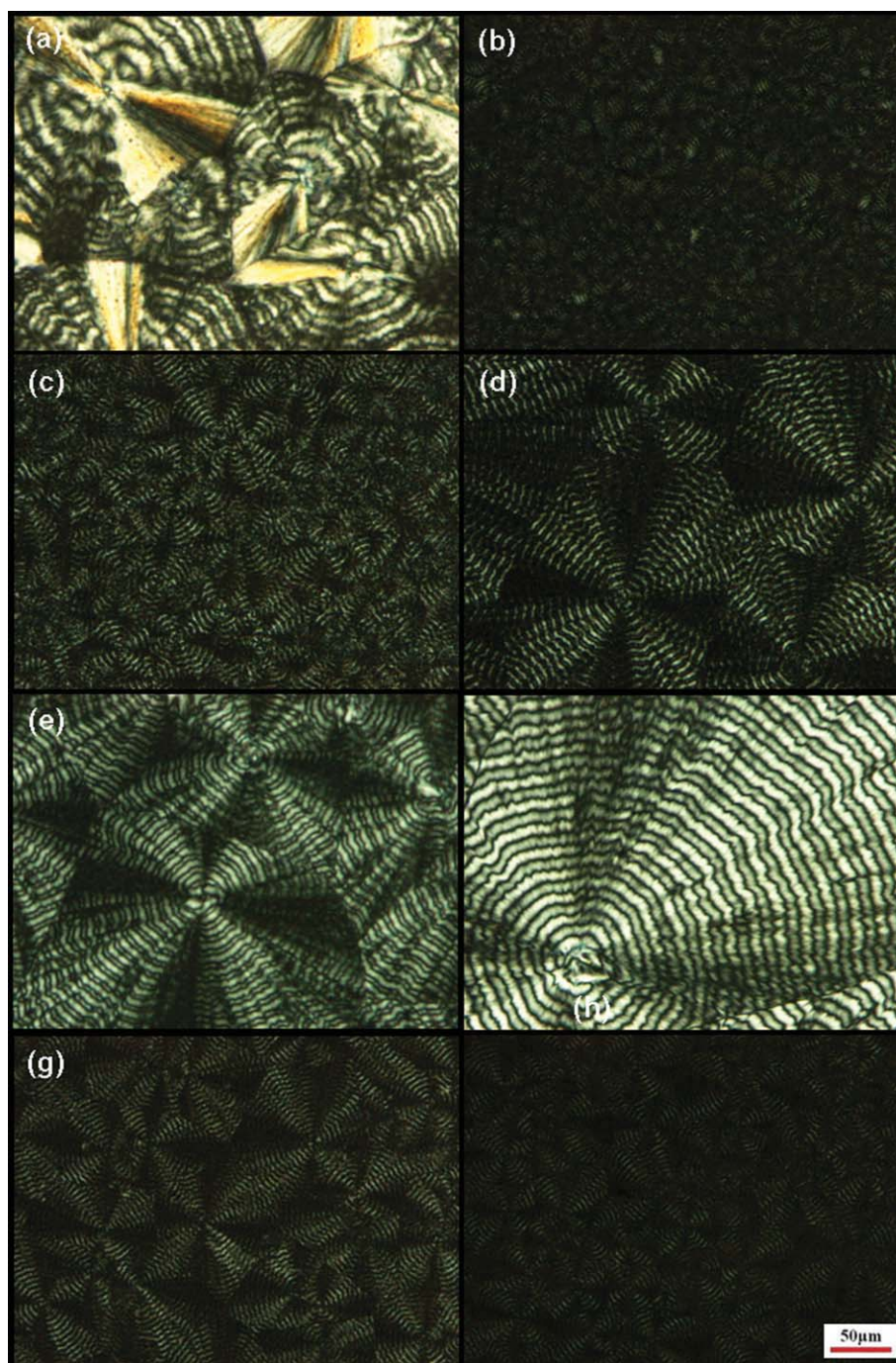


Figure 4 POM graphs for copolyesters of (a) PBS crystallized at 80°C, (b) $\text{PBS}_{80}\text{G}_0\text{LA}_{20}$ crystallized at 30°C, (c) $\text{PBS}_{73}\text{G}_9\text{LA}_{18}$ crystallized at 45°C, (d) $\text{PBS}_{76}\text{G}_{11}\text{LA}_{13}$ crystallized at 60°C, (e) $\text{PBS}_{68}\text{G}_{28}\text{LA}_4$ crystallized at 75°C, (f) $\text{PBS}_{65}\text{G}_{35}\text{LA}_0$ crystallized at 90°C, (g) $\text{PBS}_{54}\text{G}_{40}\text{LA}_6$ crystallized at 55°C, and (h) $\text{PBS}_{41}\text{G}_{50}\text{LA}_9$ crystallized at 50°C, respectively. The scale is the same for all photos. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

reported,⁴¹ the PBS tended to form the monoclinic crystal lattice. In this study, all the copolyesters exhibit two major reflection peaks at $2\theta = 19.8^\circ$ and 22.7° . When compared with pristine PBS and the $\text{PBS}_{80}\text{G}_0\text{LA}_{20}$ copolyester, the reflection peaks of the other copolyesters show a minus shift. It is suggested that all the copolyesters formed the crystals

similar to pristine PBS. However, after the incorporation of EO units into the copolyesters, the crystal lattice showed a minor change due to the existence of EO units. It is further noticed that the tiny reflection peak at $2\theta = 22.0^\circ$ should be ascribed to PEG crystals. Based on the DSC analysis, the tiny crystallization peak confirmed the crystallization of EO

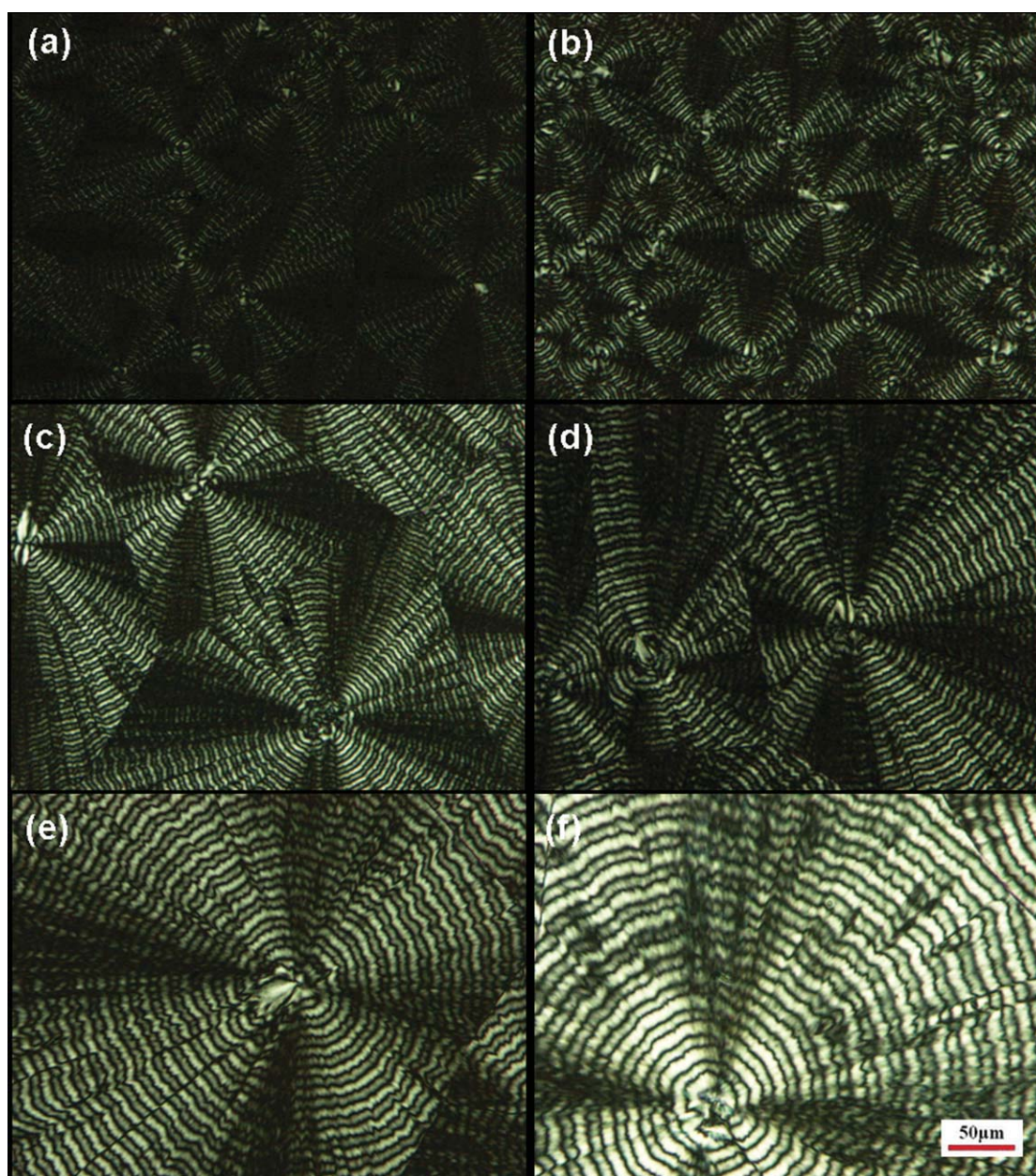


Figure 5 POM photographs showing spherulites for $\text{PBS}_{65}\text{G}_{35}\text{LA}_0$ copolyester at different temperatures: (a) 65, (b) 70, (c) 75, (d) 80, (e) 85, and (f) 90°C. The scale is the same for all photos. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

units. Therefore, both of the WAXD and DSC results indicate the formation of PEG crystals in the PBS crystal lattice. In the PBSGLA copolyesters, both of the BS and EO units are able to crystallize, leading to the formation of PBS and PEG crystals. During the cooling process, the BS units first incorporate into the crystal lattice and form the crystals. Due to the compatibility between PEG and PBS, the EO units might be stay between the lamellae of PBS crystals, facilitating the confined crystallization. In addition, the sequence length of BS units increased as the EO content increasing. The confined crystallization and increase of sequence length of BS units

finally lead to the decrease of crystallization temperature of the tiny peak although the EO content increases. However, the other EO units incorporate into the PBS crystals and affect the crystal parameters of the crystals.

The POM was further used to investigate the morphology of the copolyesters, and the results are illustrated in Figure 4. After crystallizing from melt at different crystallization temperatures, the copolyesters exhibit the different textures. For PBSGLA copolyesters, the apparent Maltese cross spherulites were observed, similar to the results in literature.^{41,42} Besides the normal extinction crosses, the double-banded extinction

TABLE IV
Mechanical Properties of the Copolyesters

Sample	Tensile strength (MPa)	Elongation (%)	Modulus (MPa)
PBS	30.9	10.1	522.3
PBS ₈₀ G ₀ LA ₂₀	11.6	178.4	226.5
PBS ₇₃ G ₉ LA ₁₈	17.3	273.0	290.6
PBS ₇₆ G ₁₁ LA ₁₃	17.4	189.6	316.8
PBS ₆₈ G ₂₈ LA ₄	19.3	182.2	321.0
PBS ₆₅ G ₃₅ LA ₀	25.0	164.0	355.2
PBS ₅₄ G ₄₀ LA ₆	15.5	261.5	246.5
PBS ₄₁ G ₅₀ LA ₉	12.8	489.0	167.5

patterns with periodic distance along the radial direction are also observed. It is found that the copolyesters having relative more content of EO and BS content form the complete spherulites. The LA units seem to interfere with the crystallization of BS units. Figure 5 shows representative POM micrographs of PBS₆₅G₃₅LA₀ copolyester spherulites, nonisothermally grown at different temperatures. The diameter of the spherulites increases with the crystallization temperature increasing. The differences in spherulite morphology may eventually lead to the change of mechanical and degradable properties.

Mechanical properties and hydrophilicity of copolyesters

It is generally accepted that the mechanical properties of the polymers are greatly influenced by many factors, such as the chemical composition, sequential structure, and the degree of crystallinity. To investigate the relationship between the factors mentioned above and the resulting mechanical properties of the copolyesters, the mechanical properties were studied and the corresponding data are listed in Table IV. It is observed that the tensile strength and modulus of the copolyesters are lower than pristine PBS.

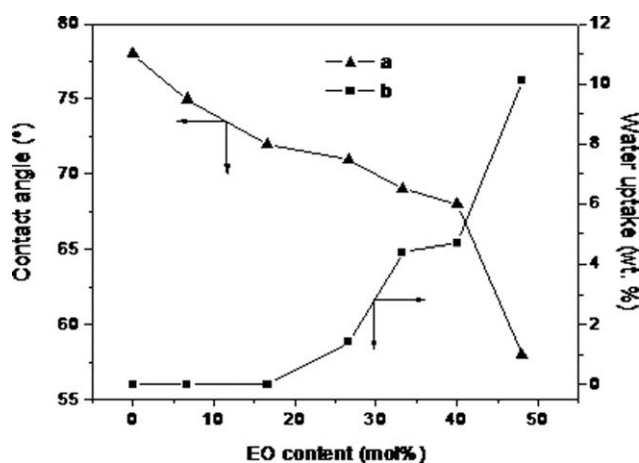


Figure 6 (a) Static water contact angles and (b) water uptake versus the EO content of the copolyester films.

However, the elongation at break of the copolyesters is higher than that of PBS, indicating the higher flexibility of the copolyesters. The increased elongation at break indicates that the toughness of PBS is improved effectively with the addition of flexible LA and EO units, so that the copolyesters can be used as flexible materials in many fields. For PBS₈₀G₀LA₂₀, PBS₇₃G₉LA₁₈, PBS₇₆G₁₁LA₁₃, PBS₆₈G₂₈LA₄, and PBS₆₅G₃₅LA₀, which had similar molar fraction ratios of PBS, the tensile strength as well as tensile modulus increased with the increasing of EO content. However, the tensile elongation at break decreased to about 164% as the feed molar ratio of EO/LA reached to 33.4/0. The increase of the PEG content in the copolyesters, as well as the decrease of the OLA content made copolyesters with longer BS sequence length and increased the crystallinity of the copolyesters, leading to the increase of the tensile strength and tensile modulus. In addition, higher content of PEG and OLA leads to the decrease of tensile strength and modulus, attributable to the decrease of BS sequence length and the composition of the copolyesters.

PBS is a kind of hydrophobic polyesters, but its hydrophilicity increased dramatically with the incorporation of hydrophilic PEG segment into the PBS main chain. As shown in Figure 6, the static water contact angle of the copolyesters decreased as the PEG content increased, indicating that the hydrophilicity of the PBS was improved after the incorporation of EO units. Additionally, the water uptake of the copolyesters increased with the increase of PEG starting feed ratios. These results suggest that

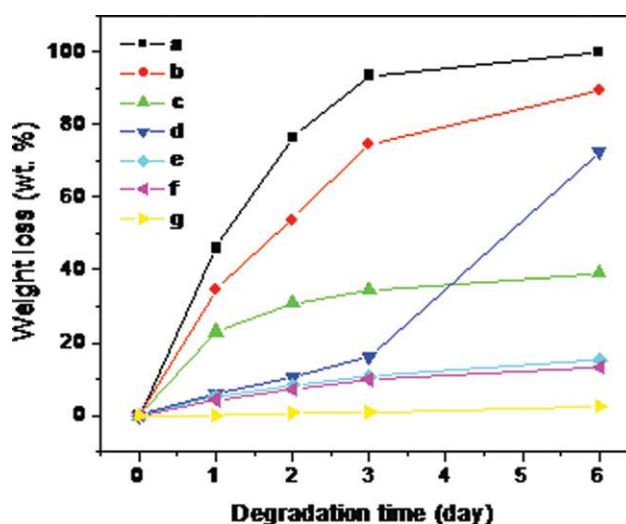


Figure 7 Weight loss versus time during enzymatic degradation for the copolyesters of (a) PBS₈₀G₀LA₂₀, (b) PBS₇₃G₉LA₁₈, (c) PBS₇₆G₁₁LA₁₃, (d) PBS₄₁G₅₀LA₉, (e) PBS₅₄G₄₀LA₆, (f) PBS₆₈G₂₈LA₄, and (g) PBS₆₅G₃₅LA₀, respectively. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

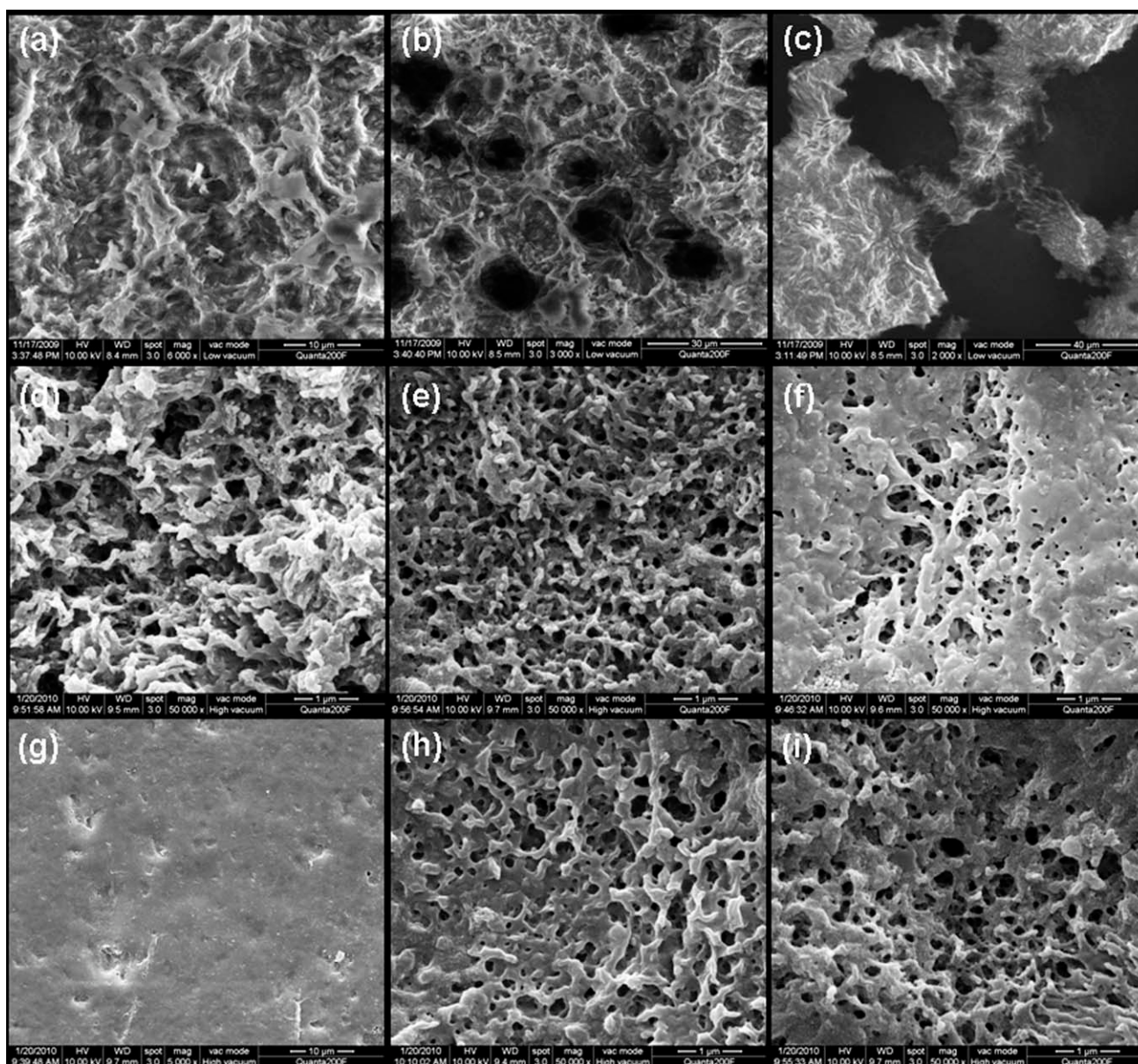


Figure 8 SEM graphs of the copolyester films surface after enzymatic degradation of PBS₈₀G₀LA₂₀ for (a) 1 day, (b) 2 days, (c) 3 days, and (d) PBS₇₃G₉LA₁₈, (e) PBS₇₆G₁₁LA₁₃, (f) PBS₆₈G₂₈LA₄, (g) PBS₆₅G₃₅LA₀, (h) PBS₅₄G₄₀LA₆, and (i) PBS₄₁G₅₀LA₉ for 3 days, respectively.

copolymerization with PEG may modify the hydrophilicity of PBS and extend its practical application.

Enzymatic degradation of copolyesters

To evaluate the biodegradability of the copolyesters in a short time scale, enzymatic degradation was performed. It is well known that the degradation behavior is significantly affected by the polymer micro- and condensed structures such as stereochemistry, hydrophilicity/hydrophobicity balance, flexibility of chains, and the morphology such as crystallinity, size and the number of crystallites and usually initiated from amorphous domains.⁴³ In this

study, enzymatic degradation is expressed as the percentage of weight loss, and the lipase of *P. cepacia* was utilized for analyzing the enzymatic degradation of copolyesters at constant temperature of 37°C.

The weight loss of the PBSGLA copolyesters during enzymatic degradation process is presented in Figure 7. It is clear that the PBSGLA copolyesters show significant weight loss due to the more content of LA units and lower degree of crystallinity. The weight loss increases with increase of the LA content. Figure 8 shows the morphology of the films of PBSGLA copolyesters after enzymatic degradation. It is observed that the film of the PBS₆₅G₃₅LA₀ copolyester without incorporation of LA units shows

no significant change after degradation, although it has enhanced hydrophilicity. The analysis of surface morphology after degradation showed corresponding evidence of weight loss curves on degradation. It is suggested that the relative degree of crystallinity and incorporation content of LA units are the main factors influencing the enzymatic degradation rate of the copolyesters with comparison to hydrophilicity.

CONCLUSIONS

Biodegradable copolyesters based on poly(butylene succinate), PEG, and OLA were successfully synthesized by the transesterification and polycondensation in the melt. The sequence length of butylene succinate (BS) decreased as the OLA feed molar ratio increasing. The incorporation of EO units into the copolyesters eventually led to the decrease of glass transition temperature, while increase the crystallization temperature, melting temperature, crystallization enthalpy, and melting enthalpy. The crystal structure of the copolyesters is similar to that of PBS except for a minor shift in peak positions due to the existence of EO and LA units. The mechanical properties of the copolyesters deteriorate after the incorporation of more content of EO units due to the changes in crystallinity and the length sequence of BS. The water uptake and contact angle of the copolyesters showed an increase and decrease with the content of EO increasing, respectively, due to the improvement in hydrophilicity. The enzymatic degradation of the copolyesters depended on the relative degree of crystallinity and incorporation content of LA units of the copolyesters.

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