

Multiblock copolymers composed of poly(butylene succinate) and poly(1,2-propylene succinate): Effect of molar ratio of diisocyanate to polyester-diols on crosslink densities, thermal properties, mechanical properties and biodegradability

Liuchun Zheng^{a,b}, Chuncheng Li^{a,*}, Dong Zhang^a, Guohu Guan^a, Yaonan Xiao^a, Dujin Wang^a

^a Beijing National Laboratory for Molecular Sciences, Key Laboratory of Engineering Plastics, Institute of Chemistry, Chinese Academy of Sciences (ICCAS), Beijing 100190, PR China

^b Graduate School of Chinese Academy of Sciences, Beijing 100049, PR China

ARTICLE INFO

Article history:

Received 23 February 2010

Received in revised form

4 May 2010

Accepted 16 May 2010

Available online 24 May 2010

Keywords:

Crosslink density

Poly(butylene succinate)

Mechanical properties

Biodegradation

ABSTRACT

In order to study the relationship between structure and properties, multiblock copolymers composed of poly(butylene succinate) (PBS) and poly(1,2-propylene succinate) (PPSu) have been synthesized by chain-extension at various molar ratios of hexamethylene diisocyanate (HDI) to polyester-diols, which have been abbreviated as *R*-values in this paper. Molecular weights of soluble fractions, gel fractions and crosslink densities have been determined. Thermal properties, mechanical properties and biodegradability have been studied and correlated with *R*-values. Crystallization of copolymers becomes difficult with increasing *R*-value. Tensile strength, flexural strength and flexural modulus tend to increase with increasing *R*-value up to 1.2, and vary little when *R*-value increases from 1.2 to 1.3, then decrease with further increase in *R*-value. Impact strength achieves a maximum value at *R*-value of 1.3. Biodegradation rate reaches a minimum value when *R*-value is 1.1. Biodegradation has been studied systematically by attenuated total reflectance Fourier transform infrared (ATR-FTIR), ¹H NMR and SEM.

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1. Introduction

In the past few decades, biodegradable aliphatic polyesters have attracted increasing interest both from material researchers and industrial workers, owing to the increasing environmental concerns about traditional nondegradable plastics. PBS, as one of the most promising aliphatic polyesters, has been widely researched and developed due to its relatively high melting point (*T_m*) and excellent processability. However, its high cost, relatively poor mechanical properties and slow biodegradation rate restrain its extensive application.

It is widely recognized that thermal properties, mechanical properties and biodegradability of polymers strongly depend on their structures, such as molecular weights, chemical structures and chemical compositions. The investigation of Fujimaki et al. [1,2] indicates that although some mechanical properties of PBS and poly(butylene succinate-co-butylene adipate) could be enhanced by increasing molecular weight, biodegradability was deteriorated instead. Therefore, extensive studies on the modification of PBS

have focused on the introduction of comonomers and change of chemical structures by means of copolymerization. Usually, aliphatic comonomers have been incorporated to adjust the biodegradation rate of PBS. As a result, various random copolymers [3–11] have been synthesized, such as poly(butylene succinate-co-butylene adipate) [3–5], poly(butylene succinate-co-ε-caprolactone) [6], poly(butylene succinate-co-L-lactate) [7], poly(butylene succinate-co-ethylene succinate) [8], poly(butylene succinate-co-butylene 2-methyl succinate) [9], etc. The influences of comonomers' chemical structures as well as copolymers' chemical compositions on physical properties, mechanical properties and biodegradability of PBS have been reported. The results showed that the copolymerization with these biodegradable aliphatic units, especially with those have side groups, could improve the degradability effectively by decreasing the crystallinity degree, but simultaneously deteriorated mechanical strengths and reduced *T_m*. Besides, the biodegradability of PBS could be enhanced by the copolymerization with polyether macromonomers [12–15], such as poly(ethylene glycol), poly(propylene glycol), etc. Although *T_m* did not depress markedly, the presence of polyethers arose another problem that was their long-term instability under environmental conditions since the oxidative reaction of ether bonds could be initiated by thermo-, photo-, or γ-radiation [16,17]. In addition,

* Corresponding author. Tel.: +86 10 6256 0029; fax: +86 10 6255 9373.

E-mail address: lichch@iccas.ac.cn (C. Li).

tensile strength inevitably deteriorated due to the introduction of flexible polyether chains.

It is well-known that aromatic polyesters are inexpensive materials with excellent mechanical properties and good thermal stability. But as they are strongly resistant to hydrolysis, as well as to bacterial and fungal attack, they usually remain unaltered in the environment. Therefore, the incorporation of aromatic polyesters into the backbone of aliphatic PBS has been explored for a long time as an attractive approach to combine the mechanical properties and thermal stability of aromatic polyesters with the biodegradability of PBS [18–25]. As a result, many investigations on the synthesis, characterization and properties of aliphatic-aromatic copolyesters, such as poly(butylene succinate-co-ethylene terephthalate) and poly(butylene succinate-co-butylene terephthalate), have been published. As expected, thermal stability and mechanical properties of PBS could be enhanced by the introduction of aromatic units. Unfortunately, the degradation rate of PBS was evidently decreased [20,21].

In our previous work, multiblock copolymers comprising of PBS and PPSu were synthesized by chain-extension reaction with HDI as a chain extender. Amorphous PPSu segment was incorporated to improve the impact resistance, reduce the production cost and extend the application of PBS [26]. The copolymers displayed extraordinary impact resistance with impact strength achieving 19 folds of PBS while retaining its tensile strength and T_m [26]. Concerning the good properties of the copolymers, it is necessary to investigate the relationship between structure and properties.

R -value is a key parameter for chain-extension reactions with diisocyanates as chain extenders. Wang et al. studied the influence of R -value on molecular weight of multiblock copolymers containing PBS and poly(L-lactic acid), when R -value was in the narrow range of 0.9–1.1, and found that maximum molecular weight was obtained when R -value was 1.0 [27]. However, no more detailed information on the influence of R -value on structure and properties, especially biodegradability, of chain-extended polymer, has been reported so far. R -value influences the mechanical properties greatly [28] as it determines the molecular weight of the resulting polymer. More importantly, when R -value is higher than 1.0, excess $-NCO$ groups on HDI will react with urethane groups to form some allophanate crosslinking points, which also affect mechanical properties remarkably [29–31]. Simultaneously, biodegradability, another main property of biodegradable polymers, is also greatly affected by R -value as it is known that the biodegradability strongly depends on molecular weight and crosslink density. In order to clarify the cause of the excellent mechanical properties, especially the high-impact strength, and the structure–property relationship, multiblock copolymers at R -values ranging from 0.9 to 1.4 were synthesized. Mechanical properties and thermal properties were investigated and related with R -values. Biodegradability, which is necessary and prerequisite for the application of biodegradable materials, was also studied in detail and associated with R -value in this article. ATR-FTIR, 1H NMR and SEM were conducted to follow the structural and surface changes during the biodegradation process. To the best of our knowledge, it is the first time to investigate the influence of R -values on the biodegradation. It is expected that this study will provide useful clues to design and develop novel copolymers by means of chain-extension with diisocyanates.

2. Experimental

2.1. Materials

HDI was kindly provided by Shandong Qingdao Xinyutian Chemical Corp.. The lipase from *Pseudomonas cepacia* (activity: 46.2 unit/mg) used for enzymatic degradation was purchased from

Sigma. All the other reagents and solvents were purchased from Beijing Chemical Reagents Corp. and used without purification.

2.2. Synthesis of the polyester-diols and multiblock copolymers

The synthesis and determination of the molecular weights for the polyester-diols, i.e., PPSu-diol and PBS-diol, were previously reported [26]. PPSu-diol is actually PPSu25 in our previous paper; the characteristics of PPSu-diol are completely the same as that of PPSu25 in the reference [26]. While the hydroxyl value, acid value and number-average molecular weight of PBS-diol are 22.58 mg KOH/g, 2.08 mg KOH/g and 4057, respectively.

The procedure to synthesize the copolymers has also been reported [26]. Briefly, the copolymers were synthesized from the chain-extension reaction between $-OH$ on bifunctional macromonomers of polyester-diols (PBS-diol and PPSu-diol) and $-NCO$ on HDI, also a bifunctional compound. The reaction between these bifunctional compounds led to the formation of a polymer with high molecular weight. Since many PBS and PPSu segments have been incorporated into a polymer chain, multiblock copolymer is resulted. Predetermined amounts of HDI were added to synthesize multiblock copolymers at different R -values. $R_{1.3}$, representing the copolymer at R -value of 1.3, is used as an example to interpret the nomenclature of multiblock copolymers. When R -values are less than or equal to 1.0, the main structure of copolymers is linear, as shown in Scheme 1(a); when R -values are above 1.0, there also exists the allophanate branching or crosslinking structure, as indicated in Scheme 1(b).

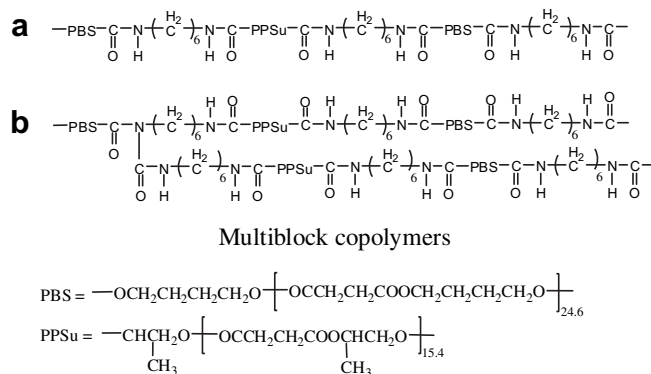
2.3. Measurements

The gel fractions of multiblock copolymers were determined by extraction with chloroform in a Soxhlet extraction apparatus until the weight of insoluble polymers did not change. Then the insoluble parts were dried at 60 °C for 12 h under vacuum. The gel fraction was calculated by the following equation:

$$\text{Gel fraction (wt\%)} = \frac{W_g}{W_0} \times 100 \quad (1)$$

where W_0 and W_g were the weights of the initial polymer and dried insoluble part of sample, respectively.

Since the allophanate groups can be selectively cleaved by aliphatic amine, crosslink densities of multiblock copolymers were determined by titration the concentration of allophanate crosslinking sites, according to the following procedures [32]: copolymer sample (3 g) was solved in butylamine ($BuNH_2$)/ $CHCl_3$ solution (1×10^{-5} mol/g), and refluxed at 40 °C for 24 h; then the



Scheme 1. Chemical structures of multiblock copolymers: (a) $R_{0.9}$ and $R_{1.0}$; (b) $R_{1.1}$, $R_{1.2}$, $R_{1.3}$ and $R_{1.4}$.

unreacted BuNH₂ was backed-titrated with HCl/ethanol solution (0.01 mol/L) with bromophenol blue as an indicator.

The molecular weight and molecular weight distribution (PDI) were determined by gel permeation chromatography (Waters 410 GPC) equipped with two Waters Styragel columns (HT6E and HT3) and a differential-refractometer detector. The measurements were taken at 25 °C, using polystyrene as standard. Chloroform was used as the eluent at a flowing rate of 1.0 mL/min.

The basic thermal parameters were determined on a Pyris Diamond DSC (Perkin–Elmer instrument) equipped with a CryoFill liquid nitrogen cooling system under N₂ atmosphere. Samples were heated to 190 °C and maintained there for 5 min to eliminate thermal histories, and then quenched to –100 °C at a rate of 200 °C/min using liquid nitrogen as a cooling agency and held there for 5 min. After that, the samples were reheated to 190 °C at 20 °C/min and held there for 5 min before they were cooled to –100 °C at the same rate. Both cooling and heating scans were recorded for analysis.

The spherulitic morphologies of polymer films with a thickness of 20 µm after being isothermally crystallized at 75 °C were examined with polarized optical microscopy (POM, Olympus Bx 51, Japan).

The impact strength was measured with an impact testing machine (CBI-137C, USA) according to ASTM D 256-97. Tensile and flexural testing was conducted on a universal tester (Instron 1122, UK) according to ASTM D 638-97 and ASTM D 790-97, respectively.

2.4. Enzymatic degradation

Film samples of polymers (10 × 10 × 0.1 mm in size) were immersed in small conical flasks containing phosphate buffer solution (pH 6.86) that were kept in a controlled incubator at 45 °C. The media was exchanged every 24 h. The concentration of enzyme in the solution was 20 unit/mL and the enzymatic concentration for the polymer was 5 unit/mg. The media was refreshed every 24 h. Each specimen was taken out at predetermined degradation time intervals, washed with double distilled water, dried at 45 °C in vacuum for 3 h and weighed. The weight loss (%) was calculated from $[100(W_0 - W_t)]/W_0$, where W_0 was the initial sample weight and W_t was the weight of dried residual specimen after degradation. Three paralleled experiments were performed for each degradation test, and then the average value was reported.

ATR-FTIR spectra of film samples at different degradation time intervals were performed using a Thermo Nicolet Avatar 6700 FT-IR equipped with an attenuated total reflectance device (Smart Orbit). The sample was scanned 32 times with a resolution of 4 cm^{–1} from 400 to 4000 cm^{–1} at room temperature.

¹H NMR spectra for the samples at different degradation time intervals were acquired with Bruker DMX-400 NMR spectrometer at room temperature using tetramethylsilane and CDCl₃ as internal standard and solvent, respectively.

The change in the surface morphology upon degradation was evaluated by SEM (JEOL JSM-6700). Prior to the analysis, the surfaces of the films were sputter-coated with platinum for 60 s.

3. Results and discussion

3.1. Gel fractions and crosslink densities of multiblock copolymers

As previously mentioned, when *R*-value is greater than 1.0, excess –NCO groups will react with urethane groups, resulting in allophanate crosslinked three-dimensional structure. The effects of *R*-value on crosslink density and gel fraction of multiblock copolymers are shown in Fig. 1. As the crosslinked network restricts the chain mobility and determines the gel fraction, the trend of gel fraction with *R*-value is similar to that of crosslink density. Both gel

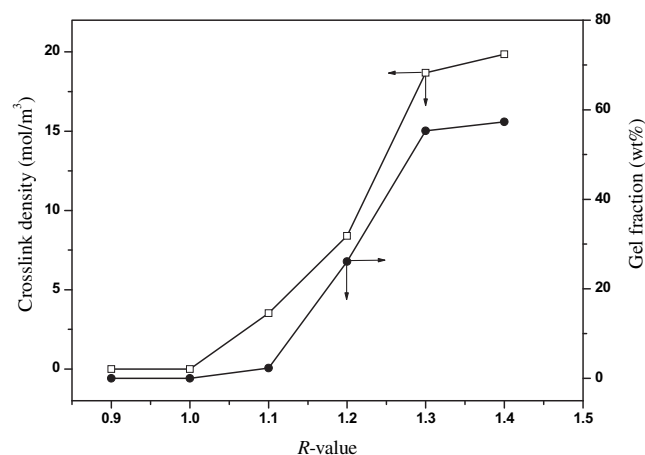


Fig. 1. Crosslink density and gel fraction of multiblock copolymers as a function of *R*-value.

fractions and crosslink densities are zero when *R*-values are 0.9 and 1.0. In the case of R1.1, although its crosslink density is evident, its gel fraction is very low (about 1.3 wt%). It can be explained as that the apparent but still relatively low crosslink density can just form a slightly crosslinked or branched structure, which is not compact enough to accommodate the solvent but causes a surprisingly high molecular weight (in Table 1). Both crosslink density and gel fraction increase steeply with *R*-value when *R*-value is between 1.1 and 1.3, and achieve a plateau level at higher *R*-values. Similar behavior has been reported by Sekkar et al. for the polyurethanes based on hydroxyl terminated polybutadiene and toluene diisocyanate [30,33,34]. The plateau level of crosslink density and gel fraction can be interpreted in the light of gelation process occurring during the chain-extension reaction at *R*-value higher than 1.3, which inhibits the diffusion of reactive groups. Consequently, many –NCO groups remain unreacted [30]. Simultaneously, the unreacted –NCO groups terminate the macromolecular chain and cause a decreased molecular weight (in Table 1). Since crosslink density is one of the most important parameters for the crosslinked network, the trend of crosslink density with *R*-value is expected to get reflected in the mechanical properties.

3.2. Thermal properties of multiblock copolymers

The correlation between *R*-value and thermal properties is studied by DSC. For this purpose, both the amorphous region and crystalline region are considered. For the amorphous region, the glass transition temperature (*T_g*) being the key feature of the amorphous phase is discussed; whereas in the case of the crystalline region, *T_m*, crystallization temperature (*T_c*) and corresponding enthalpy are considered.

Unexpectedly, as shown in Fig. 2 and Table 2, *T_g* varies little with *R*-value. It is generally regarded that crosslinks restrict

Table 1
Molecular weight of soluble fraction for multiblock copolymers.

Sample	<i>M_n</i> ^a (×10 ⁵)	<i>M_w</i> (×10 ⁵)	PDI
R0.9	0.517	1.42	2.75
R1.0	0.548	2.67	4.87
R1.1	75.6	131	1.73
R1.2	2.05	12.2	5.95
R1.3	0.234	0.789	3.37
R1.4	0.356	0.590	1.66

^a Abbreviation of number-average molecular weight.

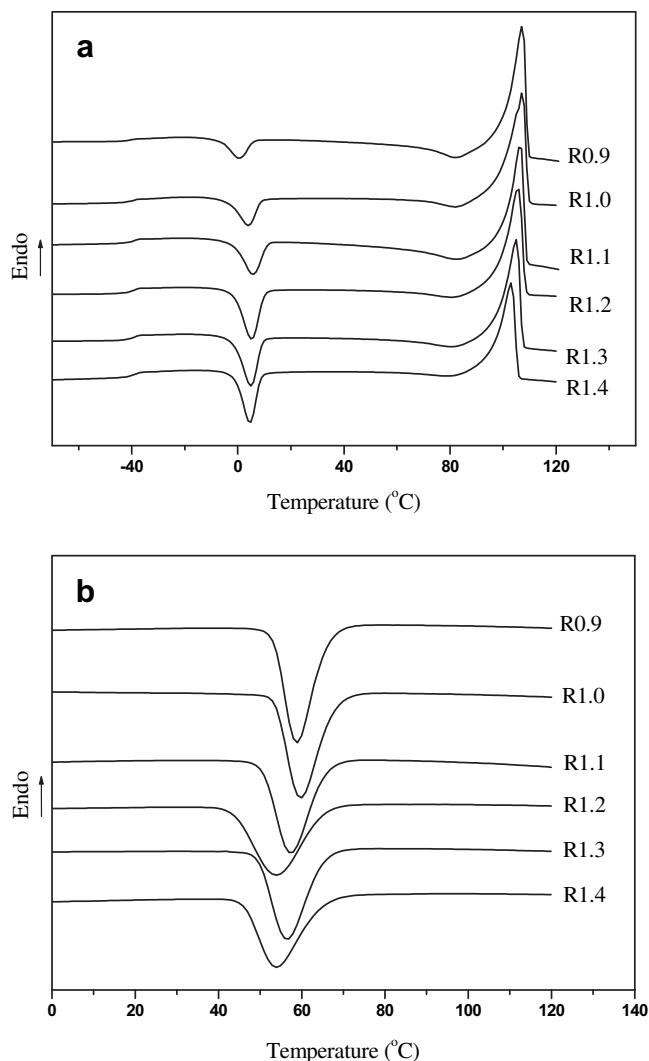


Fig. 2. DSC curves of multiblock copolymers: (a) heating scans and (b) cooling scans at a scanning rate of 20 °C/min.

mobility of macromolecular chains and thus increase T_g . However, crosslinks also reduce the crystallinity degree (X_c) (in Table 2) and increase the free volume [35], which would increase the segmental mobility in the amorphous domain. As the influence of the former on the segmental mobility may be exactly offset by that of the latter, T_g keeps almost unchanged. Similar results were reported by Sekkar et al. on the dihydroxytelechelic polybutadiene based urethanes [34].

As far as the crystalline region is concerned, it can be found from Table 2 that T_c , T_m , enthalpy of fusion (ΔH_m), enthalpy of crystallization (ΔH_c) and X_c show a decreasing trend with the increase of R -value. Generally, T_m is associated with crystal size or perfectness;

while ΔH_m , ΔH_c and X_c , which have considerable influence on material mechanical properties, are related with the amount of crystals. When R -values are less than or equals to 1.1, the decrease of T_m , ΔH_m , ΔH_c and X_c with the increase of R -value can be attributed to the increment in the weight-average molecular weight (M_w) [36,37]. For copolymers at higher R -values, the decrement in T_m , ΔH_m , ΔH_c and X_c with the increase of R -value arises from the increased crosslink density [35,38]. Crosslinking points play the role of defect centers, restrict the mobility of polymer chains through crosslinking junctions and impede the chain folding for the crystallization [35]. Consequently, perfectness or size of crystals decreases with the increase of crosslink density, which can be evidenced by the POM micrographs of polymers in Fig. 3. As imperfect or small crystals require less energy for melting, T_m reduces with increasing R -value. Concomitantly, the amount of crystals decreases, causing reduced ΔH_m , ΔH_c and X_c . Additionally, as clearly shown in Fig. 2(b), R1.2 displays a evidently wider crystallization peak as compared with other samples, suggesting a wider crystallite size distribution. It is originated from its much higher PDI (in Table 1). The wide PDI of copolymers is closely associated with the fast chain-extension by HDI [27]. The chain branching by allophanate groups further widens the PDI [28].

3.3. Mechanical properties of multiblock copolymers

Mechanical properties of multiblock copolymers have been summarized in Table 3. As shown in Table 3, tensile strength, flexural strength and flexural modulus tend to increase with increasing R -value up to 1.2, change little when R -value increases from 1.2 to 1.3, and then decrease with further increase of R -value. Impact strength achieves a maximum value of 569 J/m at R -value of 1.3, which is remarkably 558% when compared to R1.0. Simultaneously, there is noticeably 50% increase in tensile strength, 25% increase in flexural strength and 35% increase in flexural modulus as compared with R1.0. Thus, it can be concluded that feeding excess HDI appropriately is an effective and feasible approach to improve the mechanical properties and change of R -value can allow production of copolymers with a range of mechanical properties depending on the material being engineered.

In general, mechanical properties strongly depend on chemical crosslinks, which are allophanate crosslinks in the present system, and physical crosslinks, which are dominated by the X_c and molecular weight. And chemical crosslinks are usually considered to be stronger than physical crosslinks. When R -value increases from 0.9 to 1.0, the improvement in mechanical properties is attributed to the increased M_w as indicated in Table 1. When R -value is between 1.0 and 1.3, the variation of mechanical properties with R -value is associated with the change of crosslink density (Fig. 1) and X_c . The increased crosslink density with the increase of R -value is favorable to the formation of a homogenous network, which enables the polymer to distribute and absorb the stress evenly [30,39,40]. Thus, the material could absorb more stress and energy before failure and becomes both rigid and tough. Simultaneously, as shown in Table 2, an increase in crosslink density accompanies with a reduction in X_c , which deteriorates the mechanical strengths but enhances the toughness. When R -value is between 1.0 and 1.2, all the mechanical properties increase with increasing R -value since the apparently increased crosslink density plays a dominant role. Similar results have been reported elsewhere [41]. While tensile strength, flexural strength and flexural modulus vary little when R -value increases from 1.2 to 1.3, resulting from the fact that the influence of crosslink density happens to equal to that of X_c . On the other hand, since both the increase in crosslink density and reduction in X_c favor the improvement of toughness, the impact strength of R1.3 is much higher than that of R1.2. However, further

Table 2
Thermal properties of multiblock copolymers.

Sample	T_g (°C)	T_c (°C)	T_m (°C)	$-\Delta H_c$ (J/g)	ΔH_m (J/g)	X_c (%)
R0.9	-40.4	59.0	107.3	56.7	68.8	62.5
R1.0	-40.0	59.7	107.2	55.7	65.2	59.3
R1.1	-39.7	57.5	106.6	54.6	62.1	56.5
R1.2	-39.9	57.0	105.6	54.3	59.5	54.1
R1.3	-39.4	56.6	104.9	50.7	58.5	53.2
R1.4	-39.3	53.9	102.9	47.7	51.7	47.0

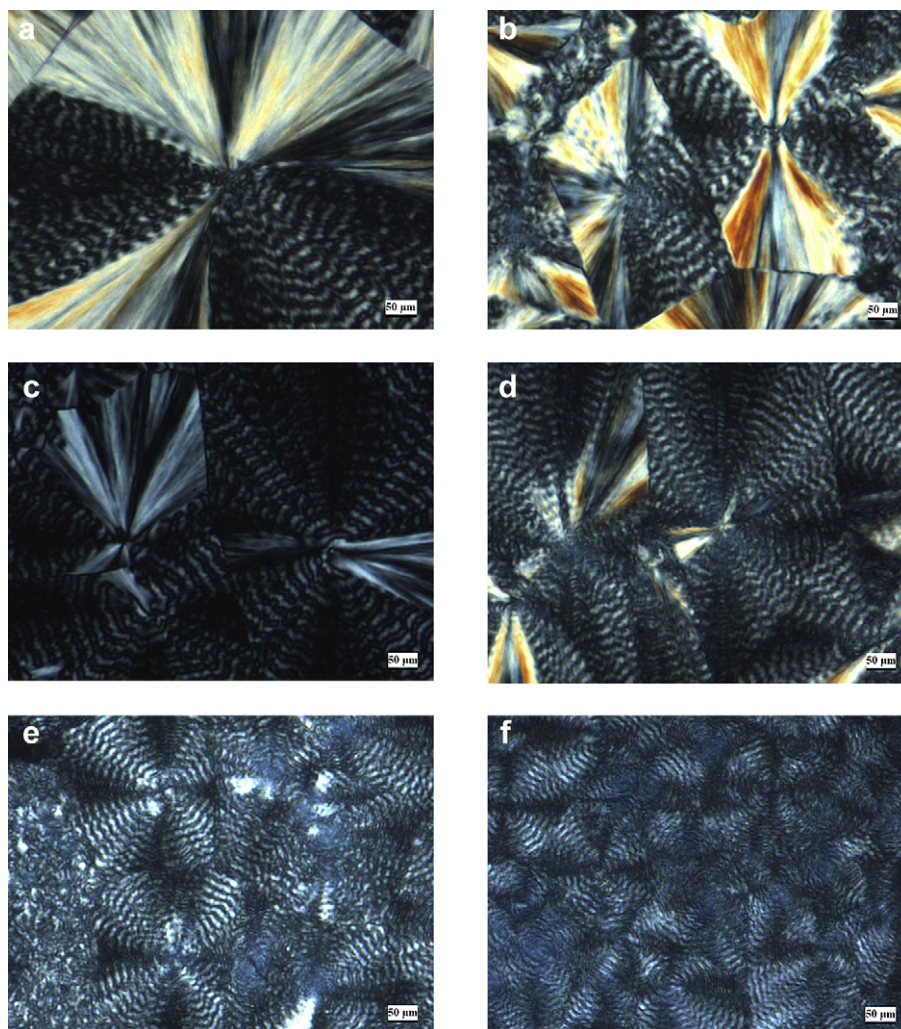


Fig. 3. POM micrographs of multiblock copolymers after being isothermally crystallized at 75 °C: (a) R0.9; (b) R1.0; (c) R1.1; (d) R1.2; (e) R1.3; and (f) R1.4.

increase in R -value decreases all the mechanical properties instead, arising from the diminished X_c . The slightly increased crosslink density of R1.4 is inadequate to compensate the loss in mechanical properties caused by the reduced X_c .

3.4. Enzymatic degradation of multiblock copolymers

The biodegradability, another very important property for biodegradable materials, is also correlated with R -value in this study. It is well-known that biodegradability of aliphatic polyesters decreases with increasing X_c or M_w and usually initiates from the

amorphous domain. As far as the multiblock copolymers are concerned, the biodegradability is also affected by the crosslink densities which depend on R -value. As shown in Fig. 4, substantial weight loss can be observed for all the investigated samples after degradation for 13 days. Besides, the degradation rate is considerably influenced by R -value and achieves a minimum value when R -value is 1.1. This signifies that the biodegradability of copolymers can be regulated according to the need. When R -value is between 0.9 and 1.1, the crosslink density is small and considered to be a less significant factor for biodegradability. While X_c decreases monotonely with increasing R -value, which would speed up the degradation. However, at the mean time, M_w of soluble fraction increases prominently with increasing R -value up to 1.1, which retards the biodegradation (Fig. 4). The reduced degradation rate with increasing R -value when R -value is between 0.9 and 1.1 suggests that the influence of M_w of soluble fraction on the enzymatic degradation is stronger than that of X_c . When R -value is greater than 1.1, degradation rate increases dramatically with increase in R -value. M_w of soluble fraction and X_c decrease with the increase of R -value as R -value is bigger than 1.1, both of which would accelerate the biodegradation. However, the crosslink density increases steeply with increasing R -value. In general, the crosslink structure deteriorates the biodegradability as it restricts the mobility of polymer chains. Nevertheless, in this system, the crosslink density

Table 3
Mechanical properties of multiblock copolymers.

Sample	Tensile strength (MPa)	Elongation at break (%)	Flexural strength (MPa)	Flexural modulus (MPa)	Impact strength (J/m)
R0.9	25.3 ± 2.3	204 ± 23	28.2 ± 1.4	359 ± 7.2	38.0 ± 3.2
R1.0	30.2 ± 3.8	86.0 ± 17	27.1 ± 2.1	352 ± 23	102 ± 8.3
R1.1	39.0 ± 2.1	120 ± 13	30.0 ± 1.6	391 ± 21	220 ± 9.1
R1.2	47.6 ± 1.2	92.0 ± 10	33.8 ± 1.3	472 ± 8.1	340 ± 13
R1.3	47.5 ± 2.1	100 ± 9.1	34.0 ± 1.1	476 ± 13	569 ± 16
R1.4	37.4 ± 1.5	165 ± 7.2	30.0 ± 2.7	391 ± 16	240 ± 16

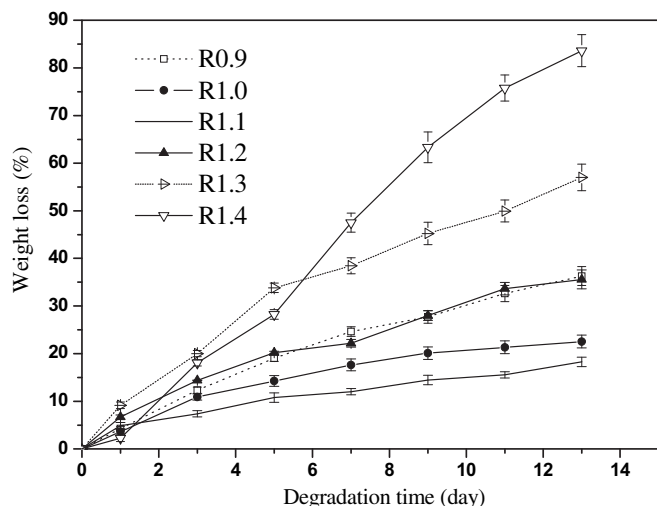


Fig. 4. Weight loss for multiblock copolymers as a function of time during the degradation process with a lipase from *Pseudomonas cepacia* at 45 °C and pH 6.86.

is not considered to be a key factor for degradation since the increase of crosslink density by increasing R -value decreases the M_w and X_c , which play dominant roles in the degradation. In addition, as the weight loss of R1.4 is above 80%, which is higher than the sol content, it can be undoubtedly concluded that the chemical crosslink bonds have been destroyed to some extent during the degradation process. Similar result has been reported by Dong et al. for dicumyl peroxide crosslinked poly[(3-hydroxybutyrate)-co-(3-hydroxyvalerate)] [42] and carbon/poly(glycerol-sebacate-citrate) elastomer composite [43].

ATR-FTIR spectra were employed to characterize the structural change of multiblock copolymers during the degradation process. As shown in Fig. 5 and Table 4, though no evident shifts can be observed for transmittance peak positions, intensity ratio of the characteristic peak of C=O at 1712 cm^{-1} to that of C–C at 1153 cm^{-1} decreases gradually along with the process of degradation. It's known that ester bonds are weak points in the copolymers and contribute to the biodegradation. Therefore, the content of ester groups decreases regularly with the progress of degradation.

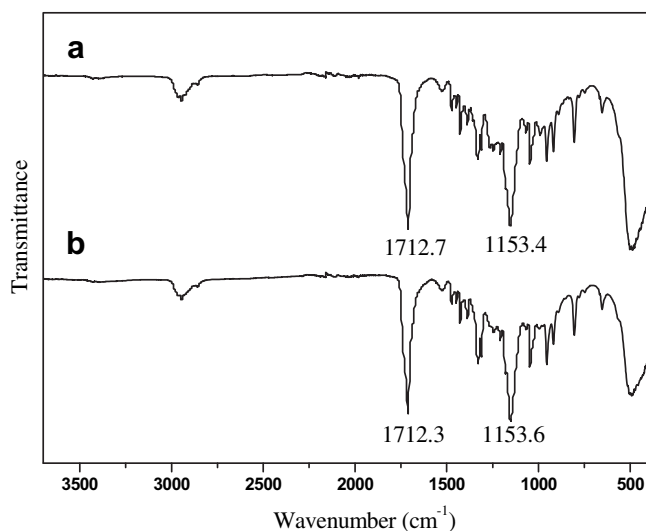


Fig. 5. ATR-FTIR spectra of R1.2 during the degradation process: (a) at day 0 and (b) at day 13.

Table 4

Intensity ratio of peak₁₇₁₂ to that of peak₁₁₅₃ and composition of copolymers at different degradation time.

Sample	Day	Intensity ratio	PPSu (wt%)	PBS (wt%)	HDI (wt%)
R0.9	0	1.58	8.03	88.0	3.97
	5	1.51	7.04	88.7	4.26
	9	1.47	6.52	88.9	4.58
	13	1.32	6.02	89.0	4.98
R1.0	0	1.60	7.88	88.0	4.12
	13	1.46	6.32	89.2	4.48
R1.1	0	1.62	8.64	86.6	4.76
	5	1.56	7.17	87.7	5.13
	9	1.53	7.01	87.8	5.19
	13	1.52	6.62	87.9	5.48
R1.2	0	1.63	8.65	86.4	4.95
	13	1.35	8.43	86.0	5.57
R1.3	0	1.61	8.35	86.2	5.45
	13	1.26	7.39	86.7	5.91
R1.4	0	1.64	7.95	86.6	5.45
	3	1.59	7.77	86.3	5.93
	5	1.47	7.58	86.4	6.02
	9	1.34	7.16	86.5	6.34
	13	1.32	6.83	85.8	7.37

^1H NMR spectra were also used to follow the structural variation during the process of degradation. No obvious change can be found in the ^1H NMR spectra (Fig. 6) upon degradation. However, there is some difference in the composition with the increase of degradation time. Weight composition of the polymers has been calculated based on the integral areas from ^1H NMR spectrum according to the following equations:

$$\text{PPSu}(\%) = \frac{158 \times A_{\delta=5.13}}{172 \times (A_{\delta=4.16}/4) + 158 \times A_{\delta=5.13} + 170 \times (A_{\delta=3.14}/4)} \quad (2)$$

$$\text{PBS}(\%) = \frac{172 \times (A_{\delta=4.16}/4)}{172 \times (A_{\delta=4.16}/4) + 158 \times A_{\delta=5.13} + 170 \times (A_{\delta=3.14}/4)} \quad (3)$$

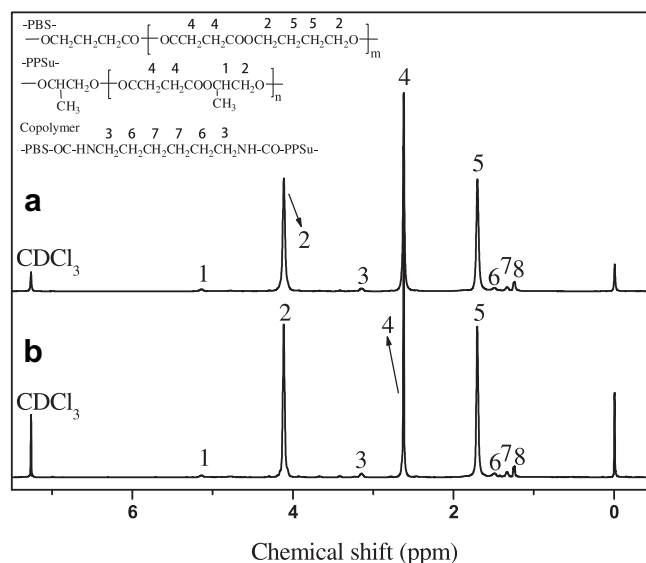


Fig. 6. 400 MHz ^1H NMR spectra of R0.9 during the degradation process: (a) at day 0 and (b) at day 13.

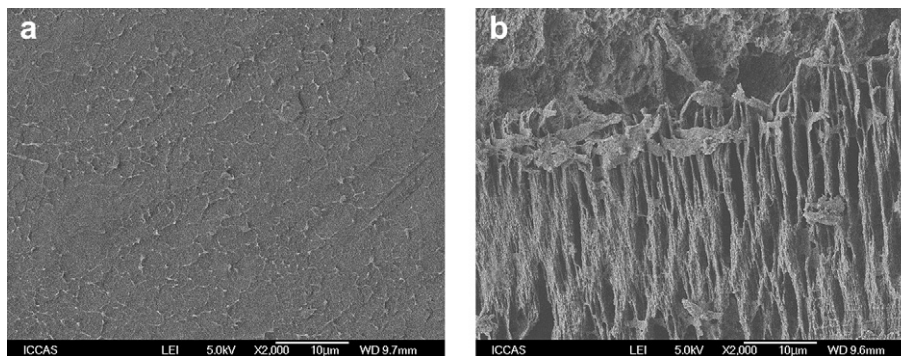


Fig. 7. SEM micrographs of R1.2 during the degradation process: (a) at day 0 and (b) at day 13.

$$\text{HDI}(\%) = \frac{170 \times (A_{\delta=3.14}/4)}{172 \times (A_{\delta=4.16}/4) + 158 \times A_{\delta=5.13} + 170 \times (A_{\delta=3.14}/4)} \quad (4)$$

where $A_{\delta=5.13}$, $A_{\delta=4.16}$ and $A_{\delta=3.14}$ designate the integral areas of methine proton of PPSu unit, methylene protons of butanediol residue in PBS unit, and methylene protons of HDI residue, respectively. 158, 172 and 170 are the molecular weights of repeating units of PPSu, PBS and HDI residue, respectively. As shown in Table 4, PPSu content in the composition decreases gradually, while content of HDI residue increases with the progress of degradation. It can be concluded that PPSu unit degrades faster than PBS unit, arising from the preferential degradation of the amorphous domain; while HDI residue that contains urethane groups degrades more slowly, due to the lack of susceptible ester bonds.

The SEM micrographs of R1.2 before degradation and after degradation for 13 days are given in Fig. 7 as representatives. Before degradation, the film exhibits a relatively smooth surface. After enzymatic hydrolysis, the film shows a rather coarse surface with many holes, suggesting that the surface has been attacked by the lipase, which would cause further hydrolysis.

4. Conclusions

Multiblock copolymers at various R -values have been synthesized to study the structure–property relationship. Gel fraction and crosslink density of multiblock copolymers increase sharply with the increase of R -value when R -value is between 1.1 and 1.3 and then reach a plateau level. M_w of soluble fraction increases with increasing R -value and achieves a maximum value when R -value is 1.1, then decreases with further increase in R -value. Crystallization of copolymers becomes difficult at higher R -value. Correlation between mechanical properties as well as biodegradability and R -value has also been established. Tensile strength, flexural strength and flexural modulus tend to increase with increasing R -value up to 1.2, vary little when R -value increases from 1.2 to 1.3, and then decrease with further increase in R -value. Impact strength achieves a maximum value of 569 J/m at R -value of 1.3, which is remarkably 558% when compared to R1.0. The crosslink density, molecular weight of soluble fraction and crystallinity degree are regarded as three main factors determining the mechanical properties of copolymers. Certain crosslink density can enhance the mechanical properties because it favors the formation of a homogeneous network and thus enables polymers to distribute and absorb the stress evenly. Biodegradation rate first decreases with the increase of R -value up to 1.1, achieves a minimum value when R -value is 1.1, then increases with further increase of R -value. Molecular weight of soluble fraction and crystallinity degree are considered to be key factors for biodegradability, while crosslink

density is regarded to be a less important factor. The large weight loss of R1.4 suggests that the gel can be degraded by the enzymes. Structural changes during the enzymatic degradation process were investigated by ATR-FTIR and ^1H NMR. The data of ATR-FTIR spectra confirms that ester bonds are weak points in the polymers and contribute to the degradation. The results of ^1H NMR spectra indicate that PPSu segment degrades faster than PBS segment, while urethane unit degrades slowest among the three.

Acknowledgements

Financially support from National High Technology Research and Development Program of China (Grant No. 2009AA033601) is gratefully acknowledged.

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