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A novel biodegradable multiblock poly(ester urethane) containing poly(L-lactic acid) and poly(butylene succinate) blocks

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A B S T R A C T

A novel biodegradable multiblock poly(ester urethane) (PEU), consisting of poly(L-lactic acid) (PLLA) and poly(butylene succinate) (PBS) blocks, has been successfully synthesized via chain-extension reaction of dihydroxyl terminated PLLA (PLLA-OH) and PBS prepolymers (PBS-OH) using toluene-2,4-diisocyanate (TDI) as a chain extender. The chemical structures and molecular weights of PEUs, containing different block lengths and weight fractions of PLLA and PBS, were characterized by ^{1}H NMR and GPC. The effects of the structures on the physical properties of PEUs were systematically studied by means of DSC, TGA, WAXD and tensile testing. The DSC results indicated that PLLA segment was compatible well with PBS segment in amorphous phase and the crystallization of PEU was predominantly caused by PBS segment, which was also confirmed by WAXD. The results of tensile testing showed that the extensibility of PLLA was largely improved by incorporating PBS segment. The PEU can be used as a potential substitute for some petroleum-based thermoplastics.

1. Introduction

In the past few decades, biodegradable polymers, especially aliphatic polyesters and their copolymers, have drawn growing attentions from both academic researchers and industrial workers due to their potential applications in both biomedical materials [1–3] and general environmentally friendly materials [4,5].

Poly(lactic acid) (PLA), as a member of aliphatic polyester family, can be synthesized via either polycondensation [6,7] of lactic acid or ring-opening polymerization [8] of cyclic lactide. The early studies of PLA mainly focus on its biomedical applications such as drug delivery [9,10], suture [11,12], and tissue engineering [13,14] due to the excellent biodegradability, biocompatibility and high tensile strength. Recently, with the increased pollution and growing costs of traditional polymeric materials, PLA has attracted increasing attention in replacement of traditional petroleum-based materials. However, disadvantages of brittleness, poor thermal stability and high costs limit its applications in general plastics.

It is well known that high-molecular-weight is the prerequisite for PLA that meets the demand of mechanical properties required in practical application. However, high-molecular-weight PLA is usually synthesized via a lengthy route of ring-opening polymerization of lactide, which makes the PLA less competitive in the market. In order to reduce its cost, many approaches, such as melt/solid state polymerization [15], solution polymerization [16], and chain-extension reaction [17], have been utilized to prepare relatively higher molecular weight of PLA. Nevertheless, these methods could not improve its toughness. Thus many methods have recently been explored to toughen PLA, such as blending or copolymerizing with flexible polymers, among which a helpful option is to introduce flexible components to the backbone of PLA to form copolymers.

A common approach to confer toughness of PLA is using flexible monomer or macromolecule to copolymerize with lactide to synthesize PLA-based random or block copolymers. For random copolymer, it is difficult to form crystalline due to irregular chain structure so that the strength is usually unsatisfied. The currently reported PLA-based block copolymers include diblock, triblock and multiblock copolymers. For diblock [18] and triblock [19] copolymers, they are commonly known as amphiphilic polymers and mainly applied in drug delivery system, where the high-molecular-weight and mechanical properties are not necessary. In the case of multiblock copolymers, for examples, multiblock copolymers PLLA–PCL [20], PEG–PLLA [21], PTMC–PLLA [22], and so on, high-molecular-weights could be achieved. They usually

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have good mechanical properties but designed for biomedical applications. Their applications will be more extensive if their costs come down.

An economical and effective way to endow PLA with toughness is chain-extension reaction of PLA prepolymer with a flexible prepolymer in the presence of chain extender. A typical example of this method is the formation of a poly(ester urethane) (PEU). PEUs with different structures usually have various properties and can be used as versatile materials from elastomers [23] to thermoplastics [24]. Many flexible molecules, such as poly(ethylene glycol) [25], poly(ethylene oxide) [26], poly(ε-caprolactone) [23,27], etc., can be used as the flexible components.

In this study, poly(butylene succinate) was used as the flexible segment. High-molecular-weight of PBS, as one of the commercially available aliphatic polyesters, has been widely researched and developed as green materials due to its biodegradability, good thermal stability, and excellent mechanical properties. Some researches [28,29] based on blends of PLA and PBS have been reported in recent years. Harada et al. [30] investigated the blends of PLA with PBS using isocyanate as a reactive processing agent and the results indicated that the blends have better impact strength and tensile strain than those of pure PLA. A triblock copolymer PLLA-*b*-PBS-*b*-PLLA [31], with the potential application in biomaterials, was synthesized through ring-opening polymerization of L-lactide using bifunctional hydroxyl capped PBS as a macroinitiator. To our best knowledge, there is no report on such a multiblock copolymer containing PLA and PBS up to now.

In this paper, we reported a convenient synthetic route for a new and inexpensive multiblock poly(ester urethane) consisting of PLA and PBS blocks, and characterized it with ^{1}H NMR, GPC, DSC, TGA and WAXD. Furthermore, we investigated the tensile properties and deformation recovery properties of PEU.

2. Experimental section

2.1. Materials

Succinic acid (AR grade) and 1,4-butanediol (AR grade) were purchased from Kelong Chemical Corporation (Chengdu, China) and were used without further purification. L-Lactic acid (LA) with 85 wt% aqueous solution was bought from Guangshui Chemical Plant (Guangshui, China), and the free water was removed by reduced pressure distillation at 80 °C for 3 h. Tetrabutyl titanate bought from Kelong Chemical Corporation was dissolved in anhydrous toluene to prepare 0.2 g/mL solution. Dihydrate tin(II) chloride ($SnCl_2 \cdot 2H_2O$) (AR grade) obtained from Jinshan Chemical Plant (Chengdu, China) and toluene-2,4-diisocyanate (TDI) (AR grade) gained from Bodi Chemical Plant (Tianjin, China) were used without further purification. All other chemicals with AR grades were used as received.

2.2. Preparation of poly(L-lactic acid) diol (PLLA-OH)

PLLA-OH was prepared by condensation polymerization of lactic acid and 1,4-butanediol with similar procedures proposed by Hiltunen et al. [32] 2 mol L-lactic acid and predetermined amount of 1,4-butanediol were charged in a 500 mL three-necked round-bottomed flask, and $SnCl_2 \cdot 2H_2O$ with 0.5 wt% amount of reactants was added in. Firstly, the temperature of the reaction mixture was steadily increased up to 160 °C in 2 h and kept for 5 h in vacuum of about 4000 Pa. Then the temperature was increased to 180 °C, while the vacuum was reduced to 150 Pa. The reaction was maintained for another 5 h. At last, the resulting product was purified by dissolving in chloroform and then precipitating in excessive methanol. The white powder product was dried to constant weight in vacuum oven at 40 °C.

2.3. Synthesis of poly(butylene succinate) diol (PBS-OH)

1.2 mol 1,4-butanediol and 1 mol succinic acid were added into a 500 mL three-necked round-bottomed flask equipped with water separator, mechanical stirrer, and nitrogen inlet pipe. The mixture was stirred for 4 h at 190 °C, then a suitable amount of catalyst tetrabutyl titanate was introduced into the flask, and then the polycondensation was carried out at 220 °C with vacuum of 30 Pa for predetermined time. The resulting product was purified using the same procedures as PLLA-OH.

2.4. Chain-extension reaction

The chain-extension reaction was performed in bulk using a glass reactor under nitrogen atmosphere. PLLA-OH and PBS-OH were put into the reactor which was vacuumed and purged with nitrogen for three times. Then the reactor was immersed in a 160 °C silicone oil bath. The reactants were stirred with a mechanical stirrer after which they were completely molten, then predetermined amount of toluene-2,4-diisocyanate was injected into the reactor. The chain-extension reaction was finished in 1 h. The resulting polymer was also purified to remove any potential insoluble product using the same procedures as PLLA-OH.

2.5. Nuclear magnetic resonance (NMR) spectroscopy

NMR spectra for the synthesized PLLA-OH, PBS-OH, and PEU were recorded with a Varian Inova 400 spectrometer and performed at ambient temperature with 5% (w/v) polymer solution in $CDCl_3$, and tetramethylsilane was used as the internal reference. The number–average molecular weights of PLLA-OH and PBS-OH were calculated from the NMR analysis.

2.6. Intrinsic viscosity

The intrinsic viscosities of PLLA-OH, PBS-OH, and PEUs were measured with an Ubbelohde viscometer at a concentration of 0.1% w/v in chloroform at 25 °C. The intrinsic viscosity values of polymers were determined by Solomon–Ciuta equation ($[\eta] = \sqrt{2(\eta_{sp} - \ln\ \eta_r)}\Big/C$).

2.7. Gel permeation chromatography (GPC)

The relative molecular weights and their distributions of prepolymers and PEUs were measured by GPC, using a Waters instrument equipped with a model 1515 pump, a Waters model 717 autosampler, and a 2414 refractive index detector. Chloroform was used as the eluant at a flowing rate of 1.0 mL/min, and a sample concentration of 2.5 mg/mL was used.

2.8. Differential scanning calorimetry (DSC)

DSC analysis was implemented on a TA Instrument DSC-Q100. Samples were quickly heated to 160 °C and maintained for 5 min to eliminate thermal history, then cooled to −50 °C at a rate of 10 °C/min, and finally were reheated to 160 °C at the same rate. Both cooling and heating scans were recorded for analysis.

2.9. Thermal stability

Thermogravimetric analysis (TGA) was used to determine the thermal stabilities of PLLA-OH, PBS-OH, and PEU. The thermograms were recorded from room temperature to 500 °C at a heating rate of 10 °C/min under N_2 atmosphere on a TA Instruments TGA-Q500. The isothermal stability of PEU was carried out to monitor the variation of intrinsic viscosity with time at the temperature above its melting temperature, from which the degradation of PEU at processing conditions could be simulated. The samples were put into an isothermal oven at 120 °C, and taken out for intrinsic viscosity testing for a given interval time.

2.10. *Wide-angle X-ray diffraction (WAXD)*

Wide-angle X-ray diffraction patterns of PLLA-OH, PBS-OH, and PEUs were recorded with an X-ray diffractometer (Philips X'Pert X-ray diffractometer) with Cu Kα radiation. The equipment was operated at room temperature with a scan rate of 2°/min scanning from 10° to 40°.

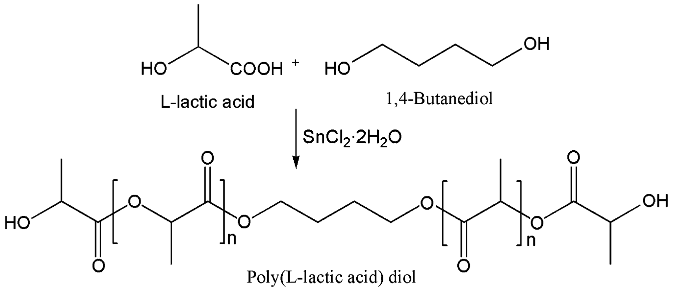
2.11. *Tensile testing*

Tensile strength and elongation at break of PEUs were measured on an Instron Universal Testing Machine (Model 4302, Instron Engineering Corporation, Canton, MA) at crosshead speed of 50 mm/min at room temperature. The samples were hot molded and shaped with a dumbbell-shaped cutter. The thickness and width of the specimens were 0.3 mm and 5 mm, respectively. The length of the sample between the two pneumatic grips of Testing Machine was 20 mm. Six measurements were conducted for each sample, and the results were averaged to obtain a mean value. Moreover, the tensile deformation recovery properties of the PEUs were investigated. The dumbbell sample was stretched to a predetermined strain at a speed of 20 mm/min at room temperature, and then the imposed strength was unloaded. The residual strain after 24 h was measured to calculate the deformation recovery rate. Five predetermined strains 20, 40, 60, 80, and 100% were utilized in our testing.

3. Results and discussion

3.1. *Synthesis and characterization of PLLA-OH and PBS-OH*

PLLA-OH was synthesized by direct polycondensation of L-lactic acid in the presence of 1,4-butanediol, using $SnCl_2 \cdot 2H_2O$ as a catalyst (Scheme 1). The chemical structure and number–average molecular weights of PLLA-OH were characterized by ^1H NMR spectra (PLLA1, Fig. 1A). The signals occurring at 1.68 (δH^d) and 4.11 (δH^c) ppm could be reasonably assigned to the inner and outer methylene protons of $-OCH_2CH_2CH_2CH_2O-$, respectively. The peaks of methyl proton and methine proton at the terminus of PLLA-OH molecular chain were observed at 1.48 ($\delta H^{b'}$) and 4.36 ($\delta H^{a'}$) ppm, while the signals of those protons in the repeating units of PLLA-OH were found at 1.58 (δH^b) and 5.18 (δH^a) ppm, respectively. The intensity of the methine proton could be used to calculate the polymerization degree (D_p) and the number–average molecular weight ($M_{n,PLLA-OH}$) of PLLA-OH according to the following equations:



Scheme 1. The synthesis process of poly(L-lactic acid) diol.

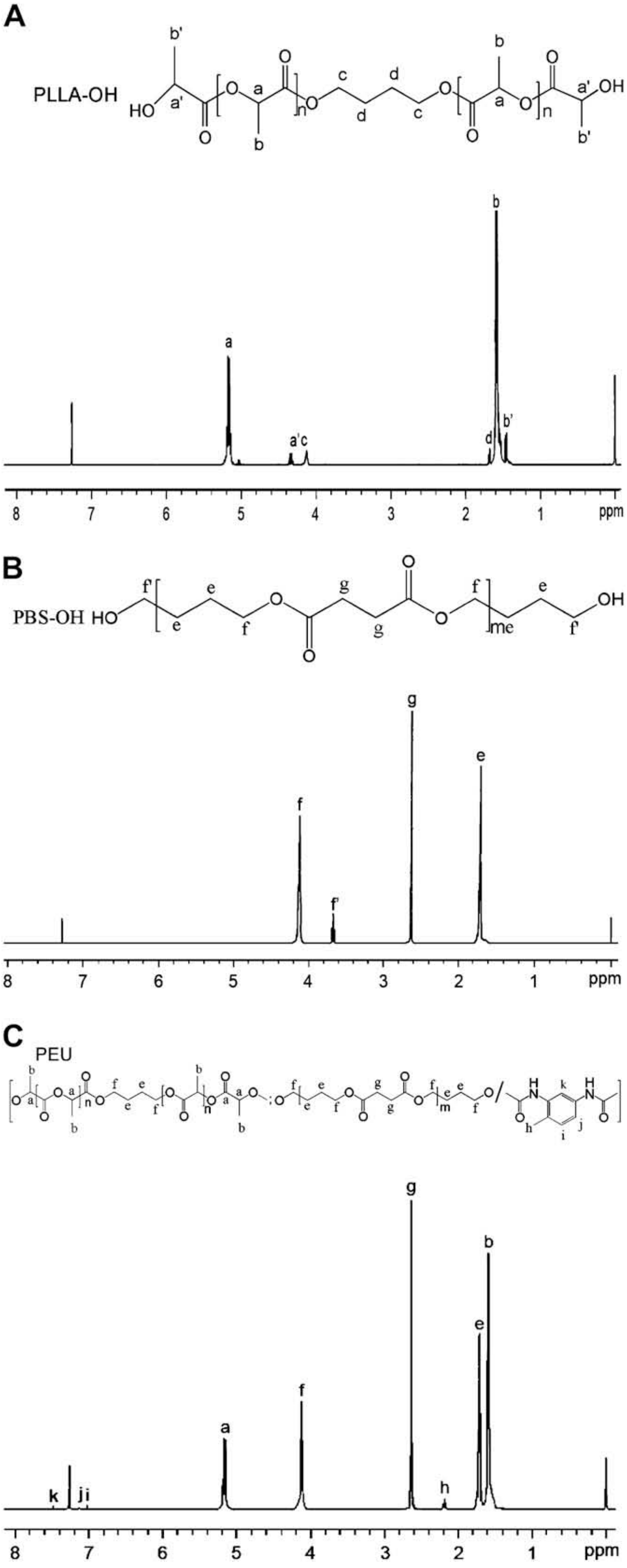


Fig. 1. ^1H NMR spectra of PLLA-OH, PBS-OH and PEU.

$$D_p = 2 \times \frac{I_{5.18} + I_{4.36}}{I_{4.36}} \quad (1)$$

$$M_{n,PLLA\text{-}OH} = 72 \times D_p + 88 + 2 \quad (2)$$

where $I_{5.18}$ and $I_{4.36}$ represent, respectively, the intensities of methine groups located in the internal and end of PLLA-OH molecular chain. 72 and 2 are the masses of repeating unit of PLLA and hydrogens at the ends of PLLA-OH molecular chain, respectively, and 88 is the mass of residue of 1,4-butanediol. The basic data for the synthesis of PLLA-OH are presented in Table 1. It was found that the $M_{n,NMR}$ was always less than theoretical value ($M_{n,Theo}$) among all the different ratios of L-lactic acid to 1,4-butanediol, which was caused by the inevitable loss of L-lactic acid during the condensation polymerization. The $M_{n,Theo}$ is calculated by the equation:

$$M_{n,Theo} = \frac{n_{LA}}{n_{BD}} \times 72 + 88 + 2 \quad (3)$$

where n_{LA}/n_{BD} is the feed molar ratio of L-lactic acid to 1,4-butanediol, 72, 88, and 2 have the same meanings as those in equation (2). In addition, the molecular weights and distribution of PLLA-OH were also determined by GPC and the results are listed in Table 1. It can be seen that the number–average molecular weight obtained by GPC ($M_{n,GPC}$) was much higher than the corresponding value calculated by NMR and the value of polydispersity increased with the increase of feed molar ratio of L-lactic acid to 1,4-butanediol.

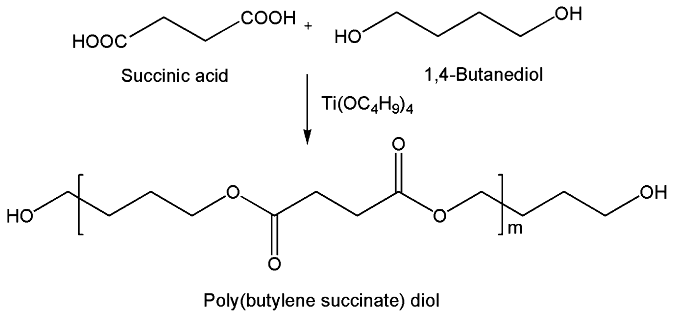
PBS-OH was prepared by condensation polymerization of 1,4-butanediol with succinic acid by two steps including esterification and successive polycondensation. Tetrabutyl titanate was used as a catalyst (Scheme 2). In order to obtain dihydroxyl terminated PBS, the feed molar ratio of 1,4-butanediol to succinic acid was fixed at 1.2:1 [31]. The molecular weight of PBS-OH was controlled by the polycondensation time. The chemical composition of PBS-OH was determined by ^{1}H NMR (PBS1, Fig. 1B). The peaks occurring at 1.67 (δH^e), 2.65 (δH^g), and 4.10 (δH^f) ppm with a same integral area are reasonably assigned to three different types of methylene protons in the repeating units of PBS.

The peak presented at 3.65 ($\delta H^{f'}$) ppm could be attributed to the methylene group linked with the terminal hydroxyl group of PBS molecular chain. The degree of polymerization and number–average molecular weight of PBS-OH can be calculated according to the intensity of methylene groups at 3.65 ($I_{3.65}$) and 4.10 ($I_{4.10}$) ppm by the following equations:

$$D_p = \frac{I_{4.10}}{I_{3.65}} \quad (4)$$

$$M_{n,PBS\text{-}OH} = 172 \times D_p + 90 \quad (5)$$

where 172 is the molecular weight of repeating unit of PBS molecular chain, and 90 is the gross mass of end chains of PBS-OH. The basic synthetic data for PBS-OH are shown in Table 2. PBS-OH was also characterized by GPC and the data are summarized in Table 2. The difference in the value of $M_{n,NMR}$ and $M_{n,GPC}$ was similar with that of PLLA-OH, and the molecular weight distribution of PBS-OH also showed a wider value with the increase of the molecular weight.



Scheme 2. The synthesis process of poly(butylene succinate) diol.

3.2. *Synthesis of poly(ester urethane)*

PEU was produced through chain-extension reaction of PLLA-OH with PBS-OH using toluene-2,4-diisocyanate (TDI) as a chain extender. The synthesis process is shown in Scheme 3 and the synthetic data of PEUs are listed in Table 3. The chemical structure of PEU was also determined by ^{1}H NMR (Fig. 1C). It was found that all the characteristic peaks belonging to both PLLA and PBS existed in the spectrum of PEU. The peak occurring at 2.20 (δH^h) ppm was reasonably attributed to the methyl protons of TDI residue. The phenyl protons of TDI unit were observed at around 7.02 (δH^i), 7.15 (δH^j), and 7.52 (δH^k) ppm. Moreover, the peaks at 4.36 ($\delta H^{a'}$) and 3.65 ($\delta H^{f'}$) ppm, belonging to PLLA-OH and PBS-OH respectively, completely disappeared in the spectrum of PEU, indicating that all the hydroxyl groups from the prepolymers were reacted completely; and proving that the methods we used to calculate the molecular weights of prepolymers were effective.

The peak intensities could be used to calculate the mass ratios of different ingredients and deduce their weight fractions (listed in Table 4) in the resulting PEU according to the following equations:

$$\frac{m_{PLLA}}{m_{PBS}} = \frac{4 \times 72 \times I_{1.58}}{3 \times 172 \times I_{2.65}} \quad (6)$$

$$\frac{m_{PBS}}{m_{TDI}} = \frac{3 \times 172 \times I_{2.65}}{4 \times 176 \times I_{2.20}} \quad (7)$$

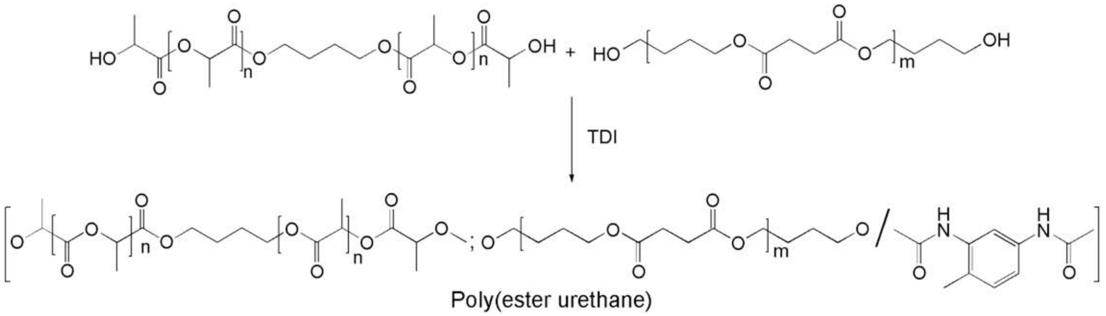
where m_{PLLA}/m_{PBS} represents the mass ratio of PLLA segment to PBS segment and m_{PBS}/m_{TDI} means mass ratio of PBS segment to TDI residue in PEU. $I_{1.58}$, $I_{2.65}$ and $I_{2.20}$ designate the peak intensities of methyl protons in the units of PLLA block, methylene protons of succinic acid residue in units of PBS block, and methyl protons in TDI residue of PEU, respectively. Numerical values 4, 3, 3, and 4 in equations (6) and (7) are the numbers of the corresponding protons occurring at 2.65, 1.58, 2.20, and 2.65, respectively. Numerical values 72, 172, and 176 are the molecular weights of repeating units of PLLA block, PBS block, and the residue of TDI in PEU, respectively.

Table 1
Synthetic data for PLLA-OH.

Sample	LA/BD (mol/mol)	[η] (dL/g)	Yield (%)	$M_{n,NMR}$ (g/mol)	$M_{n,Theo}$ (g/mol)	$M_{n,GPC}$ (g/mol)	$M_{w,GPC}$ (g/mol)	PDI
PLLA1	25:1	0.09	94.7	1800	1890	3400	5200	1.53
PLLA2	50:1	0.12	89.2	3300	3690	5300	8700	1.64
PLLA3	75:1	0.16	83.8	4600	5490	7400	12400	1.68
PLLA4	100:1	0.21	86.2	6300	7290	13800	24100	1.75

Table 2
Synthetic data for PBS-OH.

Sample	Polycondensation time (min)	[η] (dL/g)	$M_{n,NMR}$ (g/mol)	$M_{n,GPC}$ (g/mol)	$M_{w,GPC}$ (g/mol)	PDI
PBS1	15	0.12	2100	6400	8200	1.28
PBS2	30	0.17	3100	8700	13,200	1.52
PBS3	45	0.21	4300	10510	17,200	1.64
PBS4	60	0.28	6000	13700	24,200	1.77



Scheme 3. Synthetic pathway for poly(ester urethane).

The synthetic conditions were optimized from the following three aspects: M_n of prepolymers, molar ratio of NCO to OH, and feed mass ratio of PLLA-OH to PBS-OH. Firstly, the effect of M_n of prepolymers on the chain-extension reaction was studied with fixed feed ratios of PLLA-OH to PBS-OH and [NCO]/[OH]. From the data of PEU1, PEU2, PEU6, and PEU10, we found that the intrinsic viscosity ($[\eta]$) of PEUs increased first and then decreased with the increase of M_n of prepolymers. This was mainly caused by the combination of original $[\eta]$ (Tables 1 and 2) and reactivity of prepolymers. As we know, the reactivity decreases continuously with the increase of M_n of prepolymers. Although the reactants used in the synthesis of PEU1 have lowest intrinsic viscosities thus highest reactivity, the lowest molecular weight of PEU1 was caused by the lowest original $[\eta]$ of prepolymers. In the case of PEU10 with highest M_n of prepolymers, the relatively lower $[\eta]$ was due to the less reactivity of prepolymers. The highest $[\eta]$ of PEU6 among these four trials indicated that prepolymers with medium molecular weights of around 4500 g/mol were the good options to prepare high-molecular-weight PEUs.

Table 3
Synthesis of poly(ester urethane) containing PLLA and PBS blocks.

Run	M_n[a] of prepolymers		PLLA/PBS (g/g)	[NCO]/[OH]	$[\eta]$ (dL/g)
	PLLA	PBS			
PEU1	1800	2100	5:5	1:1	0.85
PEU2	3300	3100	5:5	1:1	1.09
PEU3	4600	4300	9:1	1:1	0.93
PEU4	4600	4300	7:3	1:1	1.04
PEU5	4600	4300	5:5	0.9:1	0.88
PEU6	4600	4300	5:5	1:1	1.17
PEU7	4600	4300	5:5	1.1:1	0.96
PEU8	4600	4300	3:7	1:1	1.54
PEU9	4600	4300	1:9	1:1	1.98
PEU10	6300	6000	5:5	1:1	1.07

[a] Number–average molecular weights were calculated by NMR analysis.

Secondly, the effect of the molar ratio of [NCO] to [OH] was discussed by comparing PEU6 with PEU5 and PEU7. It was clear that the highest $[\eta]$ of polymer (PEU6), like other chain-extension reactions [33,34], was achieved in a balanced stoichiometric formulation [NCO] = [OH], where [OH] = [OH from PLLA-OH] + [OH from PBS-OH]. When [NCO] < [OH], the intrinsic viscosity decreased because of incomplete reaction of hydroxyl groups. Whereas, when [NCO] > [OH], the excessive NCO groups would block chain-extension reaction then lead to reduction of intrinsic viscosity of PEU.

At last, we researched the influence of feed ratio of prepolymers on the chain-extension reaction, and found that it played a very important role in the reaction. The $[\eta]$ of PEU was considerably increased with the increasing mass content of PBS-OH in the feed ratio. The value of $[\eta]$ increased from 0.93 dL/g of PEU3 to 1.98 dL/g of PEU9 as the feed mass ratio of PLLA-OH to PBS-OH changed from 9:1 to 1:9. The reason for the change in $[\eta]$ must be the different reactivity of different kinds of hydroxyls. As we know, OH in PLLA-OH is a secondary hydroxyl group that has lower activity than the primary one in PBS prepolymer when reacting with NCO group. Therefore, the more the amount of PBS-OH in the feed ratio, the more the primary hydroxyl groups existing in the reaction system, thus the higher the chain-extension efficiency.

The molecular weights of PEUs shown in Table 4 were determined by GPC in chloroform at 30 °C with polystyrene as a standard, and the GPC elution traces for the synthesized PEUs and prepolymers PLLA3 and PBS3 are graphically shown in Fig. 2. The GPC traces of PEUs show a single peak, indicating that a complete reaction took place without unreacted prepolymer remaining [35]. From Table 4, it could be found that high-molecular-weight PEUs were successfully achieved, and the variation trend in molecular weights was similar with that of intrinsic viscosity as discussed earlier. In comparison with GPC data of prepolymers, it could be

Table 4
Compositions and molecular weights of resulting PEUs.

Sample	PLLA			PBS			TDI		Molecular weight[c]		
	M_n (g/mol)	f_{PLLA}[a] (%)	F_{PLLA}[b] (%)	M_n (g/mol)	f_{PBS}[a] (%)	F_{PBS}[b] (%)	f_{TDI}[a] (%)	F_{TDI}[b] (%)	$M_n \times 10^{-4}$ (g/mol)	$M_w \times 10^{-4}$ (g/mol)	M_w/M_n
PEU1	1800	45.88	43.17	2100	45.88	48.51	8.24	8.32	7.33	11.4	1.56
PEU2	3300	47.42	46.25	3100	47.42	48.57	5.16	5.18	6.53	14.3	2.19
PEU3	4600	86.70	84.42	4300	9.63	11.97	3.67	3.61	6.00	11.4	1.91
PEU4	4600	67.40	65.68	4300	28.88	30.66	3.72	3.66	6.43	15.3	2.39
PEU6	4600	48.12	47.17	4300	48.12	49.12	3.76	3.71	9.49	18.2	1.92
PEU8	4600	28.85	28.09	4300	67.33	68.14	3.82	3.78	9.73	23.4	2.40
PEU9	4600	9.61	9.32	4300	86.53	86.81	3.86	3.87	13.4	32.6	2.42
PEU10	6300	48.63	47.98	6000	48.63	49.16	2.75	2.86	6.96	11.6	1.66

[a] Weight fraction in the feed ratio.
[b] Weight fraction in PEU determined by NMR calculating.
[c] Molecular weights were measured by GPC with PS standards.

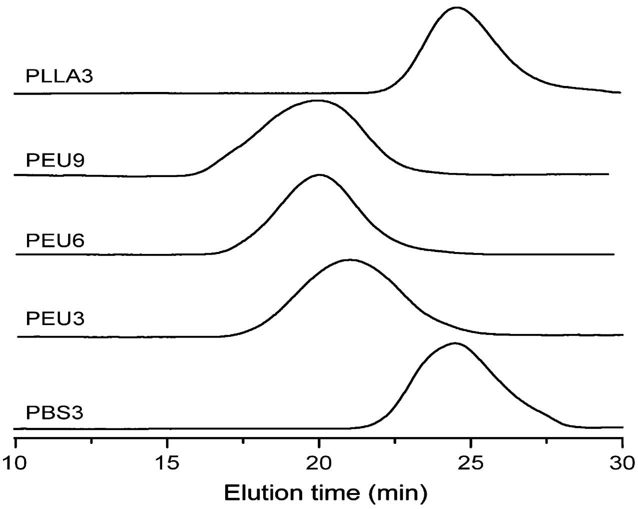


Fig. 2. GPC elution traces for synthesized PEUs as well as prepolymers PLLA3 and PBS3.

found that the molecular weight distribution of PEUs was a little wider than that of their prepolymers. This is easy to understand because the chain-extension reaction was very fast and difficult to control. Table 4 also lists the compositions of PEUs determined by NMR as mentioned above. f_{PLLA}, f_{PBS}, and f_{TDI} in Table 4 designate the weight fraction of the corresponding substance in feed ratio, while F_{PLLA}, F_{PBS}, and F_{TDI} are the corresponding weight fractions in the resulting polymer. From the data, it can be found that F_{TDI} agrees well with f_{TDI}, F_{PLLA} is slightly lower than f_{PLLA}, and F_{PBS} is slightly higher than f_{PBS}. The differences were mainly caused by 1,4-butanediol that was induced to PLLA diol but was neglected during the calculation of PEU composition, for it had same shifts as 1,4-butanediol residue in units of PBS block. The difference between f_{PLLA} and F_{PLLA} was dwindled from PEU1, PEU2, PEU6 to PEU10, which was resulted from the deduction of 1,4-butanediol content in PLLA with the increase of block length. In addition, with the same PLLA block length, the relative mass ratio of 1,4-butanediol to L-lactic acid unit in PLLA block was unchanged in PEU3, PEU4, PEU6, PEU8, and PEU9, but they also showed dwindled difference between f_{PLLA} and F_{PLLA}, which should be caused by the gradual reduction of absolute mass content of 1,4-butanediol unit accompanied by the reduction of weight fraction of PLLA segment in the PEU chains.

3.3. *Thermal behaviors and crystallization of PEUs*

DSC analysis was conducted to characterize the thermal behaviors of PLLA-OH, PBS-OH, and PEUs. The results of DSC studies are presented in Figs. 3 and 4 and Table 5. Fig. 3 shows the DSC thermograms of PEUs with various block lengths. For all the samples, only one glass transition was detected, and no crystallization peak could be observed in the cooling scan (Fig. 3a). In the heating scan (Fig. 3b), all samples exhibited cold crystallization exothermal peaks except PEU1.

It was clear that melting point (T_m), enthalpy of fusion (ΔH_m), and enthalpy of crystalline (ΔH_c) increased, while cold crystalline temperature (T_{cc}) and glass transition temperature (T_g) decreased gradually with the increase of the length of PLLA and PBS blocks. The increase of ΔH_m and ΔH_c was mainly caused by the enhanced crystallinity resulting from increased block lengths and reduced urethane linkage content, and the enhancement in the values of T_m was due to the formation of larger crystallizing chain size with the increase in the length of PBS block. While the decrease of T_g was primarily because the content of urethane linkage decreased with increasing lengths of PLLA and PBS blocks.

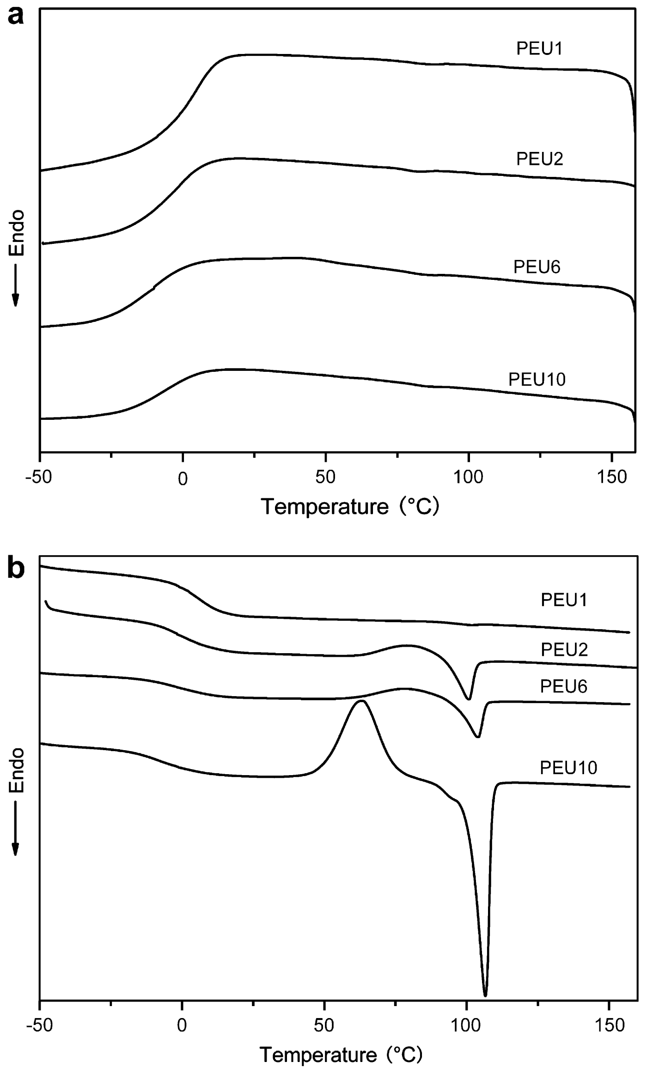


Fig. 3. DSC curves of PEUs with different block lengths: (a) cooling scan; (b) heating scan.

Fig. 4 represents the DSC thermograms of PLLA-OH, PBS-OH, and PEUs with variable compositions. The molecular weights of PLLA and PBS segments were 4600 and 4300 g/mol, respectively. We can see that all the PEUs had only one glass transition regardless of the composition. Furthermore, the value of T_g fell between those of PLLA-OH and PBS-OH and increased with the increase of F_{PLLA} in the PEU. The results indicated that PLLA and PBS segments in PEUs were well compatible in the amorphous phase, which were similar with the results obtained in triblock copolymer PLLA-*b*-PBS-*b*-PLLA [31]. For compatible system of block copolymers, the glass transition temperature value ($T_{g(fox)}$) could be evaluated by the Fox equation: $1/T_{g(fox)} = F_1/T_{g1} + F_2/T_{g2}$, where T_{g1} and T_{g2} are the T_g of individual segments, and F_1 and F_2 are the weight fractions of corresponding components. Here, the values of T_{g1} and T_{g2} were −33.0 and 51.2 °C, respectively. The $T_{g(fox)}$ and $T_{g(exp)}$ (obtained by experiment) versus F_{PLLA} are graphically presented in Fig. 5, where the T_g values of samples with F_{PLLA} at 0% and 100% were the T_g of PBS-OH and PLLA-OH, respectively. It was found that the $T_{g(exp)}$ was close to $T_{g(fox)}$ for all the PEUs, which also confirmed the compatibility between PLLA and PBS segments.

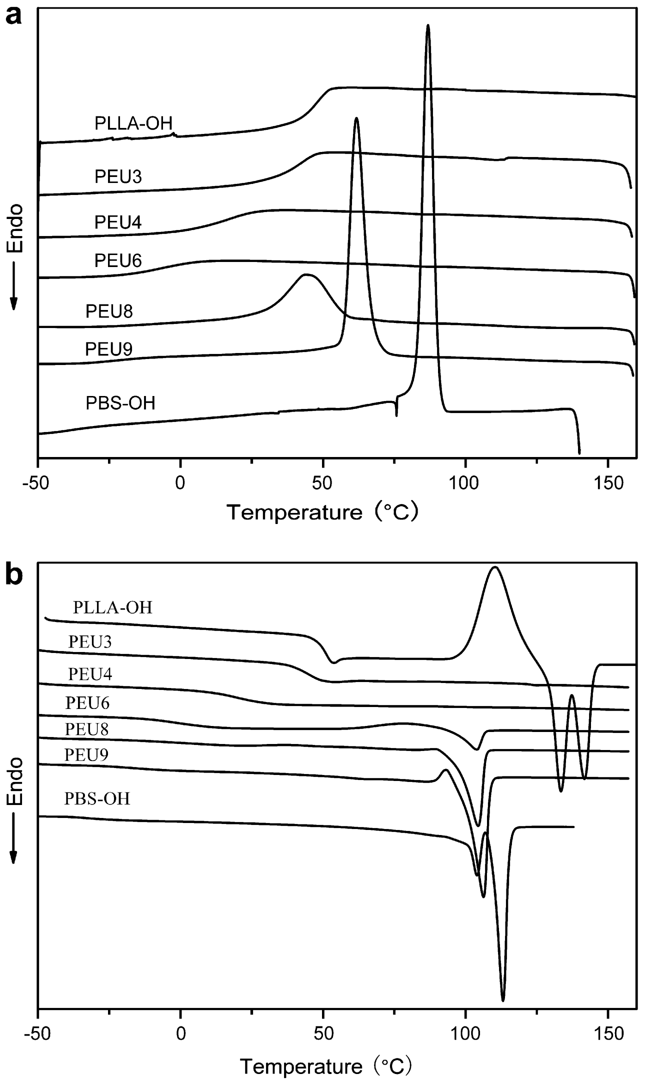


Fig. 4. DSC thermograms of PLLA-OH ($M_n = 4600$), PBS-OH ($M_n = 4300$), and PEUs with variable compositions: (a) represents the cooling scan and (b) expresses the heating scan.

Table 5
Thermal testing data of PLLA-OH ($M_n = 4600$), PBS-OH ($M_n = 4300$), and PEUs.

Sample	T_g (°C)	T_c		ΔH_c		T_m (°C)	ΔH_m (J/g)	T_d (°C)		
		T_{c1}[a] (°C)	T_{c2}[b] (°C)	ΔH_{c1}[c] (J/g)	ΔH_{c2}[d] (J/g)			$T_{0.05}$[e] (°C)	T_{c1}[f] (°C)	T_{c2}[g] (°C)
PLLA-OH	51.2	110.4	[h]	31.9	[h]	141.7	31.3	220.5	256.3	[h]
PBS-OH	−33.0	[h]	86.9	[h]	58.7	113.2	57.3	335.3	[h]	392.7
PEU1	3.1	[h]	[h]	[h]	[h]	[h]	[h]	[i]	[i]	[i]
PEU2	−2.0	78.0	[h]	2.6	[h]	100.6	6.3	[i]	[i]	[i]
PEU3	44.9	[h]	[h]	[h]	[h]	[h]	[h]	224.7	291.5	345.9
PEU4	19.7	[h]	[h]	[h]	[h]	[h]	[h]	235.4	275.5	376.4
PEU6	−2.0	79.6	[h]	8.8	[h]	104.0	7.7	232.9	270.4	396.4
PEU8	−6.4	[h]	44.2	[h]	32.0	104.4	40.5	225.2	274.2	396.5
PEU9	−17.4	[h]	61.8	[h]	54.3	106.3	56.3	270.3	272.3	396.0
PEU10	−8.3	63.6	[h]	36.1	[h]	106.6	35.4	[i]	[i]	[i]

[a] Cold crystalline temperature in the heating scan of DSC curve.
[b] The crystalline temperature in cooling scan of DSC curve.
[c] The enthalpy of crystallization in heating scan.
[d] The enthalpy of crystallization in cooling scan.
[e] Decomposition temperature of polymers at weight loss of 5%.
[f] The maximum decomposing temperature of the first stage (PLLA segment).
[g] The maximum decomposing temperature of the second stage (PBS segment).
[h] Not detected.
[i] No test.

For PEU6, PEU8, and PEU9, in which F_{PBS} was larger than F_{PLLA} and gradually increased from 49.12% to 86.86%, one melting peak was observed in the heating scan (Fig. 4a). T_m and ΔH_m of the polymers increased in going from PEU6 to PEU9 and became closer to those of PBS-OH. While in the cases of PEU3 and PEU4, in which PLLA segments were the dominant component, no melting peak was observed. For T_{cc} and ΔH_c, the similar trend was also discovered in the cooling scan (Fig. 4b). The results suggested that the melting transitions and crystallization behaviors may arise from PBS segment and be slightly affected by the PLLA segment, and also indicated that it was very difficult for PLLA segment to form crystalline in all the synthesized PEUs, which was further confirmed by WAXD testing. To explain this phenomenon, it is necessary to analyze the crystallization behavior of the prepolymers PLLA-OH and PBS-OH. We can see from Fig. 4 that the crystallization of PBS prepolymer itself was much easier than that of PLLA prepolymer, which can be concluded by comparing the DSC scan of PBS-OH with that of PLLA-OH. For PLLA-OH, there was no crystallization peak in the cooling scan and the crystallization happened in the heating scan. While in the case of PBS-OH, the crystallization was completed in the cooling scan. After copolymerization, the crystallization of PLLA segment would be significantly restricted by the crystallized PBS segment, because the mobility of PLLA segments would become more difficult after crystallization of PBS segments. In addition, the introduction of chain extender would disturb the structure of PLLA thus further restricts the crystallization of PLLA segments.

Fig. 6 displays the wide-angle X-ray diffraction patterns of PLLA-OH, PBS-OH, together with PEU4, PEU6, and PEU8. Two main peaks were observed, occurring at 2θ values of 19.5° and 22.6° for PEUs, coinciding with the characteristic peaks of PBS-OH. However, the peaks for PEUs were less sharp than those of PBS-OH and the peak intensity became weaker with the gradual decrease of PBS block content in PEUs from PEU8 to PEU6 and to PEU4. PLLA-OH had two main peaks appearing at 2θ values of 16.7° and 19.1°, which were very weak in PEU4 with an F_{PLLA} of 65.68% and even could not be detected in PEU6 and PEU8. The results were in agreement with those obtained from DSC analysis, that is, melting transitions and crystallization behaviors of PEUs were caused by PBS block and affected by the PLLA block; it was very difficult for PLLA block to form crystalline in all the PEUs.

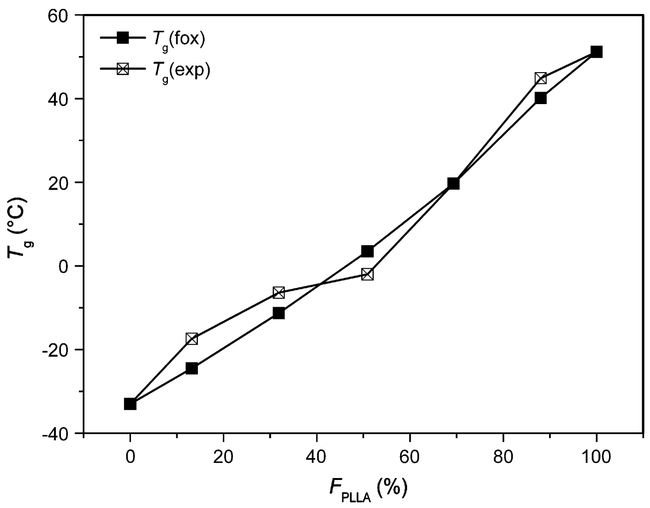


Fig. 5. The T_g of PEUs versus F_{PLLA}.

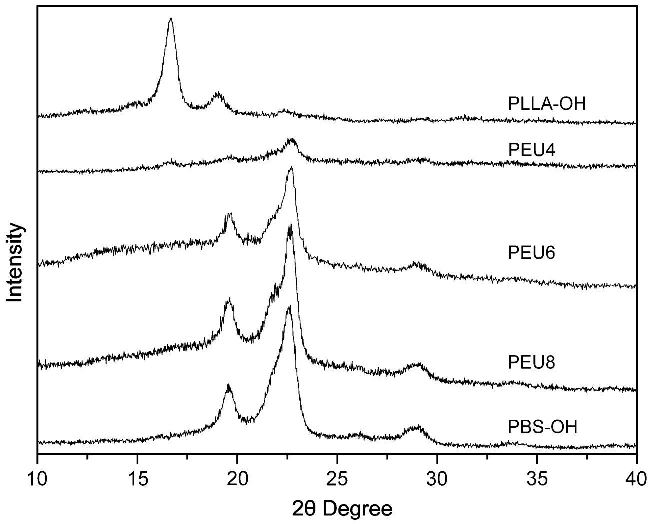


Fig. 6. Wide-angle X-ray diffraction patterns of PLLA-OH ($M_n = 4600$), PBS-OH ($M_n = 4300$), and PEU4, PEU6, and PEU8.

3.4. Thermal stabilities of PEUs

The non-isothermal stabilities of PEUs were studied using thermogravimetric analysis (TGA). The TGA results of PLLA-OH, PBS-OH, as well as PEUs are summarized in Table 5 and Fig. 7. The PEUs undergo two-stage thermal degradation. The first stage with a maximum decomposition temperature of around 270 °C is the degradation of PLLA segment, and the second stage with a maximum decomposition temperature of more than 340 °C is the thermal degradation of PBS block. All the PEUs have a higher initial decomposition temperature ($T_{0.05}$) and maximum decomposition temperature than those of PLLA-OH, indicating that all the PEUs are more stable against heat than PLLA-OH.

It is well known that pure PLLA undergoes an unexpected thermal degradation during thermal processing, which would lead to poor mechanical properties of the resulting product. In the study, we investigated the isothermal stability of the PEUs at a temperature of 120 °C which is about 15 °C higher than the melting points of PEUs. This research is very meaningful for guiding the processing of the polymers. Fig. 8 displays the effect of isothermal time on the intrinsic viscosities of the PEUs. From the data, we found that intrinsic viscosity of PEUs showed very little decrease in the first 30 min. For PEU6 and PEU8 with F_{PBS} higher than F_{PLLA}, they exhibited good thermal stabilities even exposed as long as 120 min. This would be very helpful to maintain the physical properties after thermal processing, and make them more useful.

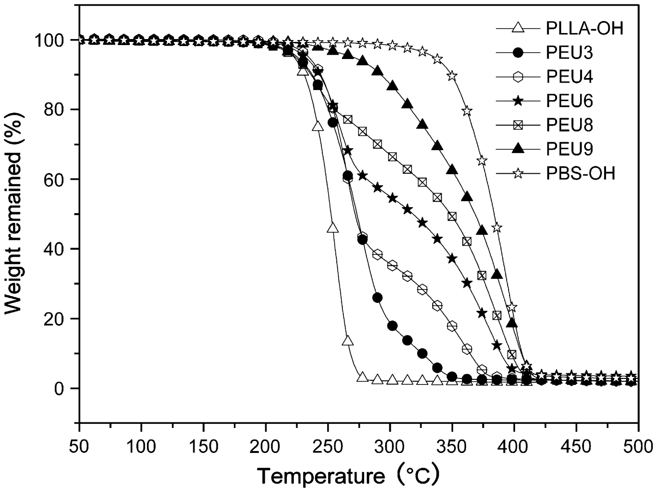


Fig. 7. TGA curves of PLLA-OH ($M_n = 4600$), PBS-OH ($M_n = 4300$), and PEUs with varying compositions.

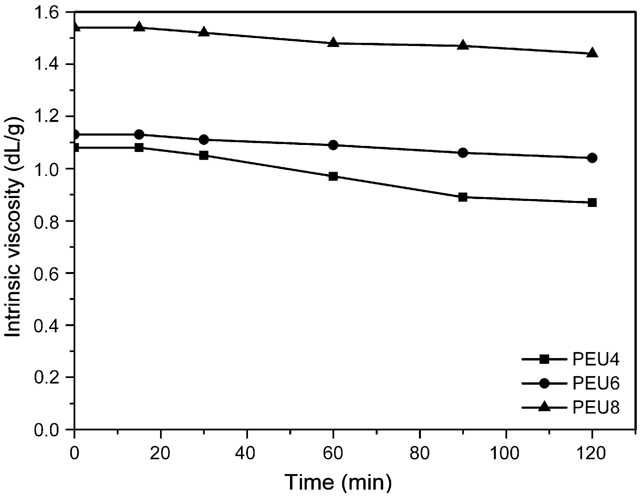


Fig. 8. Isothermal stabilities of PEUs at 120 °C.

3.5. Tensile properties

Mechanical properties of polymers are more important than any other properties with respect to practical applications. The tensile properties of the PEU samples are summarized in Table 6. There were many factors which can affect the physical behaviors of the PEUs synthesized, such as molecular weight, chemical composition, glass transition temperature, and crystallinity. For PEU1, PEU2, PEU6 and PEU10, which had similar weight fraction ratios of PLLA to PBS segments (F_{PLLA}/F_{PBS}) and glass transition temperatures (T_g) close to each other, their block lengths, crystallinity and molecular weights were the major factors to affect the tensile properties. A trend of increasing first and then decreasing in both tensile strength and elongation at break was observed with increasing lengths of PLLA and PBS blocks. The relatively lower strength of PEU1 was probably caused by lowest crystallinity; PEU6 that has a PLLA segment with a molecular weight of 4600 g/mol and a PBS segment with a molecular weight of 4300 g/mol exhibits most excellent tensile properties; and the relatively lower strength of PEU10 might be caused by the reduced molecular weight and the reduction in the elongation at break of PEU10 should result from the increased crystallinity. In the cases of PEU3, PEU4, PEU6, PEU8, and PEU9, they had almost the same content of urethane linkages, and the mass ratio of PLLA/PBS was the main reason for the variation of tensile properties. PBS segment, as discussed above, was the main contribution to crystallization of PEUs and the flexible segments. With the

Table 6
Tensile properties of PEUs.

Sample	Tensile strength (MPa)	Elongation at break (%)
PEU1	18.8 ± 0.4	426 ± 32
PEU2	25.7 ± 1.2	500 ± 41
PEU3	45.5 ± 3.5	45 ± 7
PEU4	24.3 ± 0.9	353 ± 29
PEU6	38.2 ± 1.8	562 ± 53
PEU8	39.1 ± 2.6	580 ± 50
PEU9	43.4 ± 2.1	559 ± 47
PEU10	22.2 ± 1.3	458 ± 33

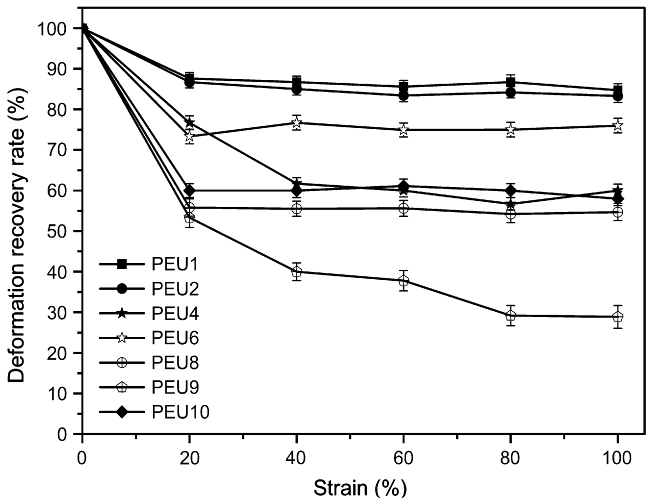


Fig. 9. The recovery properties of PEUs.

increase of F_{PBS}, higher molecular weight and higher crystallinity of PEU would be obtained, thus resulting in gradually higher strength at break. PEU3, with the highest content of PLLA segment, showed a similar strength but better toughness in comparison with PLLA. Although PEU9 had a higher molecular weight than PEU8, it exhibited a slightly lower elongation at break, which was probably due to the relatively higher crystallinity of PEU9.

The recovery properties of the PEUs were researched via tensile testing in our study. The testing procedures were as follows: PEU specimen was clamped using two pneumatic grips, the distance between the two grips was marked as L_0 ($L_0 = 20$ mm). The sample was stretched to a predetermined strain (elongation was defined as L_1) then the imposed strength was unloaded. Thereafter, the sample was placed in a plate for 24 h when the length between the two marked lines was measured and defined as L_2. The deformation recovery rate (σ) was calculated by the following equation:

$$\sigma = \frac{L_0 + L_1 - L_2}{L_1} \times 100\% \tag{8}$$

The results are graphically displayed in Fig. 9. PEU3 was not measured as its elongation cannot meet the demand of testing. For PEU1, PEU2, PEU6, and PEU10, their σ values were higher than 50%, and decreased gradually from PEU1 to PEU10. The reason for their high recovery rate was that the testing ambient temperature was higher than their T_g, so they existed in the rubbery state at testing temperature, that is, the elastic deformation was the predominant deformation. The small difference in the σ values was caused by their different crystallinities. For PEU1, it had lowest crystallinity thus showing the greatest recovery rate. Whereas, the smallest σ value of PEU10 was determined by its highest crystallinity. For PEU4, PEU6, PEU8, and PEU9, the degree of cystallinity should probably account for the variation of recovery rate. For PEU9, although it had the lowest T_g, its lowest σ value was the result of the highest crystallinity. From PEU9 and PEU8 to PEU6, as they all had a T_g higher than room temperature, the σ values increased with the decrease of crystallinity. The T_g of PEU4 is very close to room temperature, so its σ value was a little smaller than that of PEU6. These results suggested that the tensile properties of the polymers can be controlled by adjusting the structures of PEUs.

4. Conclusions

In summary, a series of poly(ester urethane)s consisting of PLLA and PBS blocks were successfully synthesized by the chain-extension reaction of PLLA-OH and PBS-OH, using toluene-1,4-diisocyanate as a chain extender. Varying the molecular weights of prepolymers and the feed mass ratio of PLLA-OH to PBS-OH, PEUs with controllable structures were prepared combining with controllable properties. Through the results of chain-extension reaction, it was confirmed that the number–average molecular weights of PLLA-OH and PBS-OH were accurately calculated via NMR characterization. GPC results showed the molecular weight of PEU increased with the increase of PBS content. DSC analysis suggested that PLLA and PBS segments were well compatible in amorphous phase, and the crystallization of PEU was predominantly caused by PBS block, which was also confirmed by WAXD study. TGA test showed that PEUs were more stable than PLLA-OH against thermal decomposition. Isothermal stability results indicated that the intrinsic viscosity of PEU could be maintained for a long time at 120 °C (processing temperature). Tensile testing proved that the toughness of PLLA could largely be improved by introduction of PBS segment. The results of recovery study demonstrated that the recoverability of PEUs could be controlled by changing the structure.

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