

# Synthesis and Characterization of Poly(ester amide)s Consisting of Poly(*L*-lactic acid) and Poly(butylene succinate) Segments with 2,2'-Bis(2-oxazoline) Chain Extending

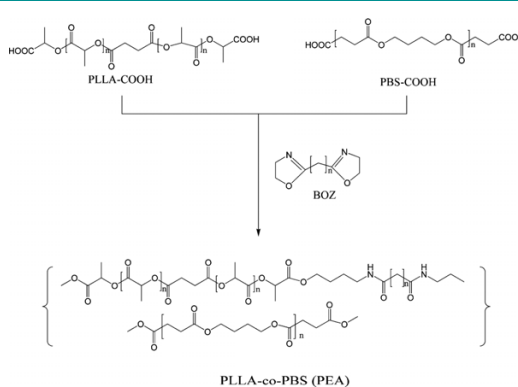
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**Abstract:** An aliphatic polyester based poly(ester amide)s (PEA) consisting of poly(*L*-lactic acid) and poly(butylene succinate) was successfully prepared *via* chain extension reaction of poly(*L*-lactic acid)-dicarboxylic acid (PLLA-COOH) and poly(butylene succinate)-dicarboxylic acid (PBS-COOH) using 2,2'-bis(2-oxazoline) as a chain extender. PLLA-COOH was obtained by direct polycondensation of *L*-lactic acid in the presence of 1, 4-succinic acid. PBS-COOH was synthesized by condensation polymerization of 1,4-butylene glycol with excessive succinic acid. The structures of PLLA-COOH, PBS-COOH, and PEAs were characterized by fourier transform infrared (FTIR) and <sup>1</sup>H nuclear magnetic resonance (<sup>1</sup>H NMR). The molar masses were determined by gel permeation chromatography (GPC). The thermal properties of PLLA-COOH, PBS-COOH, and PEAs were characterized by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC). The lattice parameters of PLLA-COOH, PBS-COOH, and PEAs were investigated by X-ray diffraction (XRD). Furthermore, The mechanical properties were characterized by tensile testing and notch Izod impact testing. The FTIR and <sup>1</sup>H NMR results demonstrated the formation of PLLA-COOH, PBS-COOH, and PEAs. The GPC measurements showed that the molar masses of copolymer PEAs decreased with increasing PBS-COOH content. The TGA analysis confirmed that the introduction of PBS improved the thermal properties. DSC data indicated that the melting temperatures of the PEAs were lower than that of the prepolymers. The results of XRD suggested that the PLLA crystal structures was destroyed by the PBS units, and the crystallization of the PEAs mainly attributed to the PBS chain segments. The introduction of PBS units into the polymer structure improved the toughness of PLLA, which was detected in mechanical properties.



**Keywords:** poly(ester amide), poly(*L*-lactic acid), poly(butylene succinate), 2,2'-bis(2-oxazoline).

## 1. Introduction

As a kind of traditional petroleum-based material, plastics have been widely used in many aspects of people's life, and provide people with a lot of convenience. However, in the booming development of the plastic industry, we also find two huge challenges recently. The conventional polymeric materials are not biological degradation, after abandoning, caused severe environmental pollution. In addition, the gradual reduction of petroleum resources impact on the sustainability of conventional plastics.<sup>1</sup> Those have motivated academia and industry to devote considerable efforts to developing new plastics, which are

synthesized by renewable and biodegradable resources.<sup>2,3</sup>

Biodegradable polyesters can be completely degraded into carbon dioxide, water and other harmless micromolecule by the microorganism of the nature, without secondary pollution. As one kind of biobased and biodegradable materials, biobased aliphatic polyesters such as poly(lactic acid) (PLA),<sup>4-7</sup> poly(butylene succinate) (PBS),<sup>8-10</sup> and their blends<sup>11,12</sup> have recently obtained more and more attention with their excellent properties.<sup>13</sup> Polylactide (PLA) is one of the most important biobased and degradable polymers with many potential applications.<sup>14-17</sup> At present, there are two synthetic routes of preparing PLLA. One is direct polycondensation of *L*-lactic acid<sup>18-20</sup> and the other is ring opening polymerization of the *L*-lactide.<sup>21-23</sup> The direct polycondensation method is difficult to obtain high molecular weight PLLA. However, high-molecular-weight PLLA is generally synthesized by the complicated procedure of ring opening polymerization of *L*-lactide, initiated with hydroxyl<sup>24,25</sup> or amine-functionalized<sup>26,27</sup> initiators, which causes PLLA to have high cost. In addition, PLLA has some inherent defects such as brittleness and poor hydrophilic.<sup>28-30</sup> In order to expand the application range

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of PLLA, we need to reduce cost and improve the toughness. To date, various preparing high-molecular-weight PLLA<sup>31,32</sup> and improving toughness methods<sup>33-35</sup> for PLA have been studied, chain extension is not only a convenient method, but also extremely effective to reduce the cost and improve the flexibility of PLLA by coupling reaction of PLLA prepolymer with another flexible prepolymer.

At present, the chain extension agents used for polyester extender chain mainly contain epoxy<sup>36</sup> maleic anhydride<sup>37</sup> or cyanate.<sup>38</sup> In the process of extender chain, some are used to extend the chain end carboxyl polymer, while some others can extend the chain end hydroxyl polymer. Oxazoline is an important coupling chain extension agent for end carboxyl polymer. Tuominen *et al.*<sup>39</sup> synthesized high molecular weight poly(lactic acid) type polyester amide copolymer with 2,2'-bis(2-oxazoline) extending prepoly(lactic acid)-diacid. Liu Shiyue *et al.*<sup>40</sup> synthesized biodegradable based polyester amides, which used 2,2-(1,4-phenylene)-bis(2-oxazoline) as chain extension agent to extend the prepolymer of adipic acid, butyl glycol and nylon-66 salt.

In this study, we prepared a novel poly(ester amide) (PEA) by using another biodegradable aliphatic polyester, poly(butylene succinate)-dicarboxylic acid (PBS-COOH) as a flexible component to copolymerize with poly(L-lactic acid)-dicarboxylic acid (PLLA-COOH) in the presence of 2,2'-bis(2-oxazoline). The copolymers were characterized using <sup>1</sup>H NMR, GPC, DSC, and WAXD. The structures, molar masses, thermal properties and the crystallization behaviour of the novel PEA were studied in detail.

## 2. Experimental

### 2.1. Materials and methods

L-Lactic acid with 88 wt% aqueous solution was obtained from Jiangsu Jiuding group (Jiangsu, China). Succinic acid (Analytical reagent grade) and ethylene glycol (Analytical reagent grade) were purchased from Enterprise group chemical reagent Co., LTD was used without further purification. 2,2'-bis(2-oxazoline) (BOZ, chemical pure grade) was bought from Dalian Chemical Plant (Dalian, China). Stannous octoate (Analytical reagent grade) and para-toluenesulfonic acid (Analytical reagent grade) were purchased from Kelong Chemical Corporation (Chengdu, China). All other chemicals with Analytical reagent grade were used as received.

#### 2.1.1. Synthesis of PLLA-COOH prepolymer

The free water of L-lactic acid was removed by reduced pressure distillation at 90 °C for three hours. The prepolymer of dicarboxylic terminated PLLA-COOH was synthesized *via* direct condensation polymerization of dehydrated L-lactic acid in the presence of 1,4-succinic acid using stannous octoate and para-toluenesulfonic acid as catalysts. The procedure was as follow: 270.0 g (3.0 mol) L-lactic acid, 4.13 g (0.035 mol) 1,4-succinic acid and 1.08 g (0.4 wt%) stannous octoate were put into a 500 mL four-neck round-bottom flask equipped with mechanical stirrer under the protection of nitrogen. When the polymerization was carried out at 160 °C, the reaction was implemented at 4 kPa for 5 h and then continued at 180 °C and 0-300 Pa for another 5 h.

The obtained polymer was purified by dissolving in dichloromethane and precipitating in excessive methanol. The white flocculent product was dried to constant weight in vacuum oven at 50 °C.

#### 2.1.2. Synthesis of PBS-COOH prepolymer

The PBS-COOH prepolymer was prepared by esterification and following polycondensation. The reaction was carried out in an exhaustively nitrogen-purged, 500 mL four-neck flask glass reactor equipped with the magnetic stirrer. 1.5 mol 1,4-succinic acid and 1.65 mol 1,4-butylene glycol were first put in reactor, and the esterification was implemented at 140 °C for 3 h. After that 0.51 g (0.1 mol% of 1,4-succinic acid) tetrabutyl titanate was added into the four-neck round-bottom flask, and the polycondensation was continued at 220 °C with vacuum of 0-100 Pa for 3 h. And then 10 g 1,4-succinic acid was put in the reactor to get PBS-COOH. The purification method was as mentioned above.

#### 2.1.3. Synthesis of PEA copolymers containing PLLA and PBS segments

The chain-extension reaction was completed in one-neck round-bottom flask filled with N<sub>2</sub>. When PLLA-COOH and PBS-COOH in the reactor were completely molten at 200 °C, a certain amount of BOZ was added into the reactor. The reaction was finished in 1 h. The copolymer was purified by dissolving in dichloromethane and precipitating in excessive methanol. Then the resultant polymer was dried to constant weight in vacuum oven at 50 °C.

### 2.2. Fourier transform infrared (FTIR) spectroscopy

FTIR spectra for the samples were characterized by Nicolet 6700 spectrometer in a range of wave numbers from 4000 cm<sup>-1</sup> to 500 cm<sup>-1</sup>. The samples of the PLLA-COOH, PBS-COOH prepolymer, and the PEA copolymers were milled into powders and then mixed and laminated with KBr at room temperature (25 °C). The resolution and scanning time were 4 cm<sup>-1</sup> and 32 times, respectively.

### 2.3. Nuclear magnetic resonance (NMR) spectroscopy

<sup>1</sup>H NMR spectroscopy were carried out by 400 Hz NMR spectrometer (Bruker, AVANCE, Switzerland) for macromolecular structure characterization. CDCl<sub>3</sub> was applied as the corresponding solvent and the tetramethylsilane (TMS) was used as the internal chemical shift standard.

### 2.4. Molecular parameters

The molecular weight of the polymers were measured by both gel permeation chromatography (GPC) and multiangle laser light scattering (MALLS) techniques at 25 °C. GPC data were collected using a Waters Corp. 515 pump equipped with OPTILAB® T-rEX Interferometric refractometer and PLGel 5 μm mixed-D-type column. MALLS data were collected by using a Wyatt Technology Corp. DAWN HELEOS II laser photometer. Chloroform was applied as the eluant at a flowing rate of 1.0 mL/min, and the samples concentration was 0.5 mg/mL. The molecular weights

and polydispersity index were calculated with the ASTRA 6 software.

## 2.5. Thermogravimetric analysis (TGA)

The thermal stabilities of polymers were performed with a TGA (Pyris Diamond, PE, America). The thermograms were recorded from room temperature to 550 °C at a heating rate of 10 °C/min under nitrogen atmosphere at a flowing rate of 30 mL/min.

## 2.6. Differential scanning calorimetry (DSC)

DSC analysis was carried out on NETZSCH (DSC-204) Instrument. The samples were quickly heated from 25 °C to 200 °C at 10 °C/min under nitrogen atmosphere, holding for 5 min to eliminate thermal history, then cooled to 25 °C at the same rate, and subsequently reheated to 200 °C at 10 °C/min to evaluate the thermal behaviour.

## 2.7. X-Ray diffraction (XRD) characterization

XRD patterns were recorded at room temperature by a XRD-6000 system with a nickel-filtered CuK $\alpha$  radiation ( $\lambda=0.154$  nm) at 40 kV and 30 mA in the  $2\theta$  range from 5 °C to 60 °C at a scanning rate of 4.0°/min.

## 2.8. Mechanical properties

Tensile tests were conducted on a Sansi Universal Testing Machine (CMT, Shenzhen, China) at a crosshead speed of 20 mm/min at room temperature according to ASTM D638. Notched Izod

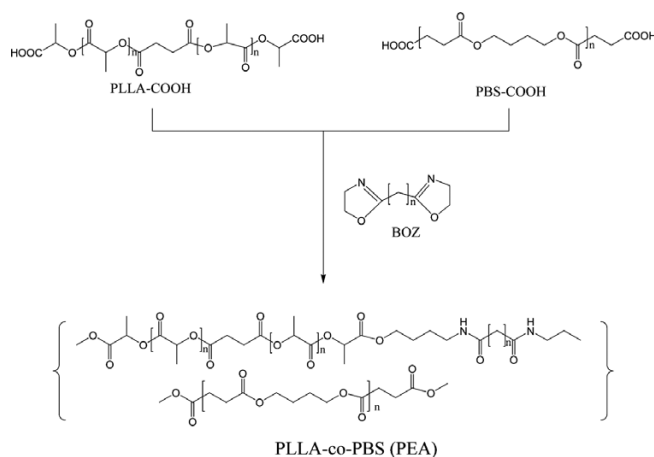
impact tests were performed according to ASTM D256 using a Ceast Pendulum Impact tester (Model Resil 50B). An average value of five replicated specimens were taken for each sample.

## 3. Results and discussion

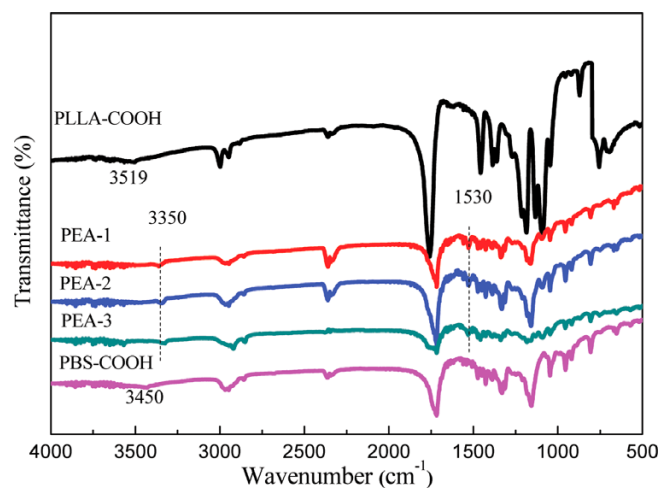
### 3.1. Synthesis of PLLA-co-PBS PEAs

The PLLA-co-PBS copolymers with different compositions were synthesized *via* chain extension of PLLA-COOH prepolymers with PBS-COOH prepolymers using BOZ as a chain extender at 200 °C for 1 h. The probable synthetic path is shown in Scheme 1. PLLA-COOH and PBS-COOH were mixed with different weight ratios before chain extension. The resulting copolymers were in sequence named as PEA-1, PEA-2, and PEA-3, respectively, which are collected in Table 1.

The functional groups present in the PLLA-COOH, PBS-COOH prepolymer, and the PEA copolymers were characterized by FTIR. The FTIR spectrum of the PLLA-COOH, PBS-COOH prepolymer, and the PEA copolymers were shown in Figure 1. It can be seen from Figure 1, that the stretching vibration bands at 3450 and 3519 cm<sup>-1</sup> assigned to the O-H in COOH groups of PBS-COOH and PLA-COOH disappeared after chain-extension reaction, which indicated that the PBS-COOH and PLA-COOH prepolymers were completely consumed. The new peak at about 3350 cm<sup>-1</sup> ascribed to the N-H vibration was found in the spectra of PEA copolymers, meanwhile the -C=N- stretching was not found in the range of around 1650 cm<sup>-1</sup>. All of above proved that the -C=N- of BOZ had been reacted completely and were absent in the resulting PEAs. It confirmed that the amount of BOZ were effective



**Scheme 1.** Preparation of PEA.



**Figure 1.** FTIR spectrum of PLLA-COOH, PBS-COOH, and PEAs.

**Table 1.** The molecular weight and polydispersity index (PDI) of PEA copolymers

Sample	PLLA/PBS (wt/wt) <sup>a</sup>	$M_n \times 10^{-3}^b$	$M_w \times 10^{-3}^b$	PDI <sup>b</sup>
PLLA-COOH	10:0	14.7	15.0	1.02
PEA-1	7:3	19.1	22.5	1.18
PEA-2	5:5	19.6	24.8	1.26
PEA-3	3:7	23.3	25.8	1.11
PBS-COOH	0:10	7.9	11.9	1.51

<sup>a</sup>Feeding weight ratios of PLLA prepolymer to PBS. <sup>b</sup>Absolute molecular weight and polydispersity indexes were measured by SEC.

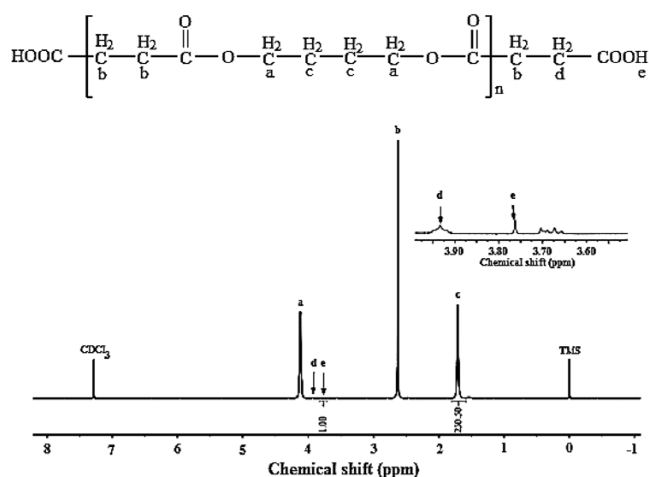


Figure 2.  $^1\text{H}$  NMR spectra of PBS-COOH.

chain-extension reaction. Furthermore, another characteristic peak of N-H vibration was also observed at about  $1530\text{ cm}^{-1}$  which provided strong evidence for the successful synthesis of PEAs.<sup>41,42</sup>

The chemical structures of PBS-COOH and PEA were characterized by  $^1\text{H}$  NMR. Figure 2 shows the  $^1\text{H}$  NMR spectrum of the synthesized PBS-COOH with the corresponding proton resonance signals assigned. Note from Figure 2 that the peak at 1.72 ppm was originated from proton of the inner methylene groups in  $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{O}-$ . The signals of methylene protons in  $-\text{OOCCH}_2\text{CH}_2\text{COO}-$  from PBS-COOH were found at 2.63–2.71 ppm. The peaks at 4.07–4.21 ppm ascribed protons of the outer methylene groups in  $-\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}-$ . Furthermore, the peaks at 3.77 ppm are the characteristic peak of  $-\text{COOH}$  groups, which is signifying that the successful synthesis of PBS-COOH. Figure 3 shows the  $^1\text{H}$  NMR spectrum of the PEA copolymer. From Figure 3, not only signals of methyne protons ( $\delta=5.10\text{--}5.23\text{ ppm}$ ) and methyl protons ( $\delta=1.57\text{ ppm}$ ) in PLLA-COOH, but also signals of methylene protons ( $\delta=4.07\text{--}4.21\text{ ppm}$ ,  $\delta=2.63\text{--}2.71\text{ ppm}$ ,  $\delta=1.72$

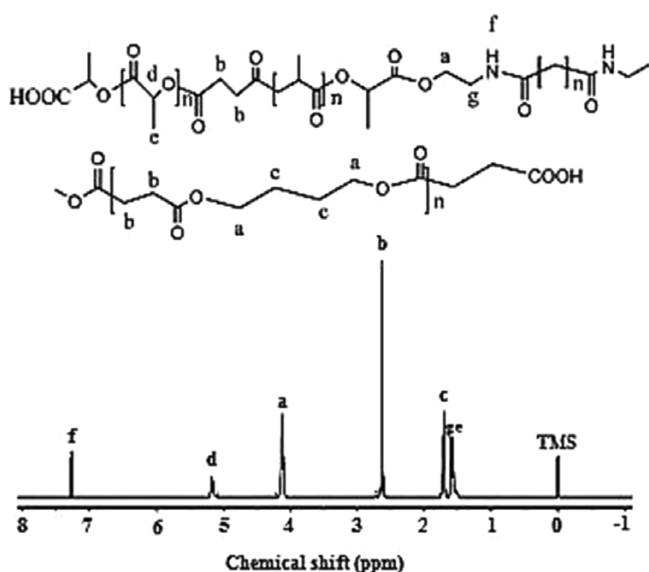


Figure 3.  $^1\text{H}$  NMR spectra of PEA.

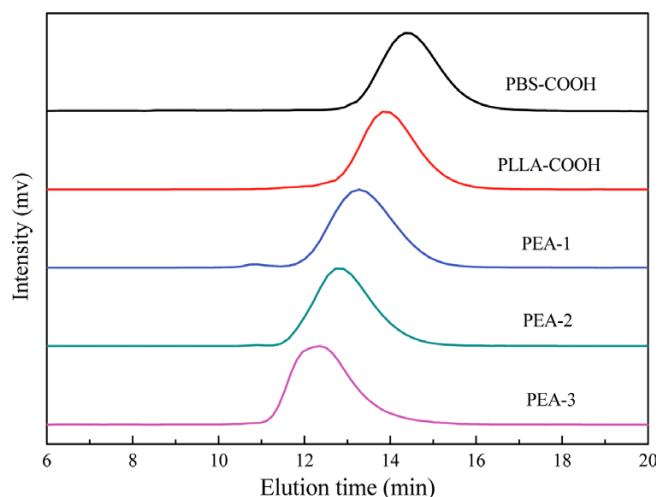


Figure 4. GPC elution traces for synthesized PEAs, PLLA-COOH, and PBS-COOH.

ppm) in PBS-COOH could be observed. Furthermore, no proton resonance signals of methyne protons in  $-\text{N}=\text{CH}-$  from BOZ were founded. These confirmed that the PLLA-co-PBS copolymers were successfully prepared *via* chain-extension reaction of poly(L-lactic acid)-diacid (PLLA-COOH) and poly(butylene Succinate)-diacid (PBS-COOH) using BOZ as a chain extender.

### 3.2. Molecular weights and polydispersity indexes of prepolymers and PEAs

The molecular weights of the PEAs, PLLA-COOH and PBS-COOH prepolymers showed in Table 1 were determined by GPC and MALLS techniques in chloroform at  $25\text{ }^\circ\text{C}$ , and the GPC elution traces for the PEAs, PLLA-COOH and PBS-COOH prepolymers are graphically shown in Figure 4. The GPC traces of PEAs show a single peak, indicating that reaction took place completely without unreacted prepolymer remaining.<sup>43</sup> In addition, it could be found from Table 1 that the molecular weights of the synthesized PEAs were more higher than the prepolymers, which could

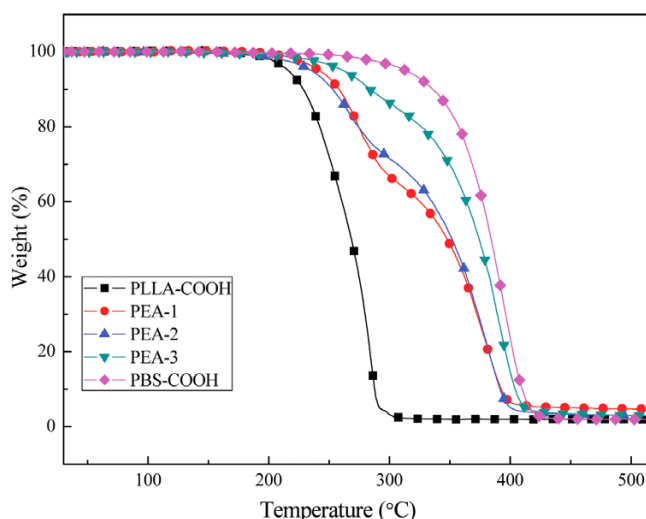


Figure 5. TGA curves of PEAs, PLLA-COOH, and PBS-COOH.



**Table 2.** TGA characteristic temperatures for polymers<sup>a</sup>

Sample	$T_{0.05}$ (°C)	$T_{max1}$ (°C)	$T_{max2}$ (°C)	$T_{0.95}$ (°C)
PLLA-COOH	215	287	n	290
PEA-1	240	268	367	n
PEA-2	235	269	383	400
PEA-3	261	271	384	412
PBS-COOH	313	n	399	417

<sup>a</sup> $T_{0.05}$ , temperature of 5% weight losing during heating process;  $T_{max1}$  and  $T_{max2}$ , temperature of maximum rate of degradation  $T_{0.95}$ , temperature of 95% weight losing during heating process. n, Not detected.

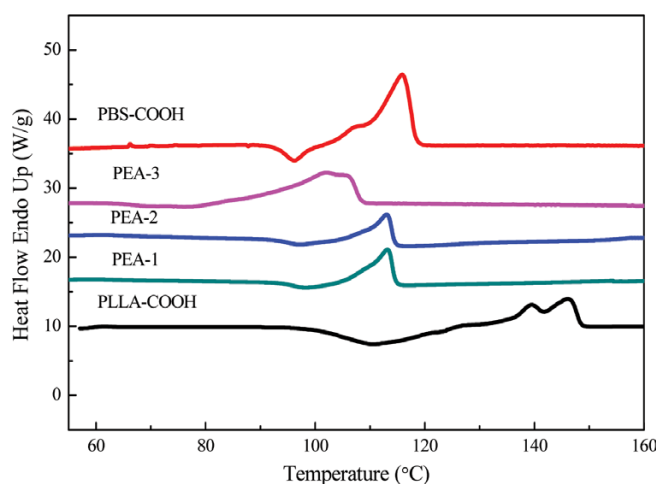
prove that the chain extension reaction was very effective. Furthermore, we can find that the molecular weight distributions of PEAs are relatively narrower than that of PBS-COOH, but wider than that of PLLA-COOH. This is easy to understand, because the structures and reactivity of the PLLA-COOH and PBS-COOH prepolymers are different.

### 3.3. Thermal properties

The thermal stabilities of the PLLA-COOH, PBS-COOH prepolymer, and the PEAs were investigated by TGA analysis. The TGA curves under a nitrogen atmosphere were shown in Figure 5, and the results are summarized in Table 2. It can be seen that the degradation process of PLLA-COOH and PBS-COOH prepolymers are the single step, while that of PEAs goes through a two-step degradation. In addition, the initial decomposition temperature ( $T_{0.05}$ ) of PBS-COOH and PEAs were much higher than PLLA-COOH, which indicated that the thermal stability of PBS-COOH and PEAs were better than PLLA-COOH. Furthermore, it was noted that the temperature of the first thermal degradation stage are around 270 °C, which owes to decomposition temperature of PLLA segment and the temperature of the second thermal degradation stage are more than 360 °C, which depends on the degradation of PBS block. Otherwise, it can be observed from TGA analysis that  $T_{0.05}$  of the PEAs increased with increasing the PBS segments in copolymers, which indicated that the thermal stabilities of the PEAs were enhanced by the increase of PBS content, and which is consistent with the conclusions of other researchers.<sup>13,44</sup>

### 3.4. Differential scanning calorimetry of PLLA-COOH, PBS-COOH, and PEAs

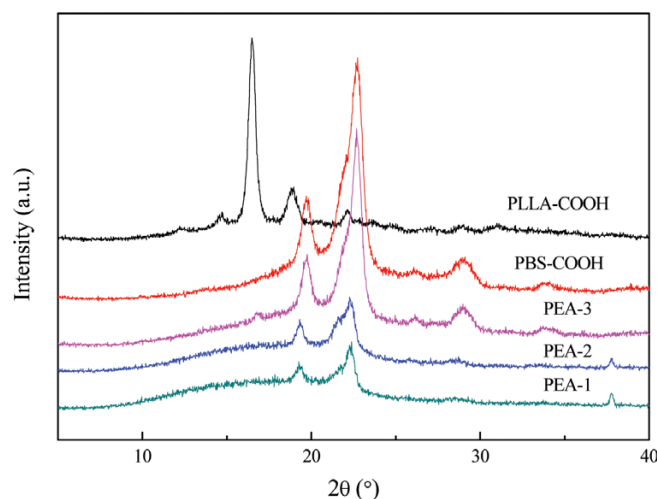
DSC analysis was used to characterize the thermal behaviors of PLLA-COOH, PBS-COOH prepolymer and PEAs copolymers. The results are shown in Figure 6. And the DSC thermograms of PEAs, PLLA-COOH and PBS-COOH are the second heated process after eliminated any thermal history. The crystallization temperature ( $T_c$ ), crystallization enthalpy ( $\Delta H_c$ ), melting tem-

**Figure 6.** DSC curves of PEAs, PLLA-COOH, and PBS-COOH.

perature ( $T_m$ ) and melting enthalpy ( $\Delta H_m$ ) were listed in Table 3. It can be found that the crystallization and melting peak of PBS-COOH and PLLA-COOH are obvious from the DSC curves, and we can note that the melting peak of PLLA-COOH shows twin peaks. That's because the crystallization rate of PLLA-COOH was relatively slow, PLLA segments could not fully crystallize with 10 °C/min heating rate of warming, and part of the crystal defect was created. In the scanning process of the second heating, the crystal defect was reheated melting in low temperature, and then crystallized and restructured again with heat releasing. The structure of the secondary crystallization was relatively perfect. As the temperature rising further, the secondary crystallization melted at higher temperature, which resulted in double molten peak. At the same time, we can also find the  $T_m$  of PEAs were lower compared to PLLA-COOH and PBS-COOH, and PEA-3 curve showed the bluntest melting peak which was an indication of the inability of forming perfect crystals. The reason was that the incorporation of copolymerization units decreased the chain regularity of the copolymers, which resulted in the decrease of the melting point of PEAs.<sup>45</sup>

**Table 3.** Thermal properties estimated by DSC analysis

Sample	$T_c$ (°C)	$\Delta H_c$ (J/g)	$T_m$ (°C)	$\Delta H_m$ (J/g)
PLLA-COOH	110	38.1	139	42.9
PEA-1	98.3	3.4	113.2	25.9
PEA-2	97.2	4.6	112.7	26.7
PEA-3	75.6	11.3	102	61.7
PBS-COOH	96.1	35.4	115	82.2



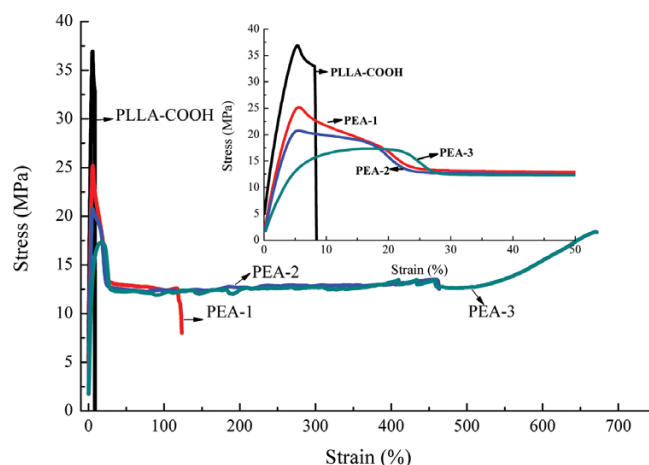
**Figure 7.** XRD patterns of PLLA-COOH, PBS-COOH, and PEAs.

### 3.5. XRD patterns

To study more about the crystallization of the PLLA chain blocks and the PBS chain segments in the PEA. The PLLA-COOH, PBS-COOH and PEAs were measured by Wide angle X-ray diffraction test. Figure 7 obviously shows that the crystal unit cells of PLLA-COOH and PBS-COOH all were  $\alpha$  crystal form. The X-ray diffraction peaks of the PLLA-COOH from (103), (010), (200), (203), and (015) planes were observed at  $2\theta=12.3^\circ$ ,  $14.7^\circ$ ,  $16.6^\circ$ ,  $18.9^\circ$ , and  $22.3^\circ$ , and the X-ray diffraction peaks of the PBS-COOH from (020), (021), and (110) planes were observed at  $2\theta=19.64^\circ$ ,  $21.88^\circ$ , and  $28.9^\circ$ , respectively. The diffraction curves of PEAs basically didn't have the crystal diffraction peak of PLLA chain segment, and mainly showed the features diffraction peak of PBS chain blocks. In addition, the relative intensity of the peaks increased gradually with increasing the content of PBS segments. All of these indicated that the regularity of the PLLA crystal structures were destroyed when the PBS units were introduced into the PEAs chains, the crystallization of PEAs mainly attributed to the PBS chain segments,<sup>46,47</sup> and the crystallization properties of PEAs are getting better and better with increasing the content of PBS segments, which is agreement with the results obtained from DSC analysis. The crystallization of PLLA blocks in PEAs are restricted by PBS chain segments.

### 3.6. Mechanical properties

Tensile testing were performed to determine the differences in properties between the synthesized polymers of PLLA-COOH and PEAs. The results of tensile strength, elongation at break



**Figure 8.** Stress-strain curves of PLLA-COOH and PEAs.

and impact strength are shown in Table 4 and Figure 8 respectively. It is evident that PLLA-COOH has superior tensile strength at room temperature but lacks flexibility which is apparent from distinct yielding and neck growth by tensile testing. On the contrary, PEAs shows a moderate strength and high elongation at break. With increasing the content of PBS segments, the tensile strength of the polymers decreased while the elongation at break almost always increased, the introduction of PBS segments and the chain flexibility may be the major factors to affect tensile properties. Although PEAs had a higher elongation at break than PLLA-COOH, it exhibited a slightly higher impact strength, which was probably due to the relatively high crystallinity of PEAs.

## 4. Conclusions

In this work, novel PEAs had been synthesized by poly(butylene succinate)-dicarboxylic acid and poly(L-lactic acid)-dicarboxylic acid, using BOZ as a chain extender. In chain extension reaction, the charge ratio of prepolymers had a marked effect on the molecular weight, which increased with increasing the PBS-COOH content. FTIR and  $^1\text{H}$  NMR spectroscopies confirmed presumed structures of the obtained novel PEAs. TGA results indicated that the initial thermal decomposition temperature of PEAs was higher than that of PLLA-COOH. At the same time, PBS segments enhanced the thermal stability of novel PEAs. The results of DSC demonstrated that the  $T_m$  of PEAs were lower compared to PLLA-COOH and PBS-COOH, furthermore, the PEAs that the two prepolymers formed have the same crystal type, the X-ray diffraction intensity of PEAs increased gradually with increasing the content of PBS segments. The crystallization behavior of PEAs mainly depends on the PBS segments, not the PLLA blocks. Tensile testing and notch Izod impact

**Table 4.** Tensile strength, elongation at break and impact strength of PLLA-COOH and PEAs

Sample	Tensile strength (MPa)	Elongation at break (%)	Impact strength ( $\text{kJ/m}^2$ )	Young's modulus (MPa)
PLLA-COOH	$36.9 \pm 0.9$	$8.6 \pm 0.6$	$12.2 \pm 0.1$	$895.1 \pm 33.8$
PEA-1	$25.2 \pm 2.1$	$123.3 \pm 21.2$	$12.7 \pm 0.1$	$677.6 \pm 29.6$
PEA-2	$20.8 \pm 1.1$	$451.1 \pm 34.2$	$13.4 \pm 0.2$	$553.8 \pm 9.8$
PEA-3	$18.4 \pm 1.7$	$610.6 \pm 55.5$	$14.9 \pm 0.1$	$362.9 \pm 36.5$

testing proved that the flexibility of PLLA could largely be improved by introduction of PBS segments.

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