Synthesis, Properties, and Degradation of Poly(butylene succinate-co-sebacicate-co-salicylicate) Copolyesters

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Abstract

Since monomers in backbone of poly(butylene succinate-co-adipate) (PBSA) are not entirely derived from bio-based sources, limiting its application in the face of increasingly stringent environmental policies. In this study, a novel full bio-based biodegradable random copolyester poly(butylene succinate-co-sebacicate-co-salicylicate) was successfully synthesized. Detailed investigations were conducted on the structural, mechanical, and degradation characteristics resulting from the introduction of salicylicate and sebacicate units. Introduction of salicylicate units effectively enhanced the mechanical performance. In comparison to PBSA, the tensile modulus of copolymer increased by 20.2% with 10% salicylic acid. Introduction of sebacicate units significantly altered the crystalline structure of copolymer and promote the degradation efficiency. Considering both mechanical strength and degradation efficiency, the copolyester with 2% salicylic acid and 20% sebacic acid was found to meet practical application requirements. Relative to PBSA, this copolymer demonstrated a 13.7% increase in tensile modulus and a remarkable 143.1% improvement in degradation efficiency. Importantly, this study focused on the effect of the bio-based rigid monomer salicylic acid and the soft monomer sebacic acid on the degradability of biodegradable polymers. The insights gained provide valuable guidance for tailoring the synthesis of degradable plastics to meet diverse degradation cycle requirements.

Keywords PBSA · Salicylic acid · Sebacic acid · Compost Degradation · Single-use Plastic

Introduction

In recent years, the problem of white pollution caused by non-biodegradable plastic has aroused great attention [1–3]. The natural degradation period of non-biodegradable plastic is estimated over hundreds of years, resulting in continuous hazards to the environment [4]. Bio-based polyester, as an alternative to fossil-based plastic, has attracted extensive research interest due to its excellent biodegradability, biocompatibility and melt processing-properties, which can effectively solve the white pollution problem [5, 6]. These polymers are advantageous in reducing the disposal cost of fossil-based single-use packaging that is associated with landfill and incineration. The biodegradable polymer could decompose and eventually convert to dioxide and water under industrial or home composting conditions. In addition to reducing white pollution, biodegradable polymers from biomass sources could also cut down on the consumption of petroleum resources [7, 8]. Apart from poly(lactic acid) (PLA) [9–11], which were increasingly being used in industry and livelihoods, poly(butylene succinate)(PBS) [12–14], and poly(butylene succinate-co-adipate)(PBSA) [15, 16] are also highly promising candidates with the potential to replace petroleum-based polymers. PBS is a biodegradable aliphatic thermoplastic polyester made from 1,4-butanediol and succinic acid [17, 18]. The mechanical properties of PBS, such as elongation at break and tensile strength are quite comparable to those of polypropylene (PP) and low-density polyethylene (LDPE) [19]. PBSA is a random copolymer obtained from the introduction of adipic acid into

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PBS polymer chain that could improve the biodegradability of PBSA over that of PBS [20–22]. This fact was found to be attributed to its lower crystallinity and polymer chain structure of PBSA [23–25]. Furthermore, to enhance the performance of PBSA or reduce the cost, blending or compounding PBSA with other materials, for example, titanium dioxide [26, 27], graphene oxide [28], organo-modified montmorillonite [29, 30], PLA [31] were widely studied. Although the performance of PBSA can be improved to a certain extent by blending or compounding with filler, its degradation rate also deceases that limits its practical application such as single-use packaging. Therefore, it is always required to find another effective method to improve the performance of PBSA while keeping its good biodegradability.

Introducing phenyl group into biodegradable polyesters could improve its mechanical performance. For example, terephthalic acid has been successfully used to improve the mechanical properties of copolymers [32, 33]. But, most phenyl monomers are rooted in petroleum resources which are increasingly scarce nowadays. If biodegradable polymers can be obtained from biomass sources, it will cut down the consumption and dependence of petroleum resources. Salicylic acid is a kind of aromatic acid containing a hydroxyl group on ortho-position making it can be taken esterification reaction. On the other hand, it is an affordable, non-toxic, bio-based and biodegradable phenolic compound, which is often used as an anti-inflammatory, antioxidant and antimicrobial agent in medicine [34–36]. In agriculture, salicylic acid works as an endogenous signaling molecule in plant growth, and it induces crop growth resistance to damage. It was shown that only a small amount of salicylic acid is sufficient to induce plant growth in agriculture and the released product from salicylic acid-based copolymer was found to be non-toxic [37–39]. These functions make it suitable as a modification agent to prepare single-use plastic [40, 41].

Except for the mechanical properties, degradation behavior is another criterion to these biodegradable polyesters. The increased degradation rate would have great potential for applications in areas that require rapid degradation, such as food waste bags and short-cycle crop mulch. Sebacic acid is a kind of long-chain aliphatic dicarboxylic acid with ten carbon atoms. Sebacic acid can also be found naturally in some plants, such as castor oil [42, 43]. Introducing sebacic acid into the polyesters can decrease its crystallinity which accelerates the biodegradation.

Given that single-use packaging plastics applications require both a fast degradation rate and viable mechanical properties, the two aforementioned bio-based monomers (including salicylic acid and sebacic acid) were introduced into PBSA, and the random biodegradable copolymer poly(butylene glycol butanedioate-salicylic acid-butylene

glycol sebacate-butylene glycol sebacate) was obtained in a two-step process. The effect of introducing salicylic and sebacic acid units on the structure, properties and degradation behavior was investigated in detail by adjusting the monomer ratio. The requirements for processability, mechanical properties and degradability of this bio-based degradable polyester were evaluated in comparison to PBSA to determine its suitability for use as a disposable plastic.

## Experimental Section

Materials

All monomers used to synthesize biodegradable polyesters are bio-based raw materials. Bio-based 1, 4-butanediol (BDO, 99.0%) was purchased from Yuanli Co., Ltd. Bio-based succinic acid (99.0%) was purchased from Land biological technology Co., Ltd. Adipic acid (AA, 99.0%) was obtained from Feiyang and Huafon chemical reagent Co., Ltd, respectively. Sebacic acid (99.0%) was purchased from Jhchem reagent Co., Ltd. Salicylic acid (99.0%) and trimethylolpropane (TMP) were purchased from Damao chemical reagent factory. Tetrabutyl titanate (TBT, 97.0%) and triphenyl phosphate (TPP, 99.0%) were purchased from Weiken and Kingfadashan Co., Ltd, respectively. All reagents were used as received without further purification.

Naming Scheme

For the clarity of expression, emphasis was initially placed on the naming scheme of polymers. 1, 4-butanediol was abbreviated to 'B'; succinic acid was abbreviated to 'S'; salicylic acid was abbreviated to 'Sa'; sebacic acid was abbreviated to 'Se'; meanwhile, abbreviation of each letter correspond the structure unit in polymer chain. For example, PBSSe20%Sa represents the poly(butylene succinate-co-sebacicate-co-salicylate). The percentage following the abbreviation represents the feeding proportion.

Synthesis of poly(butylene succinate-co-adipate-co-salicylate) (PBSASa)

As shown in Scheme 1, the copolymer PBSASa was prepared by a two-step procedure in a 20 L reactor (Polytex, Yangzhou, China). Firstly, all monomers BDO, succinic acid, AA and salicylic acid with a designed ratio were put into the reactor. The molar ratio of acid to alcohol is 1: 1.3, and the molar percentage of AA is always kept at 20% of the total acid. Then the branched crosslinker TMP (0.05% molar ratio) and the heat stabilizer TPP (0.005% molar ratio) were added into the reactor at the same time. The temperature was

Scheme 1 Synthesis route of PBSASa copolymer
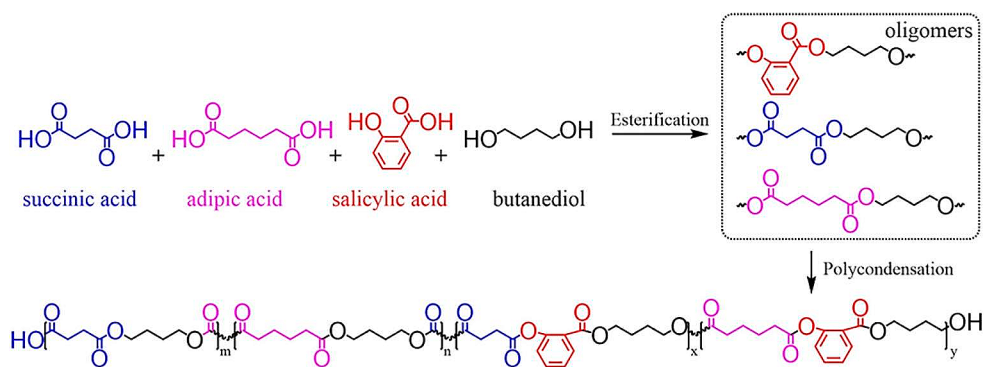
Scheme 2 Synthesis route of PBSSeSa copolymer
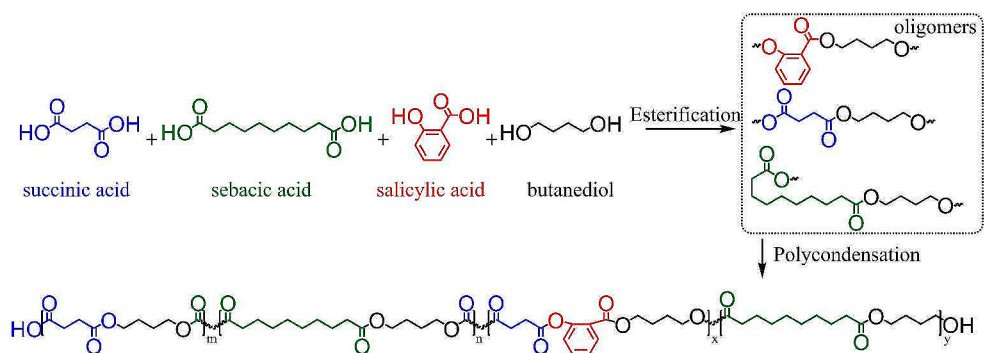
heated to 190°C after the reactor's atmosphere was replaced by nitrogen gas twice. Secondly, monomers are esterified for 3 h with stirring. The reaction generally lasts 4–6 h after the stirring power rises significantly. Finally, the copolymer was removed from the reactor for drawing, cooling and pelletizing. Change the feeding ratio of salicylic acid to 0, 2, 5 and 10% of total acid can prepare a series of copolymers corresponding to PBSA, PBSASa2%, PBSASa5% and PBSASa10%, respectively.

Synthesis of poly(butylene succinate-co-sebacicate-co-salicylicate) (PBSSeSa)

The synthesis of copolymer PBSSeSa is shown in Scheme 2. The process is similar to the synthesis of PBSASa. The molar ratio of acid to alcohol is 1: 1.3, and the molar percentage of salicylic acid is always kept at 2% of the total acid. But the long-chain aliphatic acid was used sebacic acid instead of AA. Firstly, all monomers BDO, succinic acid, sebacic acid and salicylic acid with a designed ratio were put into the reactor. Then the branched crosslinker TMP (0.05% molar ratio) and the heat stabilizer TPP (0.005% molar ratio) were added into the reactor at the same time. The temperature was heated to 190°C after the reactor's atmosphere was replaced by nitrogen gas twice. Secondly, the monomers were conducted by esterification reaction under well stirring for 3 h. As the esterification finished, catalyst TBT (0.1% molar ratio) was added into the reactor, and the vacuum system was activated, the temperature was

raised to 230°C for 1 h, further raised to 245°C. The polycondensation reaction generally lasts 4–6 h, the reaction can stop when observing the stirring power rise significantly. Finally, the copolymer was removed from reactor for drawing, cooling and pelletizing. By altering the feeding amount of sebacic acid to 20, 35 and 50% of total acid, a series of copolymers corresponding to PBSSe20%Sa, PBSSe35%Sa, PBSSe50%Sa can be synthesized, respectively.

Preparation of Polyester Plate

The particles obtained by polymerization were made into $100 \times 100 \times 2.5$ mm plates at 160 °C. The plate was directly used for rotational rheology and compost degradation tests. In addition, the plate was cut into 4 mm wide and used for stress-strain testing.

Characterization

The molecular weight of copolymers was measured by gel permeation chromatography (GPC, WATERS) equipped with ACQUITY APC equipment. Tetrahydrofuran was used as the mobile phase, the injection volume was 10 μL, the column temperature was set as 40°C, and the running time was 15 min.

The hydrogen chemical shift was recorded by ^{1}H NMR spectrometer (BRUKER AVANCE 500), all tested samples were dissolved in deuterated chloroform (CDCl$_3$), and tetramethylsilane (TMS) was used as an internal reference.

The thermal decomposition behavior of copolymers was recorded by thermo gravimetric analyzer (TGA, NETZSCH TG209 F3). All samples were tested ranging from 30 to 800°C (with 20°C/min heating rate) under N_2 atmosphere.

The thermal transition was analyzed by differential scanning calorimetry (DSC, NETZSCH DSC215) with a standard heating-cooling-heating mode from 20 to 110°C (with 1 °C/min heating rate).

The FTIR spectrum of samples was recorded using a Thermo Scientific Nicolet IS20 infrared spectrometer with 16 scans per spectrum at a resolution of 2 cm^{-1}.

Polarized optical microscopy (POM) equipped with a hot stage was used to examine the nucleation behavior of copolymers.

Powder X-ray diffractograms were obtained using an Axio Scope A1 X-ray diffractometer (ZEISS) employing CuKα radiation (λ = 1.54056 Å) with a setting of 30 kV and 20 mA. The samples were analyzed from 5° to 50° (2θ) with a scanning speed of 0.5°/min.

Tensile strength, modulus and elongation-at-break of copolymers were determined and carried out using CMT4104 tester (SASTest Corporation) with a single strain rate of 50 mm/min at room temperature.

Melt flow rate (MFR) measurements were done according to ISO 1133 with the melt flow device (Zwick/Roell) under load of 2.16 kg. The copolymer specimen (5–10 g) was heated at 190°C for 240 s.

Intrinsic viscosity was recorded using Ubbelohde viscometer according to the DIN 53,728. The specimen must be completely dissolved before the test (concentration 5 mg/mL, volume 50 mL, temperature 25 ± 0.05 °C).

Dynamic viscoelastic spectra were recorded by Discovery HR-2 rheometer (TA instruments). The samples were loaded into the rheometer and equilibrated for 5 min at 120°C. Then strain sweep experiments were performed at strain 1.0% with a shear rate ranging from 0.01 to 100 Hz.

Compost degradation measurements were done in a simple self-designed oven (100 L) at constant temperature (58 ± 2°C) and humidification (50 ± 5%RH) according to DIN 13,432. All samples were buried in standard compost soil. Mass ratio of compost soil to waste vegetables is 1:1. Urea (0.4%) was used to regulate compost soil the pH value at the same time.

After degradation, the surface morphology of samples was studied using a scanning electron microscopy (SEM) device S-3400 N (HITACHI) with an accelerating voltage of 3 kV. The surface of the sample was sputter coated with a gold/palladium alloy to improve conduction and avoid charging.

Results and Discussion

Synthesis and Characterization

The copolymer was synthesized through esterification and polycondensation. Adjusting the monomers ratio, a series of polyester with different structural units could be obtained. The chemical structure of these copolymers was analyzed by ^{1}H NMR. The spectroscopy of selected copolymers PBSA, PBSASa2% and PBSSe20%Sa were shown in Fig. 1. Typical signals and corresponding assignments are signed in the spectra. The chemical shift of -O-CH$_2$- (a) and -CH$_2$- (d) in butylene unit appeared at 4.12 ppm and 1.70 ppm, respectively. The chemical shift of -CH$_2$- (b) in succinate unit located at 2.63 ppm, and peaks of 2.33 ppm and

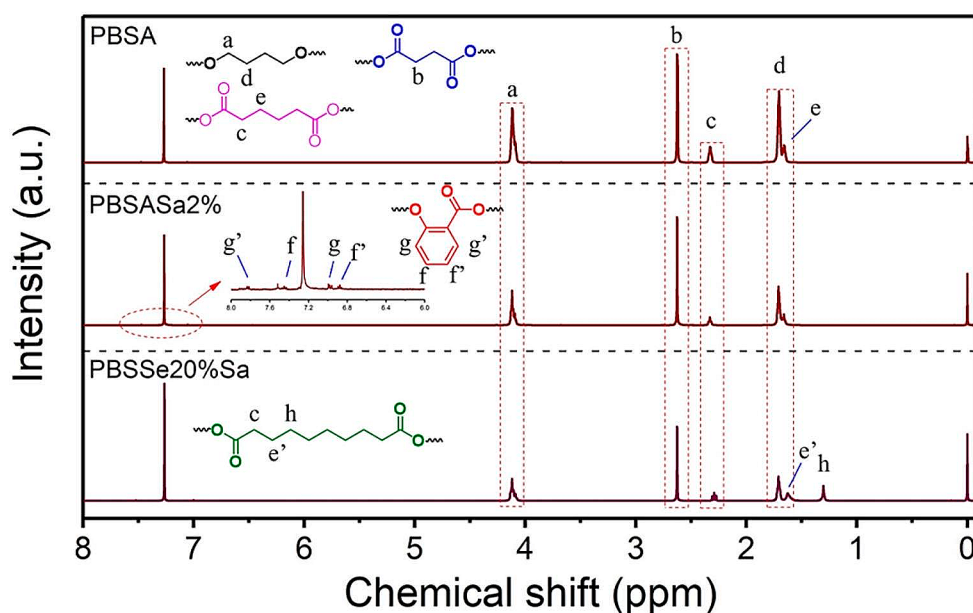**Fig. 1** ^{1}H NMR spectra of copolymers PBSA, PBSASa2% and PBSSe20%Sa.

Table 1 The molecular weight of copolymers

No.	Material	$M_n(g \cdot mol^{-1})$	$M_w(g \cdot mol^{-1})$	M_w/M_n
1	PBSA	52,250	89,792	1.72
2	PBSASa2%	61,305	97,602	1.59
3	PBSASa5%	42,704	77,590	1.82
4	PBSASa10%	46,470	75,402	1.62
5	PBSSe20%Sa	46,338	74,561	1.61
6	PBSSe35%Sa	48,890	77,440	1.58
7	PBSSe50%Sa	44,872	74,449	1.66

1.66 ppm were assigned to -CO-CH$_2$- (c) and –CH$_2$- (e) in adipate unit, respectively (Fig. 1 top). It can be seen from a slight difference between PBSA and PBSASa2% ^{1}H NMR spectroscopy, new signals at 6.97 ppm (g), 7.03 ppm (g'), 7.46 ppm (f') and 6.89 ppm (f) can attribute to hydrogen of benzene ring in salicylicate unite (Fig. 1 middle and Figure S1). In PBSSe20%Sa ^{1}H NMR spectroscopy, it is clear that the chemical shift at 1.30 ppm can be attributed to the intermediate -CH$_2$- in sebacicate unit (Fig. 1 bottom and Figure S2).

The molecular weight (M$_n$ and M$_w$) and polydispersity index (PDI = M$_w$/M$_n$) of copolymers were listed in Table 1. As the molar ratio of salicylic acid increased, the molecular weight of PBSASa copolymer decreased. This phenomenon may be attributed to the larger steric hindrance of salicylic acid compared to aliphatic acid, making challenging to achieve polyester with a higher molecular weight. Conversely, as the molar ratio of sebacic acid increased, the molecular weight of the PBSSeSa copolymer showed no significant change, suggesting that the reactivity of sebacic

acid is comparable to that of adipic acid or succinic acid. The successful synthesis of copolymers was corroborated by the results of ^{1}H NMR and GPC characterizations.

Thermal Properties of Copolymers

The TG and DSC curves of copolymers were shown in Fig. 2. The initial thermal decomposition temperature of the PBSASa copolymer decreased with the rise of the salicylic acid molar content. As the molar ratio salicylic acid increase to 10%, the temperature at 5% weight loss (T$_{5\%}$) of PBSASa decrease from 370.6 to 336.7°C (Fig. 2a and Table S1). This phenomenon could be attributed to the instability of the ester bond adjacent to the benzene ring structure of salicylic acid, which undergoes rapid decomposition at elevated temperatures (above 300°C). At low temperature (below 100°C), the addition of salicylic acid has promoted the melting temperature (T$_m$) of PBSASa copolymers. Especially, compared with pure PBSA, T$_m$ of PBSASa2% has significantly increased from 88.6 to 93.8°C, implying that benzene ring structure in salicylic acid unites restricted the movement of the chain segment (Fig. 2b, c and Table S1).

As shown in Fig. 2d, with the increase of sebacic acid, T$_{5\%}$ was elevated from 353.2 to 364.0 °C. Normally, the thermal decomposition of polyester starts from an ester bond. The sebacic acid possesses a longer carbon chain, its addition reduces the proportion of ester groups in copolymer, resulting in an improvement in the initial thermal properties. It can be seen from Fig. 2e-f, that the thermal
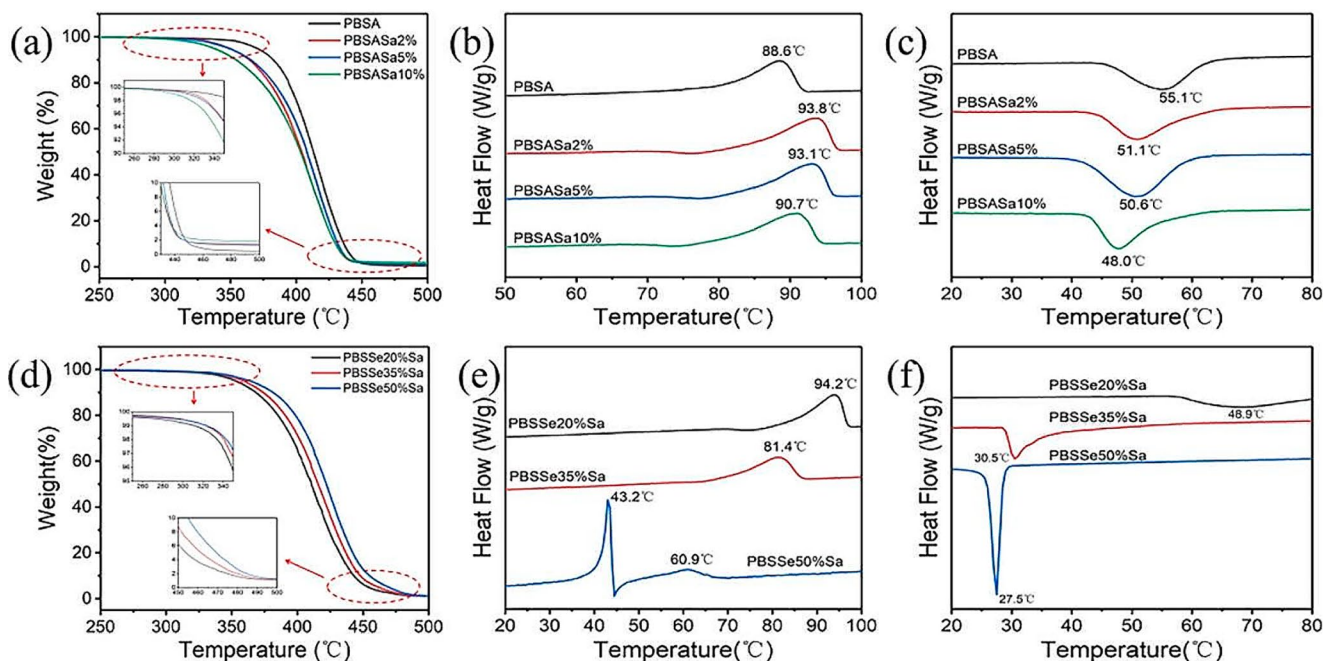

Fig. 2 (**a**) TGA curves, (**b**) DSC heating curves of PBSASa copolymers and (**c**) DSC cooling curves. (**d**) TGA curves, (**e**) DSC heating curves of PBSSeSa copolymers, and (**f**) DSC cooling curves

transition behavior of copolymers strongly depends on the molar content of sebacic acid. T_m of PBSSeSa copolymers varied from 94.2 °C to 60.9/43.2 °C, and T_c also rapidly decreased from 48.6 °C to 27.5 °C, indicating that the soft chain structure of sebacic acid unit had a decisive influence on the movement of the chain segment and crystallization.

As shown in Fig. 3, the crystal structure of copolymers was evaluated by XRD and POM. The peaks of 19.5°, 21.7°, 22.5° and 28.9° were attributed to the crystal planes of (020), (021), (110), (111) in PBSA, respectively [44]. There was no movement of the position of peaks with increasing salicylic acid molar content, demonstrating that the introduction of salicylic acid did not change the spherical crystal structure.To further investigate the crystallization, the process of crystal growth at constant temperature was studied using POM. All copolymers showed similar nucleation behavior. It can be seen that the nucleation rate of PBSA was faster than that of PBSASa2% at 70°C for 10 min. The nucleation rate of PBSASa copolymers decreaseD as the increase of salicylic acid, this result was following the trend of the cooling crystallization curve in DSC. Compared with PBSA, copolymers PBSASa exhibit some big spherical crystals therefore require more heat to melt [45]. This may be the reason why the melting temperature of PBSASa copolymers was higher than that of PBSA in DSC heating curves.

For PBSSe20%Sa copolymers, with sebacic acid substituted for 20% molar content AA, was still able to crystallize at 70°C. While further increasing the molar ratio of sebacic acid, the obtained PBSSe35%Sa can't crystallize at 70 °C, and only a small amount of spherical crystal nuclei was generated after lowering the temperature to 50°C. In addition, PBSSe50%Sa can't even complete crystallization at 50 °C, but it was rapidly hardening and shaping at 30°C without any crystal. This phenomenon was following the trend of the cooling crystallization curve in DSC and XRD curves, indicating that with the introduction of monomers with long carbon chains such as sebacic acid, the chain segments become softer and the proportion of ester bond decreases significantly, which causes a significant change in the crystallization properties.

Rheological and of Copolymers

The melt flow behavior of copolymers was evaluated according to ISO1133. MFR and intrinsic viscosity were listed in Table 2. With increasing molar content of salicylic acid, MFR of copolymers varied 5.24 to 61.98 g/10min, and intrinsic viscosity decreased significantly from 1.6122 to 1.1791 dL/g. The MFR and intrinsic viscosity trend of PBSSeSa is similar to that of PBSASa. With increasing molar content of sebacic acid, the MFR varied 32.3 to 70.18 g/10min, and intrinsic viscosity decreased from 1.3197 to 1.1655 dL/g.

Melt flow behavior in the processing and structure influence of copolymers was confirmed by rheological tests. As shown in Fig. 4a-c, with increasing salicylic acid, the storage modulus (G') and loss modulus (G") increase

Fig. 3 XRD analysis of copolymer (**a**) PBSASa and (**b**) PBSSeSa. (**c**) Polarizing optical micrographs of copolymer (specimens from left to right are PBSA, PBSASa2%, PBSASa5%, PBSASa10%, PBSSe20%Sa, PBSSe35%Sa and PBSSe50%Sa, respectively) at different time (top: 10 min, middle: 30 min and bottom: 60 min; test temperature: from PBSA to PBSSe20%Sa 70°C, PBSSe35%Sa 50°C, PBSSe50%Sa 30°C)
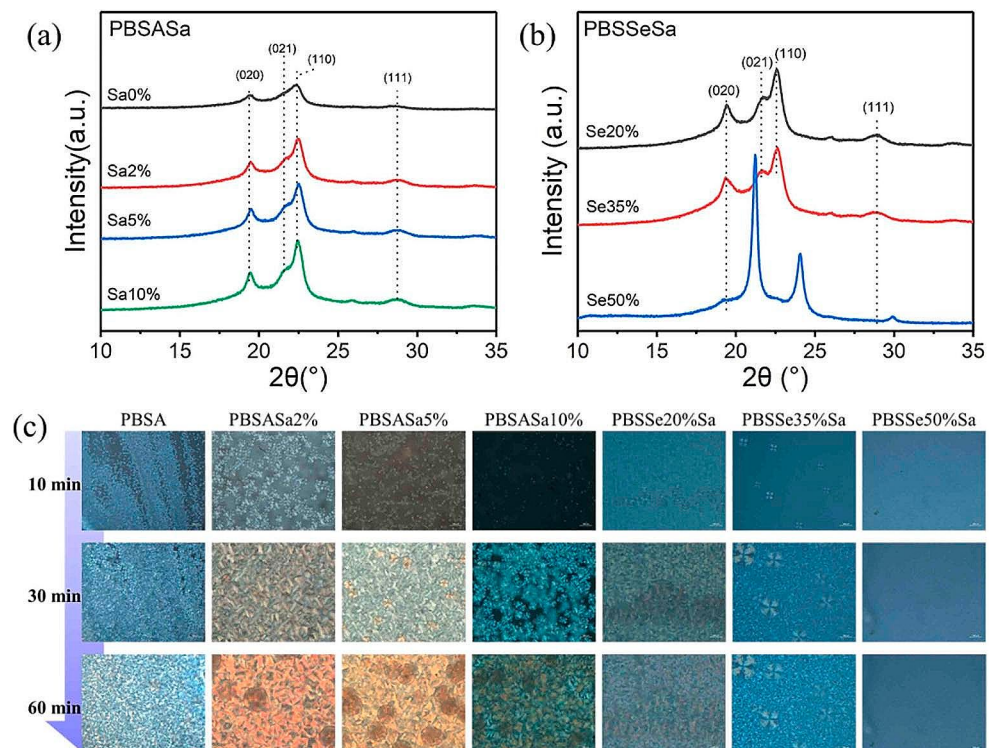
Table 2 MFR and intrinsic viscosity of copolymers

No.	Material	Average value of MFR (g/10min)	Average value of intrinsic viscosity (dL/g)
1	PBSA	5.24	1.6122
2	PBSASa2%	22.74	1.4015
3	PBSASa5%	33.98	1.3008
4	PBSASa10%	61.98	1.1791
5	PBSSe20%Sa	32.30	1.3197
6	PBSSe35%Sa	41.80	1.2934
7	PBSSe50%Sa	70.18	1.1655

and complex viscosity (η) decrease especially in the low-frequency region. This may be because the polymerization degree of PBSASa copolymer decreased by the addition of salicylic acid, and the benzene ring structure weakened the movement of molecular chains, leading to the reduction of the entanglement between molecular chains. As shown in Fig. 4d-f, with introducing sebacic acid, the G' and G'' and η trend of PBSSeSa is similar to that of PBSASa, but the variation is smaller. The introduction of sebacic acid altered the molecular flexibility, without a reduction in the entanglement between molecular chains.

Mechanical Properties of Copolymers

As shown in Fig. 5a; Table 3, the addition of salicylic acid improved the yield strength, while the elongation at break decreased obviously. The tensile strength of PBSASa copolymers varied from 14.52 to 16.95 MPa with the molar ratio of salicylic acid increasing from 0 to 10%. However, the elongation at break decreased rapidly from 333.1 to 123.27% due to the rigid structure of the benzene has been introduced into the copolymer main chain.

As shown in Fig. 5b; Table 3, with increasing sebacic acid molar ratio, by the benefit of its flexible long aliphatic carbon chain, the elongation of PBSSeSa has been improved. Compared with PBSSe20%Sa and PBSSe50%Sa, the elongation at break increased from 200.2 to 400.8%. Due to the larger ratio introduction of sebacic acid, the PBSSe50%Sa shows being like an elastomer. The tensile strength and modulus of copolymer decrease. As the molar ratio of sebacic acid increased from 20 to 50%, the tensile strength and tensile modulus decreased respectively from 16.51 MPa to 5.24 MPa and from 204.5 MPa to 73.3 MPa.

Compost Degradation of Copolymers

Degradation performance was evaluated by industrial composting test, and degradation behavior of various copolymers was recorded by photograph (Fig. 6). All specimens were put into the compost soil (Figure S3), and after 4 weeks, copolymers showed different degrees of degradation. The surface of copolymers appeared to cracks evidenced by SEM image (Fig. 7a-g). Comparing the molecular weight of the copolymers before and after degradation, it is clear molecular weight of all copolymers had dramatically decreased (Fig. 7h, I and Table S2).
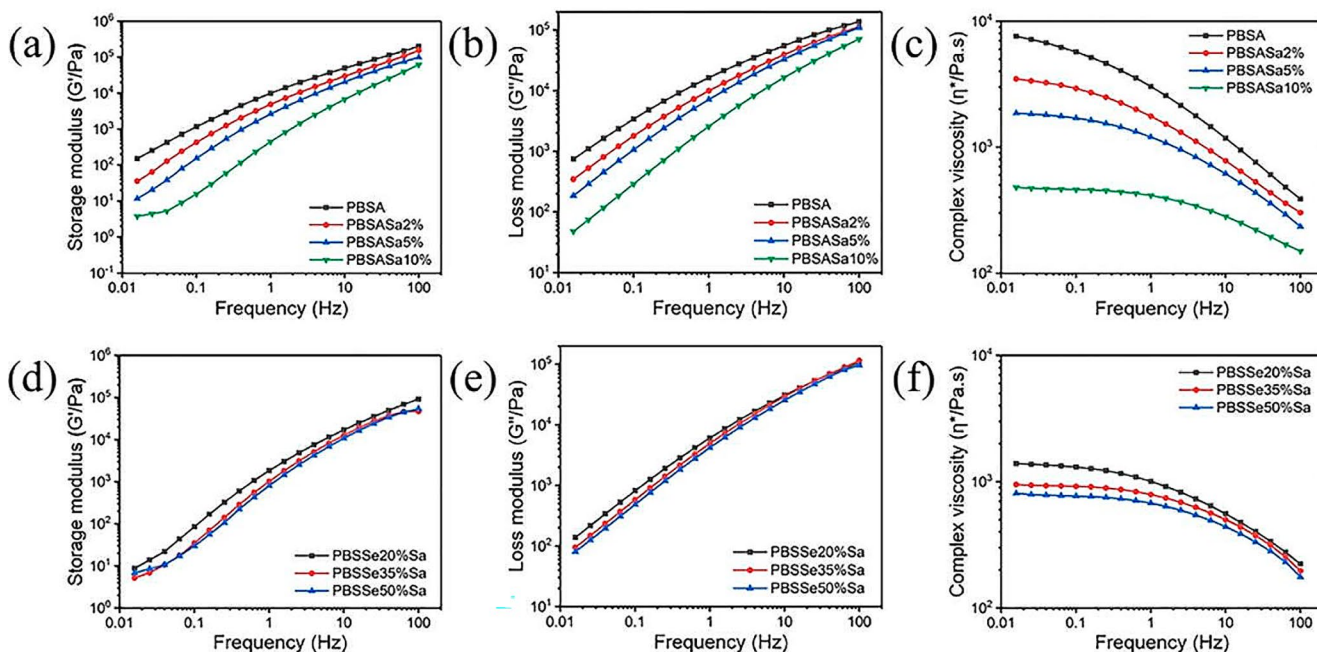

Fig. 4 Rheological properties of copolymers: (**a**) storage modulus (G'), (**b**) loss modulus (G''), (**c**) complex viscosity (η) of copolymer PBSASa. (**d**) storage modulus (G'), (**e**) loss modulus (G''), (**f**) complex viscosity (η) of copolymer PBSSeSa

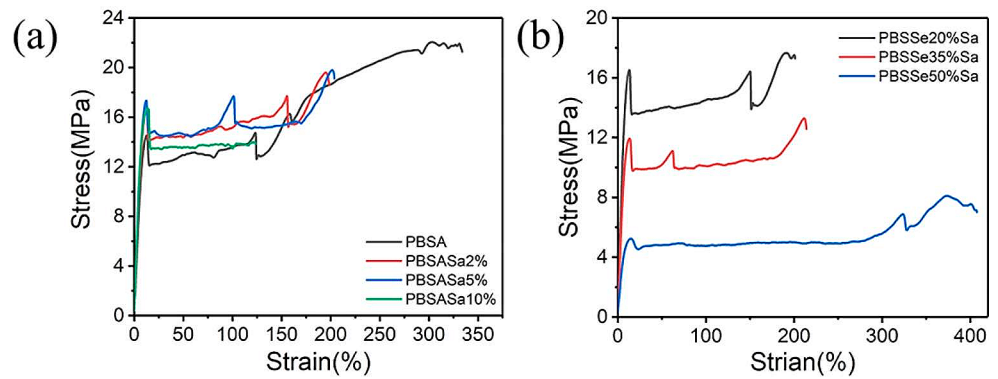**Fig. 5** Stress-Stain curves of (**a**) PBSASa and (**b**) PBSSeSa copolymers

Table 3 Tensile test data of copolymers

No.	Material	σ^a_{yield} (MPa)	ε^b_{yield} (%)	σ_{break} (MPa)	ε_{break} (%)	E (MPa)	D_{std}
1	PBSA	14.52	12.68	21.91	331.1	180.0	0.350
2	PBSASa2%	16.74	12.40	19.59	194.9	204.1	0.142
3	PBSASa5%	17.32	12.10	19.79	210.6	221.5	0.288
4	PBSASa10%	16.73	13.87	12.86	123.27	213.7	0.582
5	PBSSe20%Sa	16.51	13.1	17.51	200.2	204.5	0.288
6	PBSSe35%Sa	11.93	13.3	13.28	211.6	153.6	0.334
7	PBSSe50%Sa	5.24	15.3	7.54	400.8	73.3	0.652

σ: stress; ε: strain; E: modulus; D_{std}: standard deviation

Fig. 6 Appearance photograph of copolymers (from left to right are PBSA, PBSASa2%, PBSASa5%, PBSASa10%, PBSSe20%Sa, PBSSe35%Sa and PBSSe50%Sa, respectively) at different degradation stage (from top to bottom are 0, 1, 2, 3, 4 week, respectively)
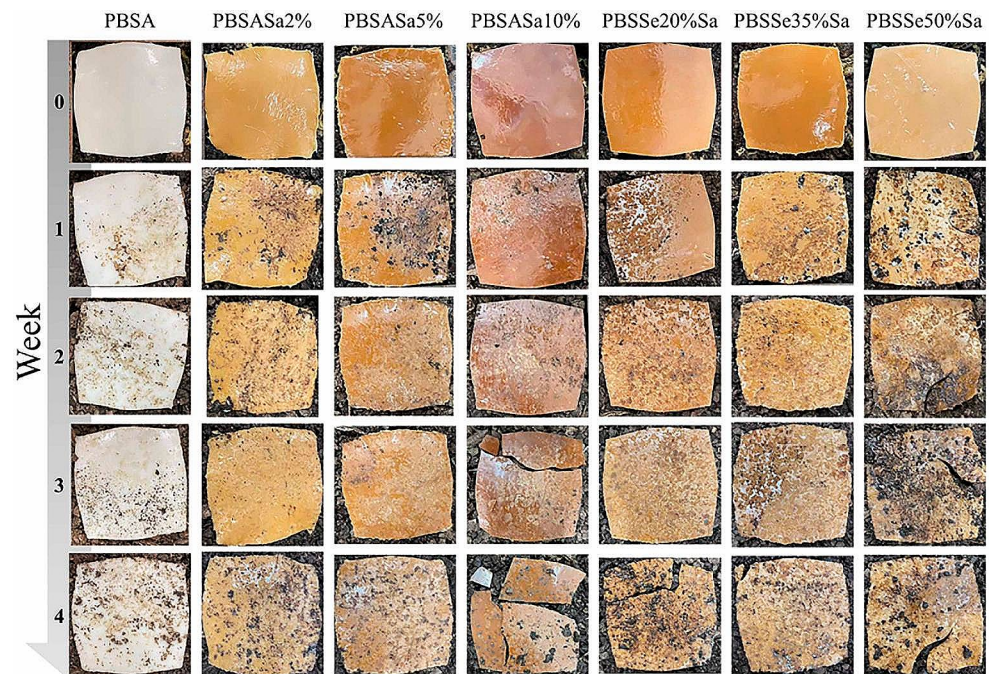
To quantify the degradation ratio of these copolymers, the weight loss was calculated according to Eq. (1):

$$W_l = \frac{m_i - m_r}{m_i} \qquad (1)$$

W_l: weight loss, %; m_i: initial mass, g; m_i: residual mass, g. As shown in Fig. 7j, the presence of benzene ring structure in copolymer chain will weaken the degradation rate. Compared with PBSA, the weight loss of PBSASa10% copolymer has reduced from 5.8 to 3.7%. The crystallization is another affecting factor for the copolymer degradation behavior. Observed by SEM image, the degradation is firstly occurred in amorphous regions. There were a few cracks that appeared in the crystallization region due to its compactness being greater than the amorphous region,

indicating insufficiency degradation. In other words, PBSASa possesses many large spherical crystals, which are more difficult to degrade than small spherical crystals. This phenomenon is consistent to with degradation weight loss curve.

The addition of sebacic acid can significantly accelerate the rate of compost degradation (Fig. 7j and Table S3). When sebacic acid was introduced to replace succinic acid and accounted for 20% of the total acid ratio, the weight loss of PBSSe20%Sa copolymer reached 14.1% after the fourth-week degradation, which was 6.0% higher than that of PBSASa%. Further, by increasing the molar ratio of sebacic acid to 50%, the weight loss reached 22.1%. It can be seen that a lot of craters appeared on the surface of copolymers after the fourth week of degradation (Fig. 7e-g). The presence of sebacic acid has reduced the crystallinity of copolymers, and the amorphous region tends to degrade prior to crystallization region, so the degradation weight loss rate of PBSSeSa is much higher than PBSASa copolymers. On the other hand, observed by SEM, a significant degradation occurred in the amorphous region, leaving deep grooves, and even the inner spherical crystals region of PBSSe20%Sa and PBSSe35%Sa were degraded with cracks, suggesting that the degradation progress has transitioned from the amorphous region to the crystalline region. In contrast, no spherical crystals were observed in PBSSe50%Sa, and generating deeper grooves than PBSSe20%Sa and PBSSe35%Sa after degradation, which was in accordance with the results of XRD, POM, and DSC test. FITR was carried out to analyze the structure change during degradation, as shown in Figure S4. It can be seen that C=O peak at 1712 cm^{-1}, which was attributed to the ester bond, obviously weakened after compost degradation. According to previous conclusions,

degradation occurs preferentially in the amorphous region. Furthermore, degradation in the amorphous region occurs first in the breakdown of the ester bonds, particularly the weakly stable ones.

Conclusion

Novel full bio-based biodegradable aliphatic-aromatic random copolymers PBSSeSa were synthesized successfully. The steric hindrance effect of salicylic acid resulted in lower molecular weight copolymers. The mechanical performance of copolymer was enhanced by introduction salicylate unit. Compare with PBSA, the tensile modulus of copolymer increased by 20.2% with the addition of 10% salicylic acid. The thermal decomposition temperature ($T_{5\%}$) of copolymer decreased from 370.6 to 336.7°C as the molar ratio of salicylic acid increased to 10%. Although the introduction of salicylate units had a minor effect on the crystallinity degree of copolymer, the nucleation rate decreased. On the other hand, the softer and longer chain structure of sebacic acid altered the crystalline behavior of copolymer, facilitating degradation. With the addition of excess sebacic acid (e.g., 50%), the spherocrystal structure of copolymer disappeared, transforming it from a plastic to an amorphous elastomer. Considering mechanical strength and degradation efficiency, the copolyester with 2% salicylic acid and 20% sebacic acid could satisfy the practical application. Compare with PBSA, the tensile modulus and degradation efficiency has increased by 13.7% and 143.1%, respectively. Depending on different application scenarios, copolyesters with different varying mechanical strength and degradation rate could be obtained by adjusting the proportions of

Fig. 7 SEM images of (**a**) PBSA, (**b**) PBSASa2%, (**c**) PBSASa5%, (**d**) PBSASa10%, (**e**) PBSSe20%Sa, (**f**) PBSSe35%Sa and (**g**) PBSSe50%Sa copolymers after compost degradation for four weeks, respectively. Molecular weight distribution curves of (**h**) PBSASa and (**i**) PBSSeSa copolymer (black and red curves represent before and after compost degradation for four weeks, respectively). (**j**) Compost degradation weight loss rate of copolymers
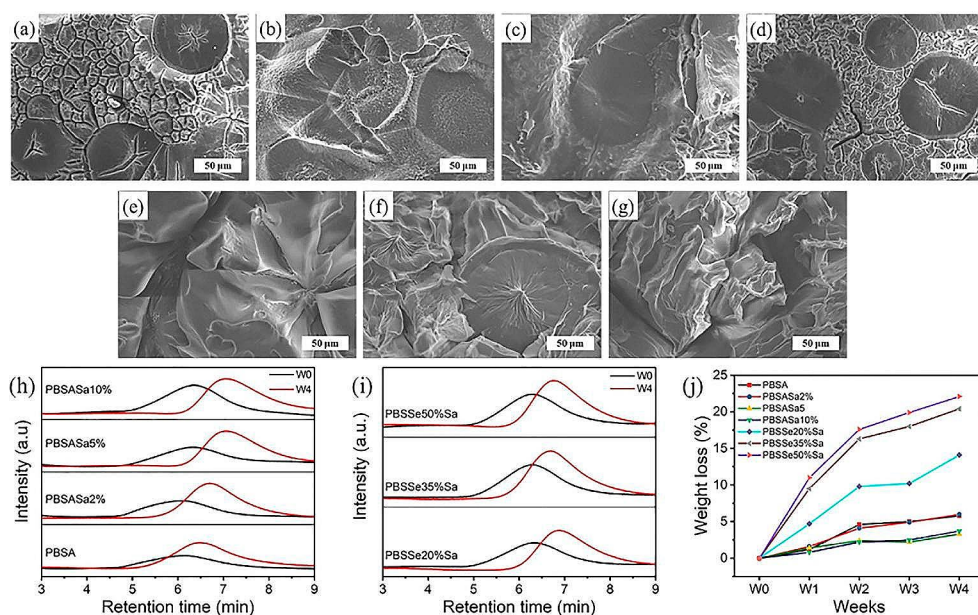
salicylic acid and sebacic acid. This research is expected to provide a generally applicable for the rational design and preparation of high-performance full bio-based biodegradable polyester plastic towards commercial applications.

Author Contributions Qiang Fu and Jianjun Li supervised the whole project. Yezhong Chen conceived the experiments. Kaijin Mai assisted characterization of materials. Yezhong Chen wrote the manuscript. Kaibo Pan proofread the manuscript. All authors commented on the paper.

Declarations

Competing Interests The authors declare no competing interests.

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