

A new biodegradable copolyester poly(butylene succinate-co-ethylene succinate-co-ethylene terephthalate)

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Abstract

To obtain a biodegradable polymer material with satisfactory thermal properties, higher elongation and modulus of elasticity, a new copolyester, poly(butylene succinate-co-ethylene succinate-co-ethylene terephthalate) (PBEST), was synthesized via direct polycondensation from three prepolymers of butylenes succinate, ethylene succinate and ethylene terephthalate (ET). The resulting copolyesters, PBEST, were characterized by ¹H-NMR, DSC, TG and WAXRD, and their melting temperature (T_m), melting heat of fusion (ΔH_m), glass-transition temperature (T_g), and thermal decomposition temperature (T_d) (1.5 wt%) were obtained. Compared to poly(butylene succinate-co-ethylene succinate) (PBES), PBEST has improved thermal properties such as higher T_m and T_d due to the incorporation of poly(ethylene terephthalate) unit into the main chains of copolyesters, but very low crystallization speeds. The degradation test of copolyesters in a compost condition shows that the degradability of PBEST is as a function of content of ET.

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1. Introduction

Recently, the amount of industrial and municipal waste has increased all over the world. Therefore, the design and development of materials capable of being degraded into safe components under specific environmental conditions have become increasingly important. Consequently, a recent trend in polymer research is focused on the development of a wide range of biodegradable polymer products with a predetermined lifetime [1–6].

Most of the synthetic biodegradable polymers are aliphatic polyesters such as poly(ϵ -caprolactone) (PCL),

poly(L-lactic acid) (PLLA), poly(3-hydroxybutyrate) (PHB), and poly(butanediol succinate) (PBS) [7–9]. Unfortunately, the application field of aliphatic polyesters in industry and agriculture were greatly limited because of their high cost and poor physical and mechanical properties. On the other hand, aromatic polyesters such as poly(ethylene terephthalate) (PET) possess excellent physical and mechanical properties and low cost compared with aliphatic polyesters, but they are very resistant to bacterial or fungal attack, and hence do not biodegrade under normal environmental conditions. Therefore, in order to obtain lower cost biodegradable polymers with both satisfactory physical properties and biodegradability, some researchers have aimed at the synthesis of copolyesters composed of aliphatic and aromatic units. Park and Cho [10] prepared

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a new type of biodegradable copolyester, poly[(butylene succinate)-co-(butylene terephthalate)]-b-poly(tetramethylene glycol), which had the improved elongation properties and elasticity. The toughness and breaking strain of the copolymers increased with increasing poly(tetramethylene glycol) content. Müll et al. [11] prepared a copolyester with low molecular weights using 1,4-butanediol and terephthalic acid and conducted the biodegradability experiment with compost test, surprisingly demonstrating that the copolyester still had biodegradability when the average sequence block was less than three. Witt et al. [12] synthesized copolyesters containing aromatic unit and showed that the copolyesters could be thoroughly biodegraded by microorganism under the compost conditions when the average sequence length of aromatic unit is more than three but its weight content is below 9%.

In this work, we report the preparation and properties of a new copolyester, poly(butylene succinate-co-ethylene succinate-co-ethylene terephthalate) (PBEST) for the first time. PBEST was prepared via direct polycondensation from three prepolymers of butylenes succinate (BS), ethylene succinate (ES) and ethylene terephthalate (ET). Poly(butylene succinate-co-ethylene succinate) (PBES) is an aliphatic copolyester and has excellent elongation behavior and biodegradability at a certain composition; in particular, its elongation at break is around 1200% when PBES contains 78 mol% of PES and 22 mol% of PBS [13]. At present, PBES copolyester has been produced for cable coating due to its low cost and easy processing properties. On the other hand, PET is a kind of widely used aromatic polyester with excellent tensile strength and thermal properties but weak biodegradability. In order to obtain a kind of low cost biodegradable polymer material with satisfactory thermal properties, higher elongation and modulus of elasticity, the molar ratio of PES/PBS in the copolyester PBEST of poly(butylene succinate-co-ethylene succinate-co-ethylene terephthalate) was controlled at around 78/22 (mol/mol) and the ratio of PET to the two prepolymers (PES and PBS) was changed, so that the new material synthesized was expected to keep a high elongation at break. Meanwhile, compared with the PBES reported previously [13], it was expected that copolyester PBEST would have better thermal and mechanical properties, such as higher melting point and modulus of elasticity than PBES due to

the incorporation of prepolymer PET into the copolyesters. The biodegradability of the copolyesters was tested by composting under a simulated municipal solid-waste (MSW) aerobic compost environment.

2. Experimental

2.1. Materials

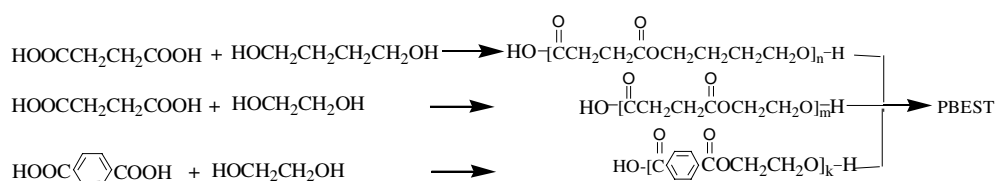
Succinic acid (SA, AR grade), 1,4-butanediol (1,4-BD, AR grade), ethylene glycol (EG, AR grade) and terephthalic acid (TPA, industrial grade) were purchased from Kelong Chemical Co. (Chengdu, China) and used without further purification. Titanium (IV) butoxide (AR grade) as catalyst was obtained from the Third Shanghai Reagent Plant (Shanghai, China).

2.2. Synthesis of prepolymers

Succinic acid (78.3 g, 0.66 mol) and 1,4-butanediol (63 g, 0.69 mol) were charged into a 250 ml three-necked flask equipped with a mechanical stirrer, a nitrogen inlet, and a distillation column. The esterification reaction was carried out at 200 °C under a nitrogen flow for 3 h with continuous removal of the released water, and then the prepolymer of PBS was obtained. The same process was applied for the synthesis of the prepolymer of PES, i.e. Succinic acid (75 g, 0.64 mol) and ethylene glycol (40.9 g, 0.66 mol) reacted at 190 °C for 5 h. For the synthesis of the prepolymer of PET, terephthalic acid (162 g, 1 mol) and ethylene glycol (81 g, 1.3 mol) were charged into a 5 l reactor, and the reaction temperature and pressure were kept at 190 °C and at 5 MPa, respectively, for 3–4 h.

2.3. Synthesis of copolyesters

The copolymers described in this work were prepared according to the synthetic route depicted in Scheme 1. First, the prepolymer of PET was charged to a three-necked flask and fully melted at 243 °C under the protection of nitrogen flow and agitation. Afterwards the blends of prepolymers of PES and PBS at a counted molar ratio were charged into the flask. The catalyst of $\text{Ti}(\text{BuO})_4$ was added 10 min later, then the reaction



Scheme 1. Synthetic route of random copolyesters of poly(butylene succinate-co-ethylene succinate-co-ethylene terephthalate).

was performed at 235 °C under a vacuum of 0.5 mmHg for 3–8.5 h.

2.4. Measurements

2.4.1. $^1\text{H-NMR}$

The compositions of copolyesters were determined by proton nuclear magnetic resonance (NMR) in CDCl_3 solvent using a Varian Gemini 400 MHz NMR spectrometer. The concentration of each sample was about 5 wt% in the solvent.

2.4.2. Intrinsic viscosity

Intrinsic viscosity was measured by an Ubbelohde viscometer in CHCl_3 at 20 ± 0.1 °C.

2.4.3. DSC

Heat histories of samples were removed and they were kept at ambient temperature for days to allow their crystallization to approach the equilibrium state prior to the DSC characterization. DSC measurements of copolyesters were carried out on a Nithids differential scanning calorimeter equipped with a liquid nitrogen cooling system under a nitrogen flow at a rate of 40 ml/min. The samples of about 8–10 mg were encapsulated in the DSC aluminum pans and then thermally treated. DSC thermal diagram was recorded at the heat speed of 10 °C/min from -70 to 170 °C, and glass-transition temperature T_g , melting point T_m , and heat of fusing ΔH_m were determined from the endothermic curves.

The samples PBEST10 and PBEST60, which are listed together with other samples in Table 1, were encapsulated in the DSC aluminum pans, respectively, then heated to 200 °C and held for 3 min to make the

samples melted completely. The melt samples were cooled to -70 °C at a cooling speed of 10 °C/min, and the crystallization temperature was recorded.

2.4.4. TGA

Thermal gravimetric traces of the prepared samples were also measured to assess their thermal stabilities. TGA (Dupont 2100) diagrams were recorded from 50 to 500 °C at a scanning rate of 10 °C/min under an atmosphere of dry nitrogen, thus a temperature T_d (-1.5 wt%) at which 1.5 wt% of original weight of a sample was lost due to its decomposition, was tentatively applied as an index to characterize its thermal stability.

2.4.5. WAXD

Wide-angle X-ray diffraction (WAXD) for typical samples was measured using an X-ray diffractometer (Philips) with $\text{Cu K}\alpha$ radiation.

2.4.6. Biodegradation

The biodegradability test by composting on a laboratory scale was conducted on the basis of ASTM D5338, which is a standard test method for determining weight loss from plastic materials exposed to a simulated MSW aerobic compost environment. MSW consisted of 28.5% shredded leaves, 11.75% shredded newspapers and computer papers (1:1), 3.85% cow feces, 4.8% meat waste (mixture of dog and cat food in a ratio of 1:1), and 12.8% food waste (mixture of freezing peanut, *Zea mays* and carrot in a ratio of 1:1:1), 31% distilled water, 2.35% wood meal, 1.2% glass bead, 1.3% urea, and 1.0% compost seed. This mixture has a C/N ratio of 20–30. The moisture content was controlled to be around 60% and the pH of the compost was above 7.0. The airflow was

Table 1
Composition, syntheses and microstructure of PBEST copolyesters

Polymer	Feed molar ratio ^a	Composition ^b	$[\eta]^c$	Reaction time (h) ^d	$n_{\text{ET}}/n_{\text{ES}}/n_{\text{BS}}^e$
PET	100/0/0	100/0/0	0.07	–	–
PES	0/100/0	0/100/0	0.05	–	–
PBS	0/0/100	0/0/100	0.08	–	–
<i>Copolyester^f</i>					
PBEST0	0/78/22	0.0/76.1/23.9	0.62	8.5	0.0/10.6/3.4
PBEST10	10/70.2/19.8	9.5/67.9/22.5	0.77	6.5	1.2/11.1/7.4
PBEST20	20/62.4/17.6	19.0/60.9/20.1	0.69	4.5	1.5/6.1/7.3
PBEST30	30/54.6/15.4	28.3/54.7/17.0	0.71	4.5	2.0/4.9/5.9
PBEST40	40/46.8/13.2	38.8/49.1/12.1	0.67	3.5	2.3/3.5/4.1
PBEST50	50/39.0/11.0	49.3/41.1/9.6	0.86	3.5	2.7/2.7/2.9
PBEST60	60/31.2/8.8	58.9/31.1/10.0	0.64	3.0	3.4/2.2/2.3

^a PET/PES/PBS feed molar ratio of prepolymers before copolymerization.

^b PET/PES/PBS molar ratio of resulting copolyester.

^c Intrinsic viscosity (dl/g).

^d Copolymerization time.

^e The number-average sequence lengths of the ethylene terephthalate (ET), ethylene succinate (ES) and 1,4-butylen succinate (BS) blocks, which were calculated according to Eq. (1) in the text.

^f Copolyester series with different contents of PET in the case of having a roughly same PES/PBS molar ratio.

maintained during the whole biodegradability test, and the bioreactor was incubated in a temperature-controlled chamber. The temperature was set at 70 °C for the first week, at 55 °C for the following four weeks, and thereafter at 40 °C. The three PBEST copolymers with various molar contents of ET, 10%, 30%, 50%, using samples of the same weight, were dissolved in CHCl_3 solvent, and then cast on the glass sheet.

All of the test specimens were dried in a vacuum chamber at 50 °C for 24 h and prepared at a size of $40 \times 25 \times 0.31$ mm. After incubation was carried out in a temperature-controlled chamber, the samples were rinsed thoroughly in distilled water and dried in vacuum to constant weight. The biodegradation rate was determined by the weight loss (mg/mg) and changes in the intrinsic viscosity. The measurement of weight loss and intrinsic viscosity for specimens was carried out each week.

3. Results and discussion

3.1. Syntheses of copolyesters

All the synthesized copolyesters have an intrinsic viscosity ranging from 0.62 to 0.86 dl/g within a reaction

time range of 3–8.5 h (see Table 1). In particular, a longer reaction time is needed for polyesters with a higher content of PES, indicating that $\text{Ti}(\text{BuO})_4$ catalyst was not so highly efficient for the synthesis of copolyesters containing high content of PES although it was a very efficient catalyst for synthesis of other copolyesters [14–16].

3.2. Structure characterization of copolyesters

The ^1H -NMR spectra recorded for the copolyesters PBEST40 were shown in Fig. 1. Resonance signals of copolyesters show the microstructure of the copolyesters. As expected, the polycondensation of three prepolymers was found to generate new chemical bond linkages, which were thoroughly different from those of parent prepolymers, such as SET, TBT and TBS, indicating the ester exchange reaction occurred among the prepolymers. For the synthesis of PBEST copolyesters, the reaction temperature reached around 235 °C, which was above the temperature of the ester bond cleavage in prepolymers, thus led to the possibility of ester exchange reaction. Meanwhile, a long reaction time was also assumed to be in favor of the ester exchange reaction.

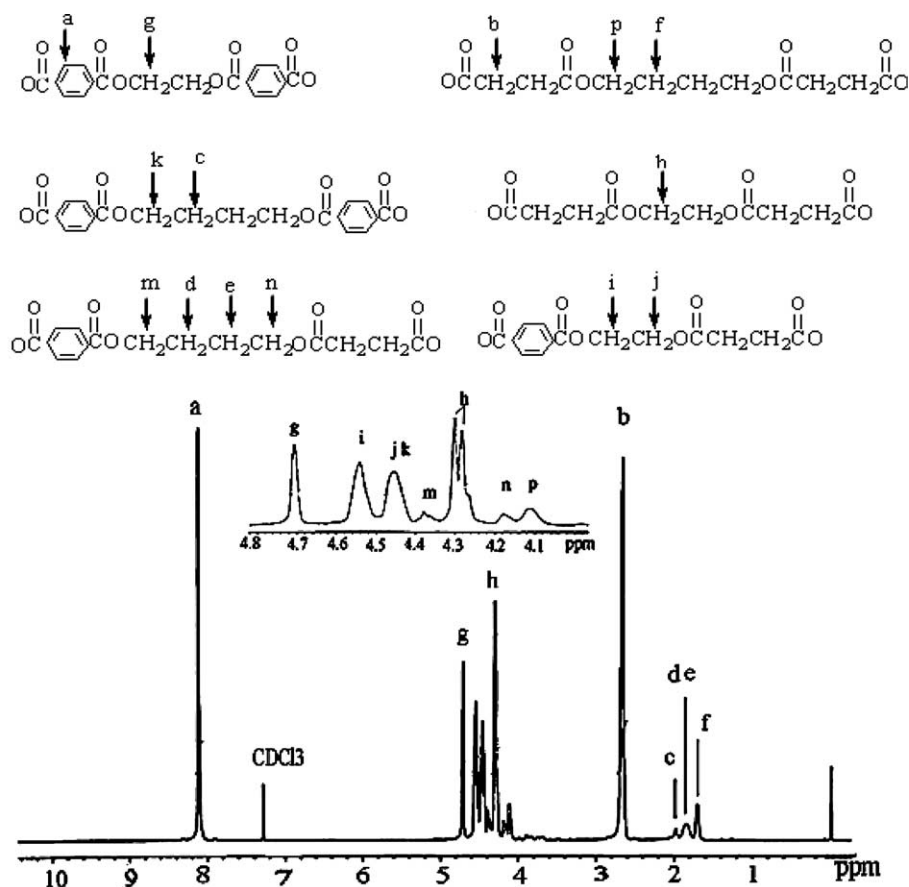


Fig. 1. 400 MHz ^1H -NMR spectra (top) of the polyester PBEST40.

The relative intensities of the dyad peaks for copolyesters PBEST were used to calculate the number-average sequence lengths of the resulting copolyesters according to the following equation:

$$n_{ET} = \frac{N_g + \left(\frac{N_i}{2}\right)}{\left(\frac{N_i}{2}\right)}, \quad n_{BS} = \frac{N_p + \left(\frac{N_a}{2}\right)}{\left(\frac{N_a}{2}\right)}, \quad n_{ES} = \frac{N_h + \left(\frac{N_j}{2}\right)}{\left(\frac{N_j}{2}\right)}, \quad (1)$$

where, N_g , N_i , N_p , N_n , N_h and N_j represent the corresponding integral areas in NMR spectrum, respectively. Fig. 2 represents the relationship of the number-average sequence lengths with the contents of ET in the copolymers. As the PET content in the copolyesters increased, the sequence lengths of the ethylene succinic (n_{ES}) and 1,4-butylene succinic (n_{BS}) units decreased, whereas the sequence lengths of the ethylene terephthalic (n_{ET}) increased. In addition, with the occurrence of extensive transesterification reactions, the sequence lengths of ethylene terephthalic in the resultant copolyesters did not vary remarkably, merely increasing from 0 to 3.4, although the feed molar ratio of PET prepolymer increased from 0% to 60%. By contrast, the sequence lengths of aliphatic units including the ethylene succinic and 1,4-butylene succinic varied much more, which could be explained by the flexibility difference between aliphatic and aromatic units leading to the different ability for forming segments during the reaction.

3.3. Thermal behavior of copolyesters

The thermal properties were characterized by means of DSC and TGA for the PBEST copolymer series. Fig. 3 illustrates the DSC thermal diagrams as a function of the ET content in the copolymers by the DSC heating scans. The change of the T_m with ET content was exhibited in Fig. 4.

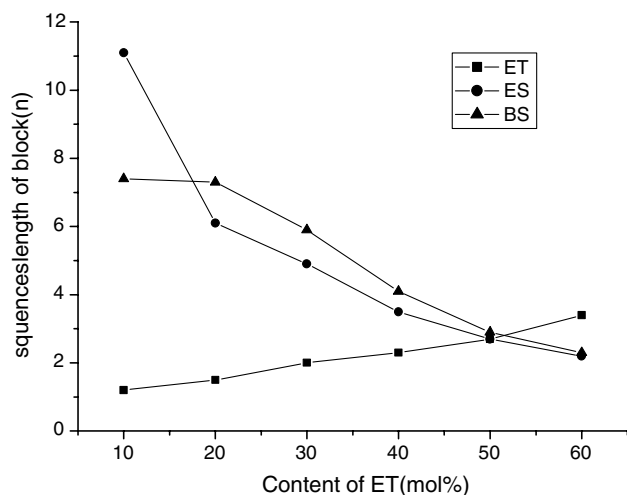


Fig. 2. The change in the number-average sequence lengths with respect to the content of ET in the copolymers.

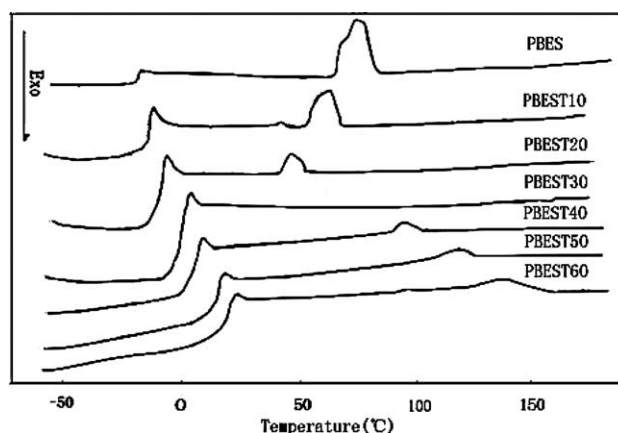


Fig. 3. DSC thermal diagrams of PBEST at the heating scan speed of 10 °C/min.

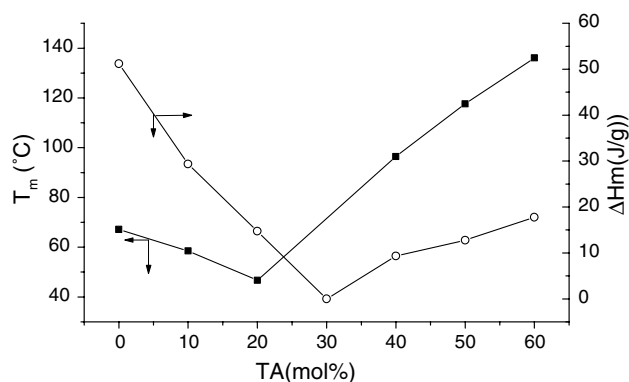


Fig. 4. Melting point (T_m) and heat of fusion (ΔH_m) for PBEST copolymers measured by DSC.

For PBES, T_m of about 67 °C is shown, while the melting peak of the PBEST containing 20 mol% of ET shifts towards a relatively lower temperature. When the content of n_{ET} is more than 30 mol%, the T_m of PBEST increases with the increase of n_{ET} content. The change of melting points with respect to content of n_{ET} is approximately in agreement with the Fox-Flory equation

$$\frac{1}{T_m} - \frac{1}{T_m^0} = -\frac{R}{\Delta H_u} \ln X_a,$$

where T_m is the melting point of copolyesters, T_m^0 the melting point of the corresponding homopolymer in copolyesters, say the melt point of PET here, and X_a and ΔH_u are molar fractions for crystalline units and fusing heat for per molar repeat units, respectively.

The relationship between T_m and n_{ET} content indicates that the copolycondensation reaction of those three prepolymers is random. The crystalline area in the copolyesters varies with the ET content, and the change will affect not only crystalline temperature but also fusing heat. Therefore, as is seen in Fig. 4, the variation of ΔH_m shows a similar tendency to that of T_m .

However, there are nine bone linkages generated in the copolymers (see Fig. 1), so that the regularity of macromolecular chains is poorer than that of other random copolyesters with simple bone linkages [10], and ΔH_m and crystallinity of PBEST are lower compared with some binary random copolyesters.

DSC traces illustrated in Fig. 3 also depict that the glass transition of the PBEST copolyester linearly moves toward a higher temperature when the molar content of ET increased, and the change is illustrated in Fig. 5. As can be seen, T_g of PBEST, ranging from -18.70 to 22.65 °C, increases linearly as the content of the PET unit increases in the copolyesters, which is in good agreement with the Fox equation [17], showing a similar linear relationship to that of a conventional random copolymer.

Table 2 summarized the T_m , ΔH_m and T_g of the copolyesters. It was seen that incorporation of the ET structure into the PBES polyester considerably increased T_g . Besides, T_m and ΔH_m pass through a minimum. For all the PBEST with different ET content, the ΔH_m decreased compared with that of PBES, indicating incorporation of the ET structure into the PBES polyester would decrease the crystallinity.

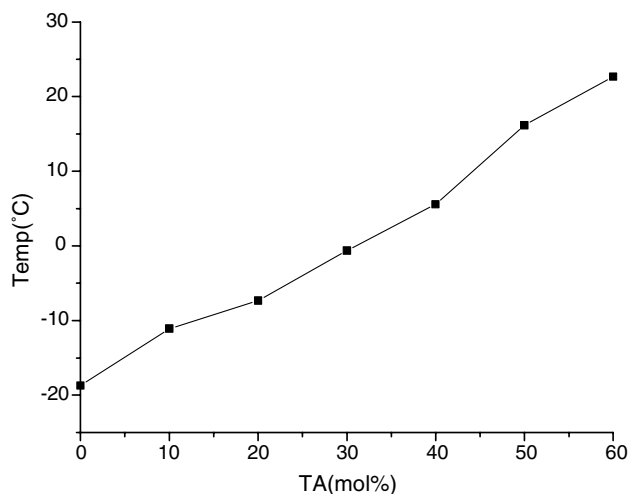


Fig. 5. Glass-transition temperature (T_g) for PBEST copolymers measured by DSC.

When PBEST10 and PBEST60 copolyesters are cooling-scanned from 200 to -70 °C at the speed of 10 °C/min, no crystalline peak is observed in cooling curves. However, both copolyesters have been proved to be crystalline by DSC heating scan. The above phenomena should be attributed to the low regularity and symmetry of the copolyester chains, which greatly lowered the crystallization speed of the copolyesters.

Fig. 6 presents the thermal gravimetric traces of PBEST copolymer, and an index of T_d (-1.5 wt%) as defined in the experimental section is tentatively applied to evaluate their thermal stabilities. The values of T_d are summarized in Table 2. T_d was between 255 and 306 °C, and a thermal stabilization enhanced by the incorporation of PET was observed clearly.

3.4. X-ray diffraction patterns and crystalline structure

Fig. 7 shows the X-ray diffraction patterns of three typical copolyesters, which contain 10, 30 and 60 mol% of n_{ET} . For the copolyester PBEST60, its WAXRD patterns show the three strong diffraction peaks at 2θ angles of 17.34° , 24.48° and 26.20° , which

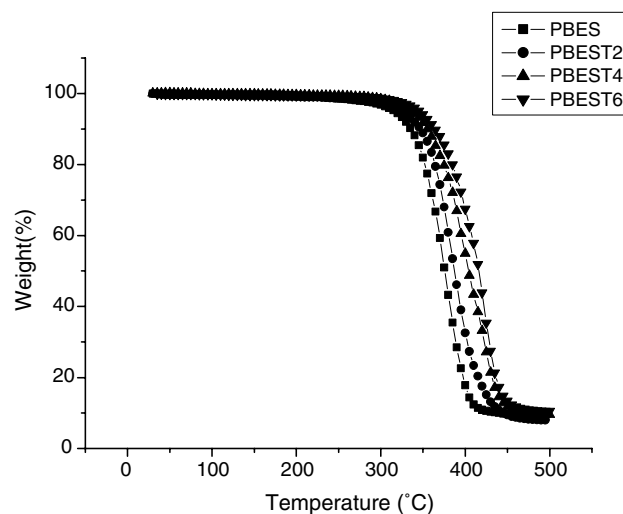


Fig. 6. TGA traces of copolyester PBEST at a scanning rate of 10 °C/min.

Table 2
Thermal properties of copolyesters

Sample code	T_m (°C) ^a	ΔH_m (J/g)	T_g (°C) ^a	T_d (-1.5 wt%) (°C) ^b
PBES	67.14	51.20	-18.70	255.00
PBEST10	58.46	29.38	-11.08	—
PBEST20	46.70	14.73	-7.33	264.00
PBEST30	Not detected	Not detected	-0.62	—
PBEST40	96.44	9.33	5.55	300.00
PBEST50	111.63	12.77	16.17	—
PBEST60	136.09	17.47	22.65	306.00

^a Melting temperature (T_m), glass-transition temperature (T_g) and melting enthalpy (ΔH_m) were registered by DSC at a heating rate of 10 °C/min.

^b T_d (1.5 wt%) was measured by TGA.

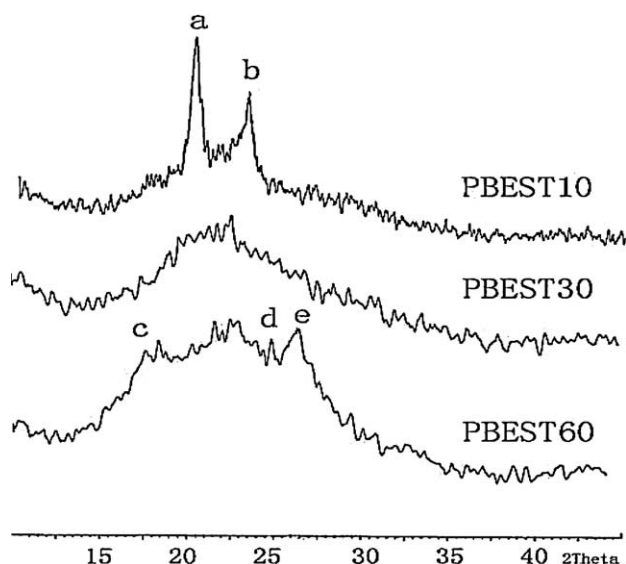


Fig. 7. Wide X-ray diffraction patterns of three copolyesters.

is similar to those of PET at the same 2θ angles, and the three diffraction peaks from small to large angles are assignable to (0 1 0), (1 1 0) and (1 0 0) planes [18], respectively. This suggests that PBEST60 has the same crystalline structures as PET, and indicates that although PES and PBS themselves can be crystallized, they are in amorphous states due to low content of ES and BS comonomers which are minor components in the PBEST60 copolyester (31.1 mol% of ES units and 10.0 mol% of BS units). The existence of ES and BS units in amorphous states results in a decrease of the crystallinity of PBEST60 compared with that of PET. As the content of PET decreases, the crystalline structures of PET in copolyesters are gradually destroyed and amorphous regions increase, which is accordance with the fact that the T_m of copolyesters shows a tendency to decline until at 30 mol% of PET content. For PBEST30, completely amorphous structures existed in the copolyester, which can be confirmed from both the wide X-ray diffraction patterns (Fig. 7) and the fact that no melting point can be detected by DSC (see Fig. 3). It is worth noting that the non-crystalline phenomenon of the ternary random copolyester, PBEST30, is different from that of some binary random copolyesters such as poly(butylene succinate-co-butylene adipate) [19] and poly(butylene succinate-co-ethylene succinate) [10], which can crystallize at any composition. With the increase of ethylene succinate in copolyester, the new crystalline structures similar to the characteristic crystalline structure of homopolymer PES were gradually formed, and the crystalline regions were enlarged. When the content of ethylene succinate largely prevails over the other units, say copolyester PBEST10, the same crystalline structures as PES homopolymer will be formed. WAXRD patterns of PBEST10 show two strong diffraction peaks at 2θ values of 20.17° and 23.18° , assigned to

(2 0 0) and (2 0 2) planes, respectively [20], further suggesting that copolyester PBEST10 has the same crystal structure as PES homopolymer.

3.5. Biodegradability under compost condition

Biodegradable copolyesters containing aromatic units have been reported recently [12,21] and various microorganisms were investigated for these aliphatic–aromatic copolyesters [22]. In this work, the biodegradability of copolymers PBEST was examined using the composting experiment. The degradation process in compost also takes place in simulated MSW aerobic compost environment, so it can be considered to be synonymous with degradation in true environment conditions, with the exception that degradation rates in composting are higher than in natural conditions due to the higher temperature.

Fig. 8 shows the biodegradability of the copolyesters, PBEST10, PBEST30, PBEST50 in compost condition.

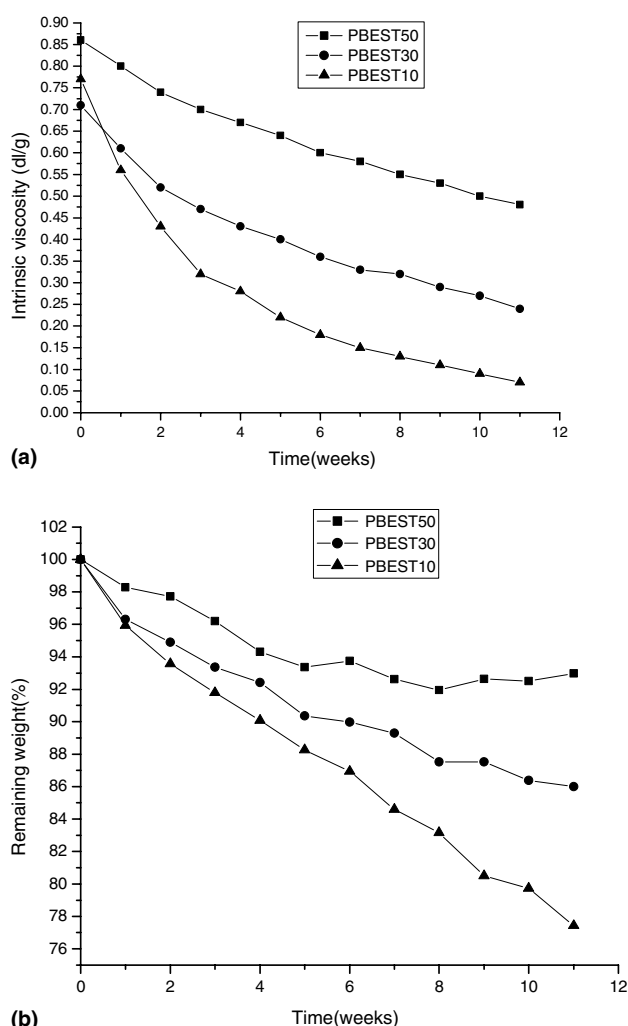


Fig. 8. The change over time of (a) intrinsic viscosity and (b) weight.

The biodegradability was hereby expressed in terms of weight loss (see Fig. 8(b)) and intrinsic viscosity (see Fig. 8(a)) as a function of the buried time for film samples. It is confirmed that each copolyester including PBEST50 was biodegraded in this kind of compost condition and the speed of biodegradability is considerably faster than that of some copolyesters mentioned in some literature [11,23]. This phenomenon may be accounted for by both the lower crystalline degree and higher specific surface area of the copolyesters. In this experiment, the thickness of the films for test is much less than that of films in other similar tests [23], which greatly increases the chance of fungus and water attacking the surface of copolyesters. The copolyesters PBEST with lower content of ET exhibited much higher degradability than those of higher ET content. In particular, copolyester PBEST50 became very weak after six weeks. On the basis of these results, it can be concluded that biodegradability in this experiment relies mainly on the ET content in copolyester. Besides, among three copolyesters tested, PBEST30 is completely in an amorphous state, but its biodegradability rate is always lower than that of PBEST10, a crystalline copolyester. This means that the effect of degree of crystallinity, as an important factor affecting biodegradability, cannot be observed in this study because the influence of the chemical structure on biological resistance is of greater significance.

In the compost test, the molecular chains were attacked by fungi, enzymes and water (60% moisture in test material). When the main chains of the copolyesters were attacked by fungi and enzymes, causing weight loss, the attacked spots would be chain ends. For this reason, the biodegradability of copolyesters was affected by many factors such as degree of crystallinity and aromatic content. However, when molecular chains were attacked by water, the attacked spots would be random, and the molecular weights of polymers would continuously decrease. The factors affecting hydrolysis are mainly hydrophilicity and steric effect of molecular units. So for the PBEST50 copolyester, although its weight loss was not obvious after six weeks (see Fig. 8(b)), its decrease in intrinsic viscosity was still noticeable (see Fig. 8(a)). However, due to the higher hydrophobic and steric effect of PBEST50, it showed a smaller decrease in intrinsic viscosity than the other two copolyesters.

4. Conclusions

Poly(butylene succinate-co-ethylene succinate-co-ethylene terephthalate) can be synthesized through the polycondensation of three prepolymers of polybutylene succinate, polyethylene succinate and poly(ethylene terephthalate). The melting temperatures of copolyesters

PBEST increase obviously compared to those of poly(butylene succinate-co-ethylene succinate), and therefore the new copolyesters are expected to find wider applications than PBES. The thermal stability of PBEST is also enhanced by introducing ET unit, which will favor the processing of the copolyesters. From a biodegradation test in a compost condition, it is concluded that the biodegradation speeds of copolyesters with lower content of aromatic units are much faster than for those with higher content of aromatic units.

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