

Synthesis, Characterization, and Properties of Biodegradable Poly(butylene succinate) Modified with Imide Dihydric Alcohol

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ABSTRACT: A series of high molecular weight poly (butylene succinate) and its copolyester containing rigid imide units were synthesized in this article. The chemical structure and composition of the copolyesters were determined by ^1H NMR spectroscopy and Fourier transform infrared spectroscopy (FT-IR). The thermal properties, crystallization behavior and mechanical properties of polymers were investigated using differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), wide-angle X-ray diffraction (WAXD) and mechanical testing. The enzymatic degradation was investigated using pancreatic lipase solution. The results showed that the melting temperature (T_m) of the copolyester decreased with the increment in pyromellitic imide unit content. However, the thermal degradation temperature (5% decomposition temperature) changed little. Meanwhile, the enzymatic degradation rate of poly (butylene succinate) was enhanced. The mechanical properties showed that the tensile strength had a trend of decrease, but the elongation at break was improved with the increment in imide units. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40807.

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INTRODUCTION

In recent decades, the universal use of nondegradable plastic products has caused serious environmental pollution.¹ The development of biodegradable polymers is an effective way to solve the problem. Aliphatic polyesters are one of the most promising structural materials for biodegradable or compostable products.² Among these biodegradable polymers, poly (butylene succinate) (PBS) with the relative high melting temperature is expected one of the most competitive materials in the future.^{3,4} However, the poorer mechanical properties and higher cost compared with other universal plastic limit its full-scale commercialization.^{5,6} So far, in order to improve its properties, a number of techniques have been used such as physical blending^{7–9} or copolymerization.^{10–17} For example, Jin et al.^{10,11} found the biodegradability of the copolyesters with phenyl units introduced into the side chain of PBS was increased because of the decrease in the relative degree of crystallinity, but its mechanical properties were not improved significantly. Jung et al.¹² synthesized new PBS copolymers containing alicyclic 1,4-cyclohexanedimethanol successfully. But its melting temperature decreased obviously. Besides, Witt et al.^{13,14} investigated the biodegradability and mechanical properties of copolymers synthesized by terephthalic acid with aliphatic diols and diacids, the results indicated that the biodegradability decreased markedly because of the introduction of aromatic units.

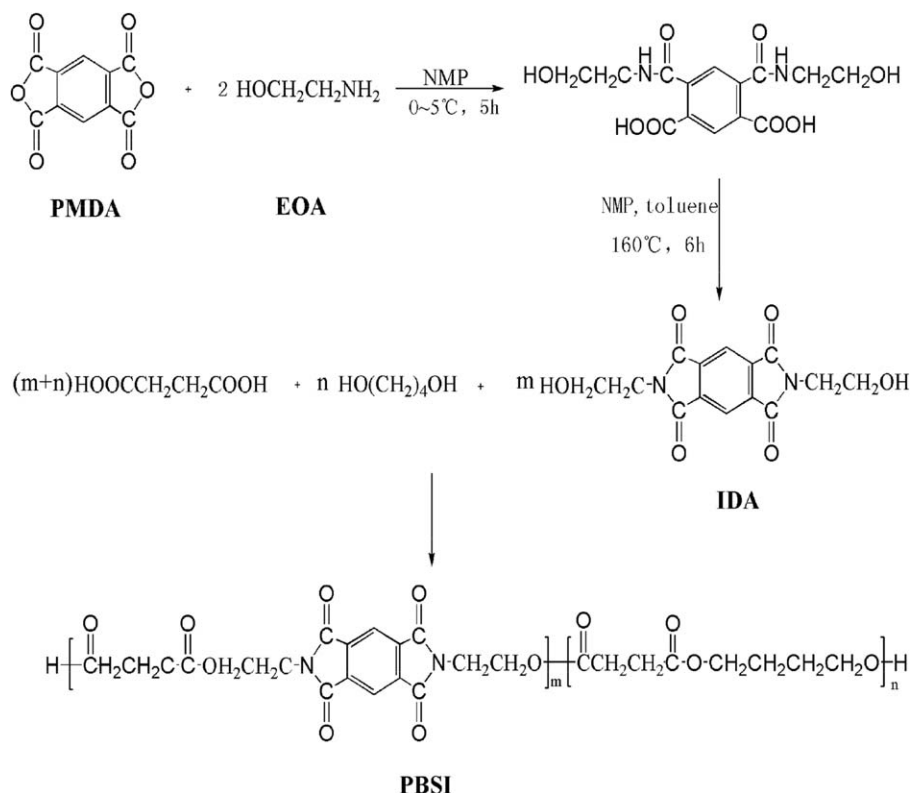
Liu et al.¹⁸ incorporated rigid imide units into the main chain of PBS and prepared a series of poly (butylene succinate) copolyesters containing trimellitic imide units (TMI). The results showed that when the imide unit content was 6.3 mol %, both the elongation at break and the tensile strength were enhanced. However, it is a two-step polycondensation technique which needs relative long time.

Chemical modification is a powerful tool for obtaining polymers with new properties and enlarging the scope of their applications. In this article, rigid imide units were incorporated into the main chain of PBS using one-step melting polycondensation. PBS and PBS copolyesters containing imide dihydric alcohol were prepared. Then their thermal, mechanical and biodegradable properties were studied.

EXPERIMENTAL

Materials

Pyromellitic dianhydride (PMDA) was obtained from Aladdin, China and purified by sublimation under reduced pressure before used. N-methyl pyrrolidone (NMP) and toluene were purchased from Chengdu Kelong Solvent Plant and NMP was distilled under reduced pressure and stored over 4Å molecular sieves. The 1,4-butanediol (BD), succinic acid (SA), ethanolamine (EOA), catalyst titanium (IV) butoxide and zinc acetate were purchased from Chengdu Kelong Solvent Plant and used



Scheme 1. Chemical structure of IDA and PBSI.

as received. The lipase used for enzymatic degradation test was purchased from Aladdin, China. All materials above are chemically pure.

Synthesis of Imide Dihydric Alcohol (IDA)

The imide dihydric alcohol (IDA) was prepared from pyromellitic dianhydride (PMDA) and ethanolamine (EOA). The synthesis process of IDA is shown in Scheme 1. At first, 109 g (0.5 mol) PMDA, 65 mL (1.0 mol) EOA and 600 mL NMP were introduced into a 1000 mL three-necked flask equipped with distillation, a mechanical stirrer, a thermometer and a nitrogen inlet-outlet system. Stirred and kept the system at 0–5°C for 5 h until the mixture was completely dissolution, then added 50 mL toluene and slowly heated the system to 160°C. Then the mixture was rigorously stirred under nitrogen atmosphere at 160°C for 6 h. The three-necked round flask was placed into refrigerator at 5°C overnight after cooling down to normal temperature in order to obtain the precipitate. The precipitate was filtered and rinsed with deionized water and acetone. Finally, the products were dried in a vacuum oven at 100°C for 18 h (yield 82%). Its chemical structure was characterized by FT-IR and ¹H NMR.

Synthesis of PBS and PBSI

The copolyesters were synthesized by one-step polycondensation techniques. The 1,4-BD (and IDA), SA were added into a 100-mL three-necked flask equipped with distillation, a mechanical stirrer, a thermometer and a nitrogen inlet tube. Heating the system gradually to 180°C until the solids were dissolved, stayed here for about 30 min until there was no water in the system, then added catalyst zinc acetate, about 30

min later heated the system to 220°C and added Titanium(IV) butoxide, kept the temperature for 1 h or more before heated it to 250°C. Subsequently, stopped the nitrogen flow, reduced the pressure of reaction system to 70 Pa for 1 h to obtain polymer. At last, poured the polymer into cold water, and then dried them in a vacuum oven for 12 h at 80°C to get a constant weight. Its chemical structure is depicted in Scheme 1 and characterized by FT-IR and ¹H NMR. The polymers were named: PBS, PBSI10, PBSI30, and PBSI50, respectively. “I” in the sample code stands for IDA, the number followed “I” represents the weight fractions of IDA+SA segment. For example, PBSI30 means that the percentage of IDA plus SA in the polymer is 30%.

Measurements

¹H-NMR spectrum of PBS and PBSI, was recorded on an INOVA-400MHz spectrometer using CDCl₃ as solvent. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 560 FT-IR spectrophotometer from 4000 to 400 cm⁻¹. DSC analysis was recorded on a DSC-60A analyzer (SHIMADZU) differential scanning calorimeter equipment under flowing nitrogen (50 mL min⁻¹) with round cycle (heating-cooling) in the temperature range from 40 to 150°C (first heating up to 150°C, then cooling down to 40°C). The rate of heating and cooling was 10°C min⁻¹. The thermogravimetric analysis (TGA) measurements were carried out on the DTG-60 simultaneous thermal analyzer (SHIMADZU) with samples weighing about 8.0 mg heating from 30 to 500°C in dynamic nitrogen environment at a heating rate of 10°C min⁻¹.

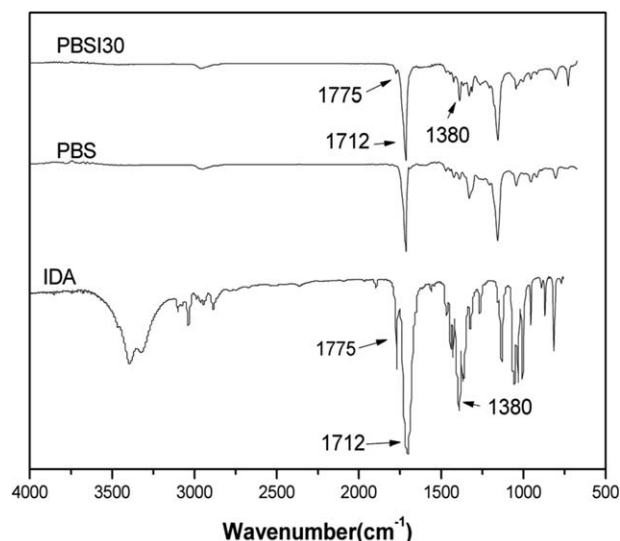


Figure 1. FT-IR spectra of IDA, PBS and PBSI30.

The inherent viscosity of the copolymer was measured with Ubbelohde viscometer at $30^{\circ}\text{C} \pm 0.1^{\circ}\text{C}$. The measurement was performed at a concentration of 0.5 g dL^{-1} in *m*-cresol.

The molecular weight and molecular weight distribution were determined by a HLC-8320GPC gel permeation chromatography (GPC) of Tosoh Corporation at 40°C . The eluent was chloroform at a flow rate of 0.6 mL min^{-1} . molecular weights were calculated against polystyrene standards.

Wide-angle X-ray diffraction (WXR) was performed at room temperature with a Rigaku Model D/max-A diffractometer using $\text{Cu K}\alpha$ radiation (40 kV, 200mA), and the experimental data were collected from 10° to 50° at a scanning rate of $2^{\circ} \text{ min}^{-1}$.

Tensile properties data were obtained using a Universal Testing Machine (Instron 5566, USA) with a full load of 10 kg. The crosshead speed was 20 mm min^{-1} . Measurements were made at room temperature using $10 \text{ mm} \times 30 \text{ mm} \times 0.1 \text{ mm}$ film samples. The polymer film was prepared on smooth glass by solution cast method using chloroform as solvent. Three individual experiments were performed and gained the average value.

To evaluate the biodegradability of the polymers in a short timescale, enzymatic degradation was used. Film samples of polymers (about $10 \text{ mm} \times 10 \text{ mm} \times 0.1 \text{ mm}$ in size) were immersed in a small conical flask containing phosphate buffer solution (pH = 6.8) that was kept in a thermostat water bath at 37°C . The media was changed every 24 h to make sure the activity of lipase. The concentration of enzyme in the solution was $10 \mu\text{g mL}^{-1}$. Each specimen was taken out every 24 h, washed by water, dried at 60°C in vacuum for 8 h and weighed. The percentage of degradation was calculated from $[100(W_0 - W_t)]/W_0$, where W_0 is the initial sample weight and W_t is the weight of dried residual specimen after degradation. Three individual experiments were performed and then gained the average value. The surface morphology of the degraded films was evaluated by SEM.

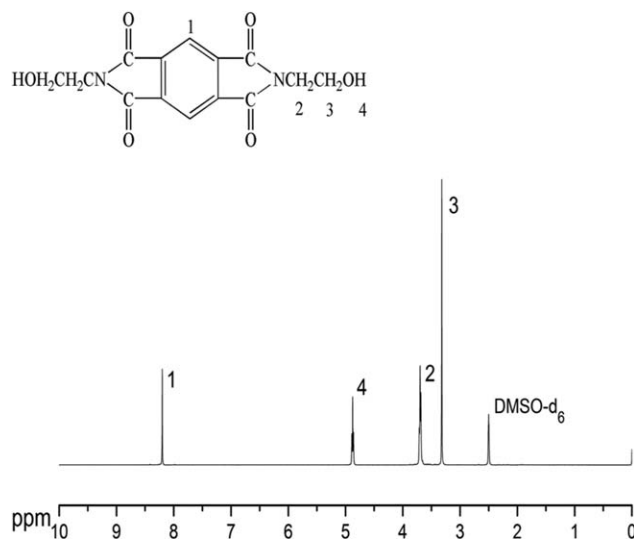


Figure 2. ^1H NMR spectrum of IDA.

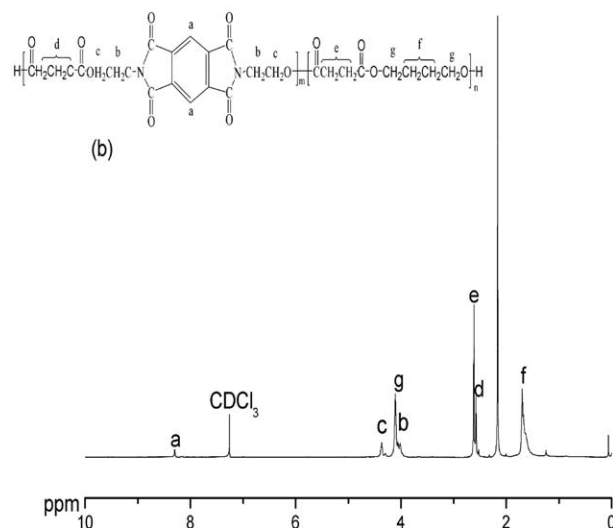
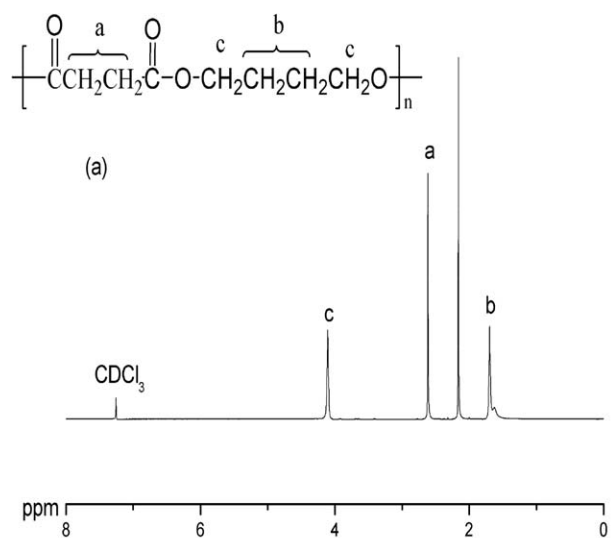


Figure 3. ^1H NMR spectrum of PBS (a) and PBSI30 (b).

Table I. Composition, Molecular Weight, and Inherent Viscosities of PBS and PBST

| Polymer | IDA (mol)/(BD+IDA) (mol) | | \overline{M}_n | \overline{M}_w | $\overline{M}_w/\overline{M}_n$ | $[\eta]$ |
|---------|--------------------------|-----------|---------------------------|---------------------------|---------------------------------|--------------------|
| | Feed (%) | Found (%) | 10^4 g mol^{-1} | 10^4 g mol^{-1} | | dL g^{-1} |
| PBS | - | - | 1.69 | 3.75 | 2.22 | 0.84 |
| PBSI10 | 4.7 | 0.5 | 1.43 | 4.28 | 2.99 | 0.62 |
| PBSI30 | 16.0 | 8.0 | 1.82 | 4.41 | 2.42 | 0.72 |
| PBSI50 | 30.8 | 14.7 | 1.42 | 4.52 | 2.63 | 0.67 |

RESULTS AND DISCUSSION

Structure and Components of IDA and the Copolyesters

To learn the chemical structure of IDA and the copolyesters, FT-IR was utilized at first. As shown in Figure 1, the characteristic absorption peaks at 1775 and 1712 cm^{-1} are due to asymmetrical and symmetrical C=O stretching vibrations of imide rings and the 1380 cm^{-1} is own to C—N—C stretching vibration. The results indicated that the IDA segment was introduced in PBS.

The ^1H NMR spectrum shown in Figures 2 and 3 was used to confirm the chemical structure of IDA and the copolyesters. In Figure 3, the chemical shift at 3.96 and 3.39 ppm was assigned to the proton 2 and proton 3. The proton 1 and proton 4 showed chemical shift at 8.31 and 4.84 ppm.

In Figure 3(a), the peak appearing at 2.63 ppm (proton a) was assigned to protons from the succinic acid; peaks at 1.65 ppm (proton b) and 4.1 ppm (proton c) originated from central and terminal protons of the 1,4-butanediol, respectively.

From Figure 3(b), the signals at 8.31 ppm (proton a), 4.00 ppm (proton b), and 4.20 ppm (proton c) were assigned to protons from IDA. The methylene protons of succinic acid resonated at 2.55 ppm (proton d) and 2.63 ppm (proton e), respectively. The methylene protons of 1, 4-BD resonate at 4.1 ppm (proton g) and 1.65 ppm (proton f), respectively.

Based on the above assignments of peaks, the chemical structure of IDA, PBS and PBSI were confirmed adequately.

The ratio of IDA and BD units in the copolymers was calculated on the basis of the corresponding resonance intensities of proton a and proton f, and the results were shown in Table I. The reason for that IDA proportion in the copolymers was lower than the corresponding feed ratio might be the lower reactivity of IDA in the course of polycondensation. The inherent viscosities of the polymers measured with Ubbelohde viscometer and GPC molecular weight are also shown in Table I. The high and narrow molecular weight distribution indicated that the experiment in Scheme 1 was successful.

Thermal Properties of PBS and PBSI

The thermal behaviors of copolymers were evaluated by DSC and TGA under nitrogen atmosphere. The DSC curves and data of PBS and PBSI samples were shown in Figure 4 and Table I. First, the melting temperature (T_m) of the PBSI was decreased from 117.5°C (PBS) to 90.6°C (PBSI30) when the IDA units

was added in PBS, which was in good agreement with the general rule of copolymers. The sharp decreasing on T_m is due to the fact that the randomized sequential structure leads to a very short PBS segment, thus only very small and rather imperfect

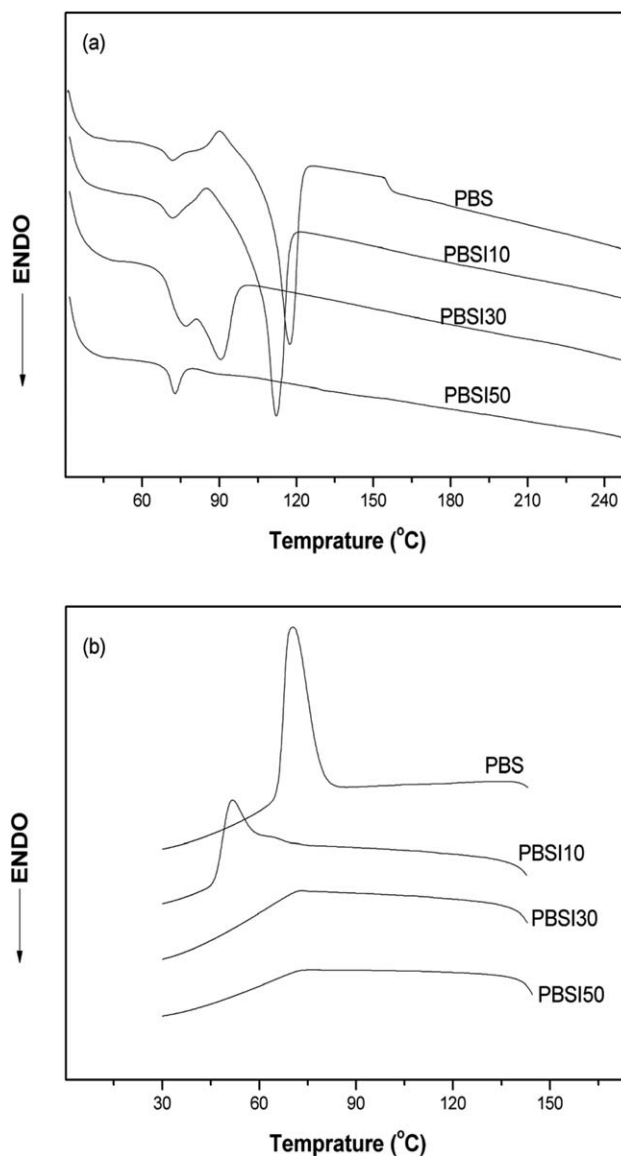


Figure 4. DSC curves of PBS and PBSI: (a) for heating scan, (b) for cooling scan.

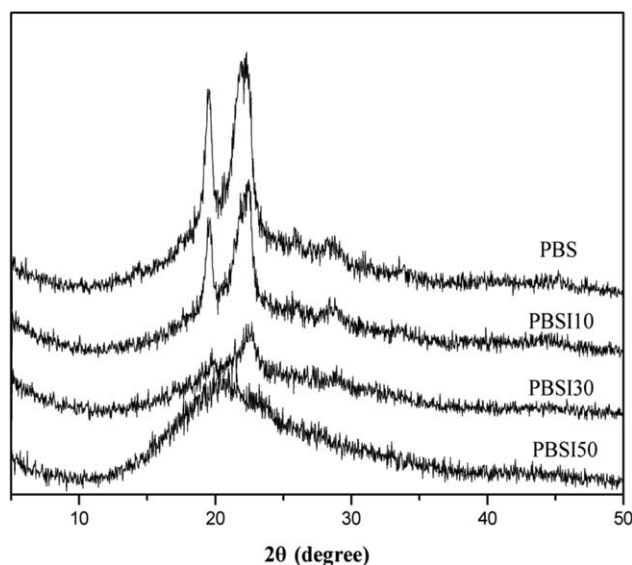


Figure 5. XRD patterns of PBS and PBSI.

spherulites resulted.¹⁹ The PBS and PBSI except PBSI50 showed double melting peaks, which was attributed to the melting of some amount of the primary crystallites and the melting of the more stable crystals, respectively.²⁰ That is to say, the amount of stable crystals decreased with amount of IDA increased in copolyesters and there were only some primary crystallites in PBSI50.

Then the crystallization temperature (T_c) should be paid attention to. It can be seen that the T_c of PBS is higher than PBSI. The degree of supercooling ($\Delta T = T_m - T_c$) is an important parameter for determining the crystallizability of a polymer.²¹ Generally speaking, the crystallizability becomes poorer as the ΔT increased. As can be seen in Table I, the ΔT of PBSI10 (60.4°C) is higher than that of PBS (46.9°C), that is to say, the crystallization rate and crystallizability of PBSI10 is lower than that of PBS. PBSI30 and PBSI50 crystallize too slowly to detect its T_c , but it is obvious that the crystallizability of PBSI30 and PBSI50 is getting lower because the more IDA in PBS breaks the regular chain of PBS more fiercely. The results above can be confirmed by the X-ray diffraction patterns. The X-ray diffraction patterns of PBS and PBSI were shown in Figure 5. PBS showed main peaks at $2\theta = 19.4^\circ$, 22.4° , and 28.6° , which were the signs of the presence of crystallites.²² The intensity of diffraction peaks of PBSI was attenuated as the content of IDA increased. This implied that IDA disturbed the crystallization of the PBS molecular chain and the perfection of crystals was reduced.

Table II. Thermal Properties of Copolymers

| Polymer | T_m (°C) | T_c (°C) | ΔT (°C) | T_d (°C)5% |
|---------|------------|------------|-----------------|--------------|
| PBS | 117.5 | 70.5 | 47.0 | 345.5 |
| PBSI10 | 112.1 | 51.8 | 60.3 | 339.2 |
| PBSI30 | 90.6 | - | - | 343.1 |
| PBSI50 | - | - | - | 347.2 |

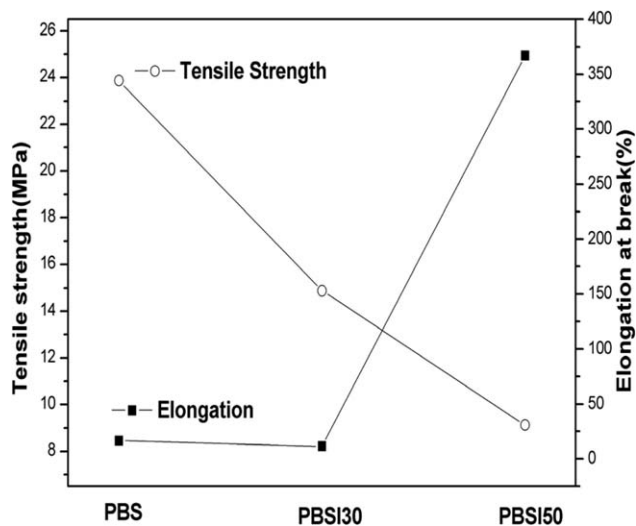


Figure 6. Mechanical properties of PBS and PBSI.

It is well known that aromatic polyimide units are well recognized because of their high thermal stability. Nevertheless, the data of TGA listed in Table II shown that the imide units affect the decomposition temperature (5% decomposition temperature) of PBS little. The decomposition temperature of PBSI had no distinct increasing compared with PBS might because the preferential cleavage of weakened ester units in the copolymer chains.²³

Mechanical Properties of PBS and PBSI

The results of the mechanical testing of the copolyester were shown in Figure 6. Compared with PBS, the tensile strength of PBSI decreased while the elongation at break of PBSI50 (367%) is 22 times higher than PBS (16.4%). It is well known that the tensile strength decreased because the regular chain of polymers and crystallinity of polymer decreased. There is no data of PBSI10 because PBSI10 can not form a 10 mm × 30 mm × 0.1 mm film sample at the same condition.

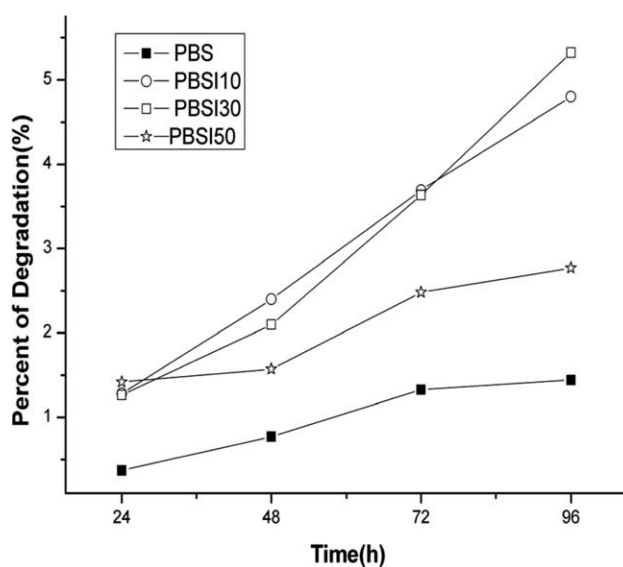


Figure 7. Weight changes of PBS and PBSI over the course of enzymatic degradation.

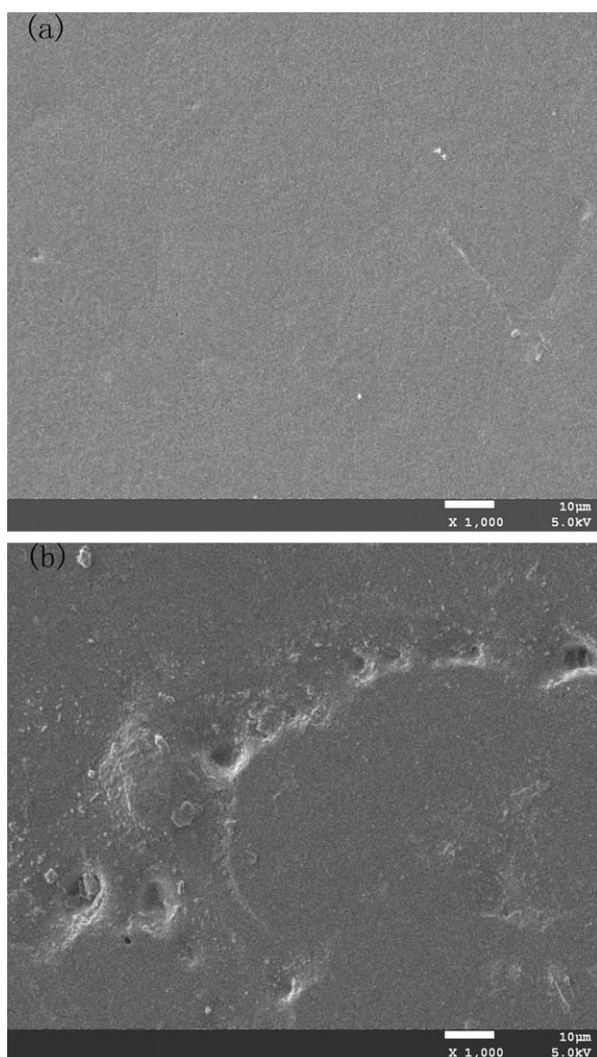


Figure 8. SEM micrographs: PBSI30 before (a) and after (b) enzymatic degradation.

Enzymatic Degradation

The biodegradation of aliphatic polyesters is significantly affected by crystallinity, molecular weight, and chemical structure of the polymer, and usually started from amorphous domains. The weight loss of PBS and PBSI was given in Figure 7. Compared with PBS, the enzymatic degradation rate of PBSI is higher; the reason might be the introduction of IDA breaks the regular chain of PBS which leads to the decrease degree of crystallinity and the dimension of the spherulites.¹⁸ That is to say, the increase of amorphous domains results in the increase of enzymatic degradation rate of PBSI. However, the enzymatic degradation rate of PBSI50 is not the fastest; this can be explained by the fact that the increase of IDA in PBS chain has two opposite effects on the degradation rate. On one hand, IDA in PBS decreased the crystallinity degree of copolymers, resulting in an increase in degradation rate. On the other hand, the increasing of IDA means the increasing of lesser biodegradable benzene ring, which limits the degradation rate. The interplay between these two will determine the resultant degraded rate.

The surface morphology of PBSI30 before and after enzymatic degradation was characterized by SEM as indicated in Figure 8.

The film showed a coarse surface after enzymatic hydrolysis indicating that the surface has been attacked by lipases which would cause further hydrolysis.

CONCLUSIONS

In this article, poly (butylene succinate) and poly (butylene succinate) copolyesters containing rigid imide units were synthesized. The chemical structure and composition of the copolyesters were confirmed by FT-IR and ¹H NMR adequately. The results showed that the experiment in Scheme 1 was feasible and successful.

The thermal properties, mechanical properties and enzymatic degradation of polymers were studied. The DSC results showed that the melting temperature (T_m) of the copolyesters decreased from 117.5°C (PBS) to 90.6°C (PBSI30) with the increase of IDA segment introduced in PBS. For DTG data, the decomposition temperature of PBSI changed little compared to that of PBS (345.5°C). The results of chemical properties showed that the tensile strength of PBSI was lower than PBS, but the elongation at break was enhanced, for PBSI50 (367%) is 22 times higher than PBS (16.4%). At last, the enzymatic degradation results indicated that the biodegradability of PBS was improved effectively. But when IDA increased enough, for example PBSI50, the biodegradability decreased.

All of the results obtained indicated that the elongation and biodegradability of PBS were improved effectively, so that the copolyesters investigated could be used as biodegradable plastic in some applications. It is expected that this research will extend the application of PBS.

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