

Effect of Molecular Weight on the Properties of Poly(butylene succinate)*

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Abstract Poly(butylene succinate) (PBS) with different molecular weight was synthesized from 1, 4-butanediol and succinic acid by direct melt condensation. The synthesized PBS was identified by ¹H-NMR and FTIR spectrometry. The molecular weight was calculated from the intrinsic viscosity, and its value was between 20000 and 70000. The crystallization behavior and crystal morphology as function of molecular weight were investigated by DSC and PLM, respectively. The mechanical properties and hydrolytic degradation behaviors related with change of molecular weight were also studied in this work. The results demonstrated that the properties of PBS were determined by both molecular weight and crystallization properties (crystallinity as well as crystal morphology). Our work is important for the design and preparation of PBS with proper molecular weight for its practical application.

Keywords: Poly(butylene succinate); Molecular weight; Properties.

INTRODUCTION

Poly(butylene succinate)(PBS) has attracted increasing attention due to its excellent biodegradability and acceptable mechanical properties^[1]. As an eco-friendly polyester, PBS has been widely applied in agriculture, forestry, civil engineering and other fields^[2–5]. The synthesis of PBS and other aliphatic polyesters was first studied by Carothers in 1930s. However, the PBS obtained at that time was of low molecular weight, which made it weak and brittle^[1, 3]. After that, as the environment problem caused by the industrial plastic waste is getting serious, more and more researches have been done to improve the molecular weight of the aliphatic polyesters. PBS with a molecular weight high enough for practical applications has been successfully produced in the 1990s with the use of new catalysts and coupling reaction^[3]. In recent years the technique for the synthesis of aliphatic polyester is becoming more mature. The molecular weight of PBS reaching about 100000 has been reported *via* direct melt condensation^[2, 6–9].

In order to obtain PBS with useful mechanical properties, it is required to have relatively high molecular weight. Nevertheless, the performance of a polymer cannot be always improved with increasing molecular weight, especially in the case of semi-crystalline polymers such as PBS, since both molecular weight and the crystallization behaviors have effects on the properties of crystalline polymers. Thus it is important to study the correlations between molecular weight and crystallization behavior, and its effect on the properties of PBS. To our knowledge, there is little research on the influence of the molecular weight on the properties of PBS^[10–15]. Although Song *et al.*^[12], studied the influence of molecular weight on the crystallization and hydrolysis of PBS.

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The number average molecular weight in their work is relatively low (less than 20000) and cannot be used in industry as a structure material. Therefore, in this work, we first synthesized PBS with molecular weight by direct melt consideration, and the molecular weight is between about 20000 and about 70000, which is high enough for industrial applications. Then the effect of molecular weight on the crystallization behavior and crystal morphology, the mechanical properties and hydrolytic degradation behaviors were investigated. It was found that PBS with molecular weight in the range of 40000–50000 could have the best mechanical properties, while PBS with the highest molecular weight had the fast rate of hydrolytic degradation.

EXPERIMENTAL

Materials

Succinic acid (SA) was supplied by Kemiou Chemical Reagent Corporation (Tianjin, China), while 1,4-butanediol (BD), tetrabutyl titanium and triphenyl phosphate (TPP) were purchased from Kelong Chemical Corporation (Chengdu, China). All chemicals were of analytical grade and used without purification.

Synthesis of PBS

Succinic acid (200 g, 1.7 mol) and 1,4-butanediol (175 mL, 2 mol) were charged into a home-made reactor together with tetrabutyl titanium and TPP (tetrabutyl titanium as catalyst, TPP as the stabilizer). With stirring, the reaction mixture was heated at 180 °C for 2.5 h under nitrogen atmosphere. Then the temperature was progressively increased to 220 °C, and the pressure was reduced to 80 Pa for condensation polymerization. The reaction was stopped when the electric current driving the stirring rod reached the designed value, at which the sample had different molecular weight. The samples were named as PBS-1, PBS-2, PBS-3, PBS-4, PBS-5 and PBS-6 according to their molecular weight, respectively. After polymerization, the production was extruded into cold water from the reactor by compressed nitrogen, and afterwards the polyesters maintained at room temperature in order to be cooled and were vacuum dried at 50 °C for 24 h. Finally, the as-prepared samples were injection-molded into tensile testing bars with dimensions of 4.0 mm in width, 2.0 mm in thickness and 40 mm in length using a mini-injection system (Thermo Scientific) at a melt temperature of 140 °C and a mold temperature of 50 °C.

Molecular Structure

The molecular structure was determined by proton nuclear magnetic resonance (¹H-NMR) spectra and FTIR spectra. ¹H-NMR spectra were recorded at 25 °C in deuterated chloroform using a Varian Unity INOVA (400 MHz) spectrometer with tetramethylsilane as the internal standard. The FTIR spectra were recorded between 400 cm⁻¹ and 4000 cm⁻¹ on a Nicolet-560 infrared spectrometer.

Molecular Weight

The intrinsic viscosity was measured by a Ubbelohde viscometer at a concentration of 0.4 g/dL in chloroform at 25 °C. Intrinsic viscosity was calculated after the Solomon-Ciuta equation^[16]:

$$[\eta] = [2\{t/t_0 - \ln(t/t_0) - 1\}]^{1/2}/c \quad (1)$$

where c is the concentration of the solution, t is the flow time of solution and t_0 is the flow time of pure solvent. The number-average molecular weights (M_n) of the products were calculated by using the Berkowitz equation:

$$M_n = 3.29 \times 10^4 [\eta]^{1.54} \quad (2)$$

Crystallization Behavior

Thermal analysis was carried out using a Perkin-Elmer Pyris-I differential scanning calorimeter with a Universal Analysis 2000. For nonisothermal crystallization, the samples were first heated to 150 °C at 100 K/min. The samples were held at that temperature for 3 min to erase any thermal history and cooled to 30 °C at 10 K/min (first cooling). Then, the samples were heated to 150 °C again at 10 K/min (second heating). Crystallization peak temperature was obtained from the first cooling traces. Subsequent melting behaviors of PBS were studied from the second heating traces.

The crystallinity index X_c was calculated using the following equation:

$$X_c = \Delta H_m / \Delta H_m^0 \quad (3)$$

Where ΔH_m is the melt enthalpy of the crystal phase of the samples, The value of ΔH_m^0 is the theoretical melt enthalpy for 100% crystallinity which was taken as 110 J/g for PBS^[17].

For isothermal crystallization, the samples were held at 150 °C for 5 min to eliminate any thermal history, cooled to the crystallization temperature (T_c) at a cooling rate of 100 K/min then maintained at T_c until the crystallization was completed. After that, the samples were heated to 150 °C at 10 K/min.

Crystal Morphology

The crystalline morphology was studied on a polarized optical microscope equipped with a hot stage. Samples were first annealed at 150 °C for 3min then cooled to different temperatures at 100 K/min, and then the development of spherulites were recorded *via* digital camera.

Tensile Properties

An Instron universal testing machine was used to evaluate the tensile properties under a cross head speed of 50 mm/min. At least five samples were used for each measurement and the results were averaged to obtain a mean value.

Hydrolytic Degradation

The hydrolytic degradation of the PBS specimens was carried out in a 1 mol/L NaOH solution at 37 °C. The dimension of the samples molded by hot pressing was 30 mm × 9 mm × 0.5 mm. The specimens and solution were put in a water bath device with gentle shaking. After a fixed period of time the samples were picked out and washed with distilled water to remove any traces of NaOH solution and then dried to a constant weight in a vacuum oven at 50 °C.

RESULTS AND DISCUSSION

Identification

The PBS samples prepared in our work were studied by ¹H-NMR, and the result is shown in Fig. 1. The peaks of the PBS ($\delta = 4.1$, $-\text{CH}_2-$ of 1,4-butanediol unit; $\delta = 1.7$, $-\text{CH}_2-$ of 1,4-butanediol unit; $\delta = 2.6$, $-\text{CH}_2-$ of succinyl unit) are clearly observed. More identification of PBS comes from the FTIR spectrum, as shown in Fig. 2. The characteristic peaks of PBS in the region at 2924 cm^{-1} and 1155 cm^{-1} corresponding to the stretching

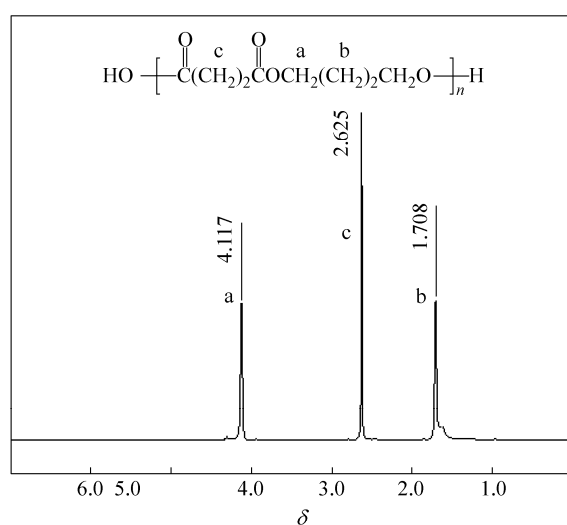


Fig. 1 ¹H-NMR spectrum of PBS

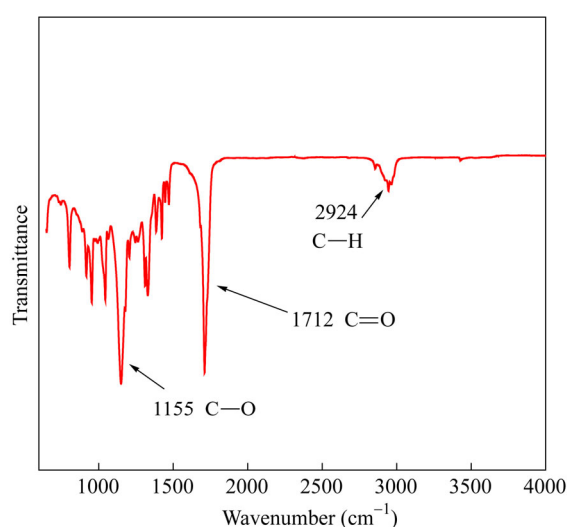


Fig. 2 FTIR spectrum of PBS

vibration of CH₂ and C—O stretching vibration in the ester group can be observed. Both NMR and FTIR results suggest that PBS with defined molecular structure has been successfully obtained in this work.

Molecular Weight

The intrinsic viscosities of all the samples prepared are listed in Table 1. The viscosities are ranged from 0.75 dL/g to 1.53 dL/g, and their corresponding molecular weight can be calculated *via* equation: $M_n = 3.29 \times 10^4 [\eta]^{1.54}$. It can be seen the molecular weight is between 20000 and 70000, which is high enough for industrial application.

Table 1. Intrinsic viscosity and molecular weight of PBS

Sample	PBS-1	PBS-2	PBS-3	PBS-4	PBS-5	PBS-6
Intrinsic viscosity (dL/g)	0.75	0.92	1.01	1.15	1.30	1.53
M_n	2.1×10^4	2.9×10^4	3.3×10^4	4.1×10^4	5.0×10^4	6.3×10^4

Crystallization Behavior

The non-isothermal crystallization of PBS with different molecular weight was investigated by DSC, and the result is shown in Fig. 3.

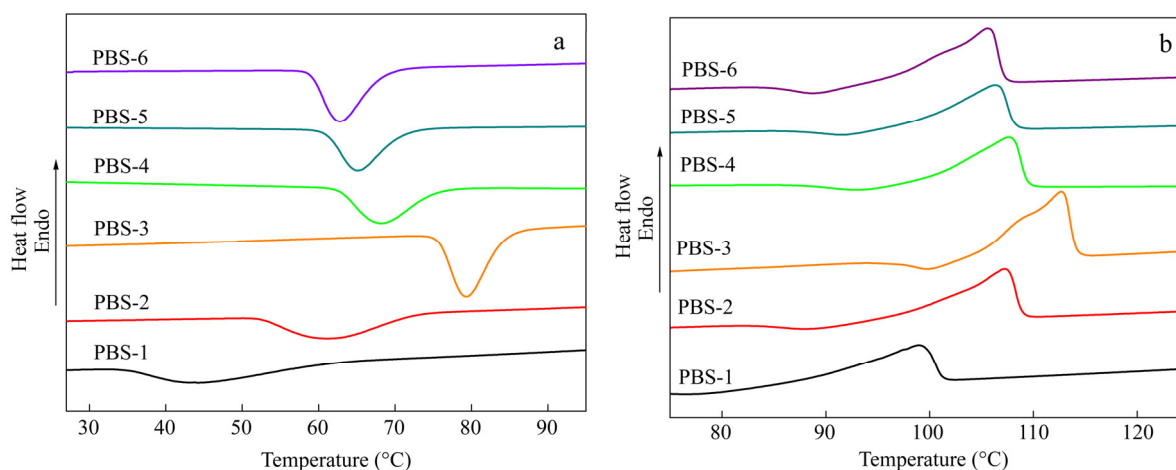


Fig. 3 DSC curves in the cooling (a) and heating (b) process of PBS with different molecular weight

It could be seen that in the low molecular weight range less than 40000 (PBS-1, PBS-2 and PBS-3), the T_m , T_c and crystallinity are all increased with increasing of molecular weight, and the cooling or melting peaks become narrow. This result indicates that the crystallization of PBS becomes easier and more perfect with increasing molecular weight. This result coincided with the work done by Song^[12] and this phenomenon was also observed for other polymers such as poly(3-hexylthiophene)^[18], PES^[11] and poly(ethylene glycol)^[19, 20]. We think the most possible reason is the decreased effect of end groups with increasing of molecular weight, as in the case of PEO crystallization^[18, 21]. For example, the high-density end groups on the PBS with low molecular weight could act as crystal defects^[12], which will slow down the overall crystallization process. In the high molecular weight range (PBS-3, PBS-4, PBS-5, PBS-6), however, the T_m , T_c and crystallinity are decreased with the increasing of the molecular weight. This can be understood as due to the increased chain entanglement and decreased molecular motion. The crystallization temperature (T_c), melting temperature, and crystallinity of PBS with different molecular weight are listed in Table 2. In our study, the sample PBS-3 has the highest T_m , T_c and crystallinity which are 113 °C, 79 °C and 65.5%, respectively. By the way, according to the literature^[19], the melting point of the PBS with molecular weight in the vicinity of 70000 is 114 °C. This experimental result is different from ours, which may be due to the differences in the polymerization process.

Table 2. Crystallization properties of PBS samples with different molecular weight

Sample	PBS-1	PBS-2	PBS-3	PBS-4	PBS-5	PBS-6
T_m (°C)	99.0	107.2	113.0	107.7	106.4	104.5
T_c (°C)	44.7	61.3	79.4	68.2	64.9	60.2
ΔH (J/g)	57.5	63.5	72.2	59.6	56.5	48.7
X_c	52.3	57.7	65.6	54.2	51.4	44.3

To further analyze the effect of molecular weight on the crystallization of PBS, the isothermal crystallization was carried out at different crystallization temperatures. As an example, the crystallization curves of PBS-4 are presented in Fig. 4(a). As can be seen, the time to reach the maximum of crystallization peak increases as the crystallization temperature increases. In this way, the half time for crystallization can be determined as the time of the peak point. The crystallization half time of PBS as a function of molecular weight is shown in Fig. 4(b). We cannot provide the data of PBS-1, as it is difficult to crystallization at test temperatures. As observed, the half time is increased as increasing of temperature for all the samples. PBS-3 shows the shortest half time thus fast crystallization rate at all the crystallization temperatures investigated among all samples. This result is consistent with that obtained *via* non isothermal crystallization. Again the balance between the effects of end groups and entanglements plays the role to determine the final crystallization rate.

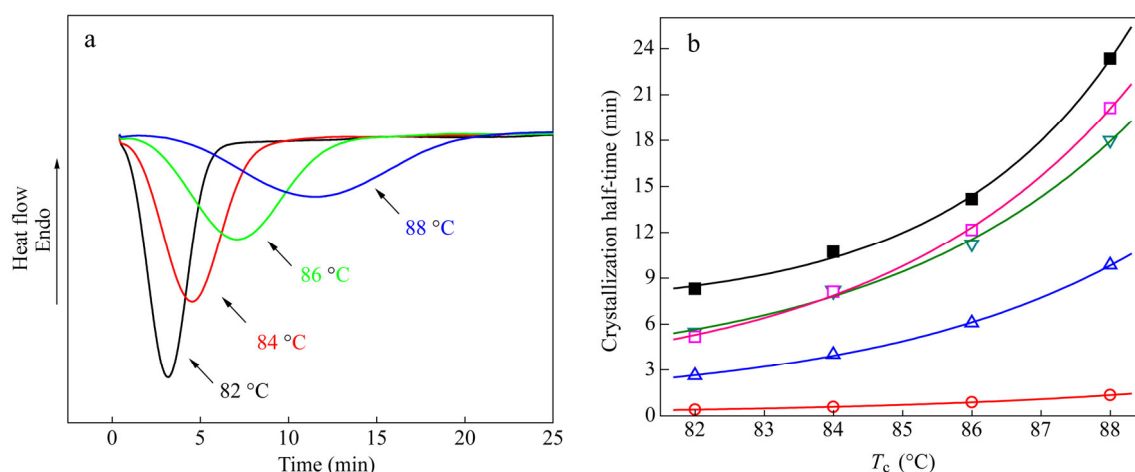


Fig. 4 Crystallization curves of PBS-4 at different temperatures (a), and T_c dependence of the crystallization half-time (b) [(■) PBS-2, (○) PBS-3, (Δ) PBS-4, (▽) PBS-5 and (□) PBS-6]

Crystal Morphology

The crystal morphology was investigated *via* PLM. Figure 5 shows the spherulite-like morphology of PBS with different molecular weight. The pictures were obtained after PBS was crystallized at 75 °C from the melt. Relatively big and clear branching textures can be observed for PBS with low molecular weight. With increasing of molecular weight, the spherulites become smaller. With further increasing molecular weight, the spherulite size increases again. The reason for this phenomenon is that the spherulite size is closely related to the nucleation density of the test sample. As the molecular weight increases ($< 4 \times 10^4$), PBS crystallization ability and nucleation density increase. This causes an increase in number of spherulites and, consequently, a decrease of spherulite size. A further increase in molecular weight causes a decrease of the crystallization ability and nucleation density of PBS, which makes the spherulites grow larger and sparse. As the molecular weight increases, the branching texture becomes dense, and even complicated morphology with internal messy birefringence can be observed for PBS with the highest molecular weight. This is probably due to the increasing entanglement density which hinders the formation of ordered lamellar structure^[22].

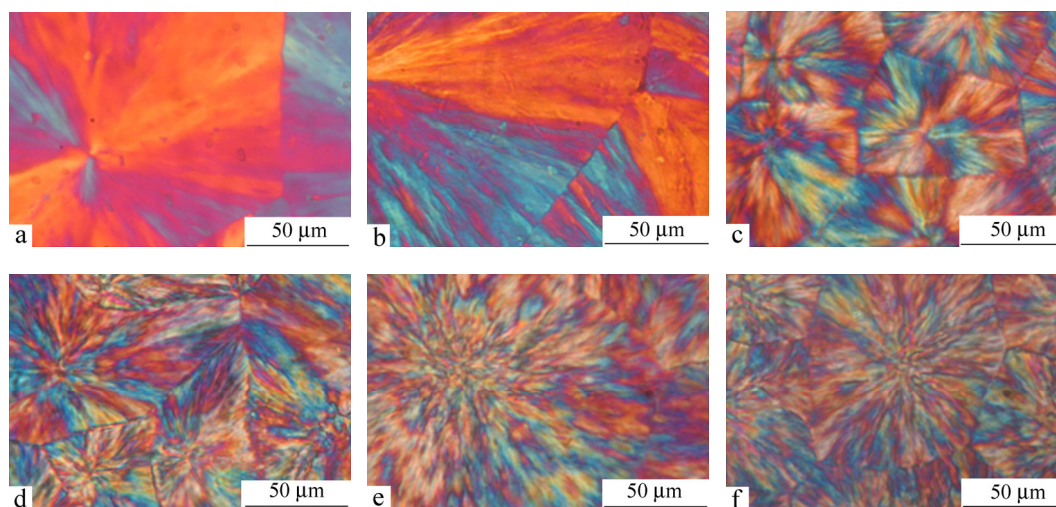


Fig. 5 The spherulite morphology of PBS crystallized at 75 °C from the melt: (a) PBS-1, (b) PBS-2, (c) PBS-3, (d) PBS-4, (e) PBS-5 and (f) PBS-6

Mechanical Properties

As a new kind of biodegradable material, the mechanical performance of PBS has attracted more and more attention in recent years, but less is known about the effect of molecular weight on its mechanical properties.

As illustrated in Fig. 6 and Table 3, The trend for the modulus, yield strength and elongation at break of PBS are all increased with molecular weight increasing up to 40000 (PBS-4), then these properties are decreased with further increasing of molecular weight. This result indicates the best mechanical properties are neither for the sample with highest crystallinity nor for the sample with the highest molecular weight. Again the balance between them determines the final mechanical properties. It should be noted that the crystallinity of the samples used for mechanical property test (given in Table 3) is a little different from that of the raw polymers which have been heated to 150 °C for erasing thermal history before the test (given in Table 2). This is because the processing thermal history also has certain effects on the crystallinity. But still, the effects of molecular weight on the variation trend of crystallinity are consistent in the two results.

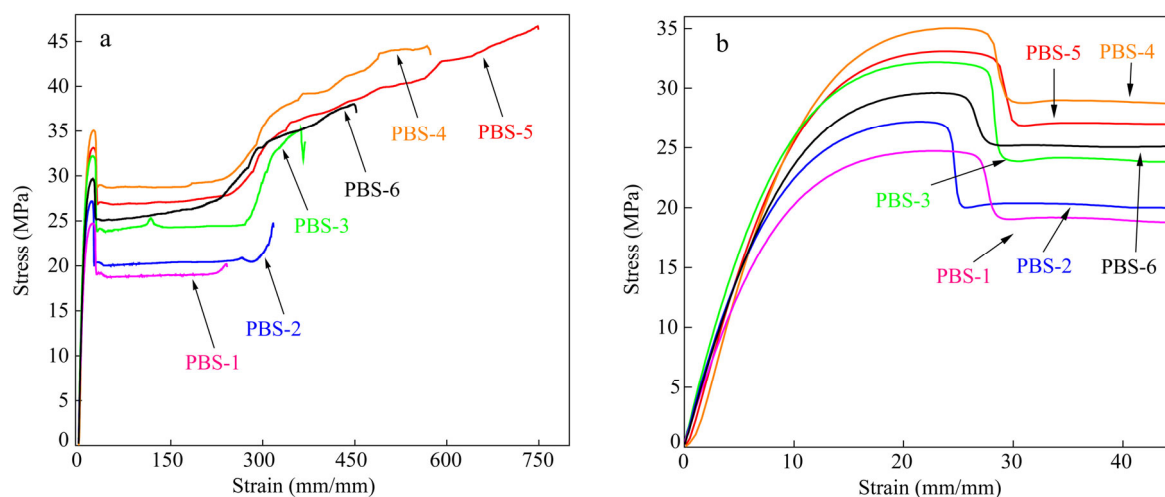


Fig. 6 Stress-strain curves of PBS samples with different molecular weight

Table 3. Crystallinity and mechanical properties of the injection-molded PBS specimens

Sample	PBS-1	PBS-2	PBS-3	PBS-4	PBS-5	PBS-6
ΔH (J/g)	58.7	65.2	71.9	59.9	57.4	50.5
X_c (%)	53.4	59.3	65.3	54.4	52.1	45.9
Yield strength (MPa)	24.8 ± 0.6	27.9 ± 1.6	32.7 ± 0.6	34.5 ± 0.4	31.5 ± 0.9	29.7 ± 0.5
Elongation at break (%)	254.6 ± 48.1	310.3 ± 12.1	392.8 ± 32.5	572.0 ± 13.0	636.9 ± 38.6	457.7 ± 5.6
Modulus of elasticity (MPa)	287.2 ± 16.9	359.0 ± 14.4	396.3 ± 3.1	387.2 ± 8.4	361.9 ± 5.4	342.7 ± 5.5

Hydrolytic Degradation

In order to investigate the effect of molecular weight on the hydrolytic degradation of PBS, the weight loss of polymorphic PBS films with different molecular weight was monitored, and the result is shown in Fig. 7.

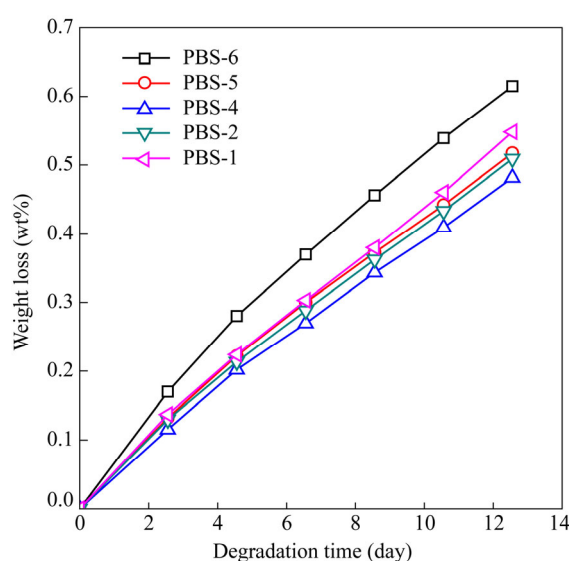


Fig. 7 The weight loss of PBS samples with different molecular weight as a function of hydrolysis time in the 1 mol/L NaOH solution

The weight loss of all samples increases almost linearly with hydrolytic degradation time. Not very much difference can be observed for PBS with intermediate molecular weight (PBS-2, PBS-3, PBS-4 and PBS-5). PBS with the highest molecular weight (PBS-6) shows obviously the first fast degradation rate and PBS with the lowest molecular weight (PBS-1) has second fast degradation rate. This result indicates that the crystallinity of the test samples plays an important role in determining the hydrolysis rate. It also further supports the conclusion that the hydrolytic degradation takes place preferentially in the amorphous region rather than in the crystalline region^[17, 18]. It is worth mentioning that the PBS-1 shows a relatively faster degradation rate than the other samples which has the similar degree of crystallinity. This can be attributed to two reasons: First, the PBS-1 has a very low molecular weight that could not form enough entanglement to prevent the polymer chain hydrolyzed by NaOH from being striped by solution. Second, the carboxyl end-group concentration is relatively high in PBS-1 sample and it can accelerates ester bond cleavage^[23].

CONCLUSIONS

Poly(butylene succinate) with different molecular weight was synthesized by direct melt condensation. The PBS-3 with molecular weight of about 33000 has the fast crystallization behavior, which shows the highest T_m , T_c and crystallinity. When the molecular weight is lower than 28.000, the molecular weight is the main factors affecting

the mechanical properties. The mechanical performance is evidently improved by increasing molecular weight. When the molecular weight is relatively higher, the influence of crystallinity on the mechanical properties of PBS becomes obvious. The molecular weight has no evident influence on the hydrolytic degradation rate. The sample which has higher crystallinity showed a lower degradation rate, however if the molecular weight of PBS is lower than 20000, it also can have an acceleration effect on the hydrolytic degradation of the sample.

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