High molecular weight poly(butylene succinate-co-furandicarboxylate) with 10 mol% of BF unit: Synthesis, crystallization-melting behavior and mechanical properties

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ABSTRACT

In this study, high molecular weight poly(butylene succinate-co-furandicarboxylate) with 10 mol% of butylene furandicarboxylate unit (PBSF10) was synthesized and its crystal structure and crystallization-melting behaviors were investigated by means of WAXD, SAXS, DSC and POM. The tensile properties were also assessed. The crystal structure of PBSF10 is found to be the same as that of poly(butylene succinate) (PBS). The SAXS result indicates that PBSF10 had the same thicknesses of crystalline region and transition zone, but larger thickness of amorphous region, indicating that the BF units are mostly excluded from the crystalline region and located in the amorphous region. Therefore, PBSF10 is less crystallizable than PBS. But PBSF10 still exhibits rapid nonisothermal and isothermal crystallization. Because of high molecular weight and good crystallizability, PBSF10 exhibits superior tensile properties: modulus 370 MPa, strength at break 38 MPa and elongation at break 230%.

1. Introduction

Biobased and biodegradable polymers are deemed as green and sustainable materials from cradle to grave. Manufacturing and using biobased and biodegradable polymers instead of some non-degradable ones has been proved to be an effective way to realize the carbon-neutral circle [1,2] and to solve, at least partially, the white pollution problem resulted from discarded polymeric materials [3]. Poly(lactic acid) (PLA) [4,5] and poly(butylene adipate-co-terephthalate) (PBAT) [6–9] are the most representative rigid and flexible biodegradable polymers, respectively. They have been successfully commercialized and extensively used into a variety of fields from disposable daily necessities to mulch films. PLA is a biobased polymer but PBAT is not yet. As 2,5-furandicarboxylic acid (FDCA) emerged as a new biobased aromatic monomer in the recent decade [10,11], some new biobased aliphatic-aromatic flexible copolymers [12–20], including poly(butylene succinate-co-furandicarboxylate) (PBSF) [12,13,16,17] and poly(butylene adipate-co-furandicarboxylate) (PBAF) [14–17], emerged as biodegradable polymers.

Synthesis, thermo-mechanical properties, hydrolytic and biological degradation of FDCA-based copolymesters have been reported in recent years [12–20]. As FDCA has similar molecular structure as that of terephthalic acid (TPA) [11], these biobased copolymesters
display thermo-mechanical properties comparable to the TPA-based counterparts [6–9,21–25]. It was reported that PBAFs with an butylene furandicarboxylate (BF) unit content below 50% are enzymatically degradable in the presence of lipase from porcine pancreas [14] and PBSFs with BF content less than 20% possess good compost biodegradability as well [13]. Our previous study demonstrated the hydrolytic [16] and compost [17] degradation of PBSFs and PBAFs with 40–60 mol% BF unit. Therefore, PBAF and PBSF copolymers appear to be promising biobased and biodegradable polymers with attractive performance and potentially wide applications.

In general, thermo-mechanical properties of aliphatic-aromatic copolymers are strongly composition-dependent [8,12,15,16,21,22]. Usually, copolymers containing around 50 mol% aromatic unit exhibit good biodegradability and better comprehensive thermo-mechanical properties. For an example, the commercialized PBAT copolymers often contain about 45% butylene terephthalate (BT) unit. However, such copolymers with “middle” composition are often less crystallizable than the aliphatic- or aromatic-rich copolymers [8,12,15,21,22]. In our previous studies, we reported the synthesis and composition-dependent thermo-mechanical properties of PBSF [12] and PBAF [15] in the whole composition range. These copolymers are less crystallizable at 40–60% BF but have good crystallizability at 10% BF. It is well-known that poly(butylene succinate-co-adipate) (PBSA) copolymers with 10–20% BA unit are deemed as chemically modified PBS products [26,27] and have been commercialized together with PBS. Similarly, PBSF copolymers with BS-rich composition may also find practical applications as modified PBS thank to good crystallizability [12], compost degradability [13] and tunable property, and therefore deserve more attention and research to better understand the structure-property relationship of these FDCA-based copolymers.

As one of a series of study on PBSF/PBAF copolymers [12,15–17], in this study, we report the synthesis, crystal structure, crystallization kinetics, melting behavior and mechanical properties of high molecular weight PBSF containing 10% BF unit (PBSF10) and PBS. The crystal structure was studied with WAXD and SAXS. The nonisothermal and isothermal crystallization and melting behaviors were investigated with DSC. And the spherulite growth was investigated with POM and analyzed with Lauritzen-Hoffman equation. The tensile properties were also assessed.

2. Experimental

2.1. Materials

Succinic acid (SA, Anhui Sanxin Chem. Co., China), 1,4-butanediol (BDO, Sinopec Yizheng Chem. Fibre Co., China) and tetrabutyl titanate (TBT, ≥99.0%, Aladdin) were all used as received. Highly purified 2,5-furandicarboxylic acid (FDCA) purified with our previously reported method [15] was supplied by Satar Chem. Co., China. Some possible impurities like 5-formyl-2-furancarboxylic acid and acetic acid were completely undetectable in its 1H NMR spectrum (not shown here).

2.2. Synthesis

PBS and PBSF10 were synthesized from BDO, SA and FDCA (optional, 10 mol% in diacid) via a two-step melt polycondensation procedure. In brief, the monomers (diol/diacid molar ratio 2:1) were added into a 250 mL four-necked round flask under mechanical stirring and N2 inlet and then heated to 170 °C. TBT (0.1 mol% based on diacid) was added and the esterification reaction was conducted at 170 °C for 1 h, 180 °C for 2 h and 190 °C for 1–2 h up to over 98% esterification degree. Finally, the polycondensation reaction was performed under vacuum (<240 Pa) at 230 °C for 1 h and 240 °C for 2–5 h until Weissenberg effect emerged. The products were vacuum-dried at 40 °C for more than 24 h and stored in a desiccator before characterization and testing.

2.3. Characterization

The 1H NMR spectrum was recorded with an AC-80 spectroscopy (400 MHz, BRUKER). Deuterated chloroform was used as solvent and tetramethylsilane as internal reference. δ (CDCl3): 4.11 (4H, t), 2.63 (4H, s), 1.71 (4H, m) for PBS; 7.21 (2H, d), 4.40 (4H, t), 4.36 (2H, i), 4.15 (2H, t), 4.11 (4H, t), 2.63 (4H, s), 1.92 (4H, m), 1.85 (2H, m), 1.77 (2H, m), 1.71 (4H, m) for PBSF. The molecular weight and its distribution were measured at 30 °C by a gel permeation chromatography (GPC, Waters 1525/2414) equipped with a differential refractive index detector (DRI, Water 2414). Chloroform was used as eluent. The concentration of sample solution was about 3 mg/mL, and the eluent flow rate was 1.0 mL/min. Polystyrene standards were used for calibration. The intrinsic viscosity was measured at 25 °C by an automatic viscosity tester (ZONWON IVS300, China) equipped with a Ubbelohde viscometer with a diameter of 0.88 mm. Mixture of phenol and tetrachloroethane (3/2 w/w) was used as solvent. The solution concentration was 5 mg/mL. The intrinsic viscosity was calculated via Billmeyer empirical formula [η] = (n2p + 3lnηi)/4 C [28].

The wide angle X-ray diffraction (WAXD) pattern was recorded using a XPert Pro X-ray diffraction system (PANalytical B.V. Company, Netherland) with Cu Kα radiation (1.54 Å), working at 40 KV and 200 mA. The sample was scanned from 2θ = 5° to 2θ = 60° with scanning rate of 2°/min. The small angle X-ray scattering pattern was recorded using XEUSS SAX. S system (XENOCS SA, France) with CuKα radiation (1.54 Å), working at 40 KV and 200 mA. The sample was scanned from 2θ = 0.1° to 2θ = 3.6° with scanning rate of 0.05°/min.

The thermal transition was recorded with differential scanning calorimetry (DSC) on a Q200 thermal analyzer (TA Instruments). A standard heat-cool-heat program with heating/cooling rate of 10 °C/min was performed between −50 and 150 °C. The temperature was held at 150 °C and −50 °C for 5 min respectively before cooling and second heating. For isothermal melt crystallization and melting, a sample was heated to 150 °C and kept for 5 min, then cooled rapidly to the crystallization temperature and held at this
temperature for enough time (10–85 min) in order to crystallize completely. At last, it was re-heated to 150 °C at 10 °C/min.

Spherulite growth was observed with a polarized optical microscope (POM, ECLIPSE E600W POL). The sample was heated at 10 °C/min to 150 °C and held for 3 min, then rapidly cooled at −100 °C/min to the crystallization temperature (T_c) and crystallized at T_c for enough time to observe and record the growth of spherulite.

The tensile properties were measured with a Zwick Roell Z020 testing machine according to ASTM D638. Dumbbell-shaped tensile specimens with thickness of 2 mm were prepared by injection with a HAAKE MiniJet II injector. All the specimens were kept in standard atmosphere of 25 °C and 50% relative humidity for at least 48 h before testing. The crosshead speed was 10 mm/min. For each sample, at least five specimens were tested in parallel.

3. Results and discussion

3.1. Synthesis and chain structure

PBS and PBSF10 were synthesized via a two-step melt polycondensation procedure. The intrinsic viscosities of them were of 1.37 dL/g and 1.91 dL/g, respectively. And the weight average molecular weights of them were of 162,500 and 193,700 g/mol, respectively. The molecular weights were much higher than those reported in our previous study [12] (see Table 1) because much purer FDCA monomer and optimized reaction conditions were used in this study. The lower and escalating esterification temperature program was helpful to depress the etherification side reaction and therefore to reach high esterification degree (> 98%). Both highly pure FDCA and high esterification degree allowed us to reach the high molecular weight. Using the same monomer and reaction conditions, PBSF40-60 with very high M_w (162,000–167,000 g/mol) were also synthesized in our very recent reports [16,17]. The higher molecular weight resulted in some difference in thermal transition and mechanical properties, which will be discussed in the next sections. The copolymer composition of PBSF10, namely, the percentage of butylene furandicarboxylate (BF) unit, was determined from the 1H NMR data, as previously reported [12,16]. It was 10.2 mol%.

3.2. Crystal structure

It was interesting to study the influence of the existence of BF unit on the crystal structure of PBSF10. The crystal structure of PBS and PBSF10 was investigated with wide angle X-ray diffraction (WAXD). Fig. 1 shows the WAXD pattern of PBS and PBSF10 samples sufficiently annealed at 95 °C. Both samples show typical profiles of semicrystalline polymers, presenting evident reflection characteristic of crystalline region, which are superimposed over bell-shape baseline due to the presence of amorphous region. It is known that PBS forms a monoclinic crystal lattice with crystal cell parameters: a = 0.523 nm, b = 0.908 nm, c = 1.079 nm, and β = 123.87° [29]. PBS shows intense diffraction peaks at 20.2°, 22.5°, 23.1° and less intense reflection at 29.5°, which are ascribed to the (0 2 0), (0 2 1), (1 1 0) and (1 1 1) planes [29]. Almost the same diffraction peaks appeared at the same position for PBSF10,

![Fig. 1. WAXD patterns of PBS and PBSF10.](image-url)
indicating that PBSF10 has the same crystal structure of PBS. Therefore, it can be concluded that the small amount of BF unit in PBSF10 is completely excluded from the PBS crystalline phase and locates at the amorphous phase. The WAXD patterns were analyzed by peak-fitting and the ratio of the total area of all crystalline reflexes to that of all reflexes was defined as the crystallinity.

The crystallinities of PBS and PBSF10 are 46% and 39%, respectively.

To better understanding the difference in crystal structure between PBS and PBSF10, they are further characterized with small angle X-ray scattering (SAXS). The normalized one-dimensional correlation function (1DCF), \( K(z) \), is correlated with the scattering intensity \( I(q) \) with Eq. (1), in which \( q \) is the scattering vector and equal to \( 4\pi\sin(\theta)/\lambda \) (\( \lambda \) is the scattering wave length) and \( z \) is the spatial coordinate along the normal direction of lamella. The 1DCF analysis results of the SAXS data were obtained using the Mathematica 9.0 software and shown in Fig. 2. The crystal structure parameters including lamella long period (\( L_p \)), thickness of the crystalline region (\( L_c \)) and thickness of the transition zone (\( t \)) were obtained from the figure through a so-called graphing method.

The thickness of the amorphous region (\( L_a \)) was calculated from Eq. (2). The results are listed in Table 2. It can be seen that PBS and PBSF10 have the same thicknesses of crystalline region and transition zone (3 nm and 1 nm), but PBSF10 has larger thickness of amorphous region than PBS (6.3 nm vs. 6.0 nm). Therefore, PBSF10 has a larger long period than PBS (10.3 nm vs. 10.0 nm). This result validated that the BF unit is excluded from the PBS crystalline phase and locates at the amorphous phase, and therefore, accounted for the less crystallinity of PBSF10. In conclusion, incorporating 10 mol% BF unit into PBS chain did not change the crystal structure of PBSF10 but thickened the amorphous region of the lamella.

\[
K(z) = \frac{\int_0^{\infty} q^2 I(q) \cos(qz) dq}{\int_0^{\infty} q^2 I(q) dq},
\]

\[
L_a = L_p - L_c - t
\]

3.3. Nonisothermal crystallization and melting behavior

The nonisothermal melt crystallization and followed melting behavior were studied with DSC. The thermograms of PBS and PBSF10 are shown in Fig. 3. In comparison with PBS, PBSF10 showed decreasing crystallization and melting temperature (\( T_c, T_m \)) and enthalpy (\( \Delta H_c, \Delta H_m \)), but they still retained high enough crystallizability and showed higher glass transition temperature (\( T_g \)). The \( T_c, T_m, \Delta H_c \) and \( \Delta H_m \) of PBSF10 decreased by 29.2 °C, 12.3 °C, 15.0 J/g, 15.5 J/g, respectively, but the \( T_g \) increased by 8.5 °C. The decrease in crystallizability is in accordance with the WAXD results. As the molecular weight of both PBS and PBSF10 was higher than those in our previous study [12], their crystallizability decreased and therefore, their \( T_c, T_m, \Delta H_c \) and \( \Delta H_m \) decreased accordingly, as shown in Table 1. On the other hand, PBSF10 has clearly higher thermal transition properties than PBSF45 (\( T_m: 101.6 \) °C vs 73.1 °C [16]; \( \Delta H_m: 49.6 \) J/g vs. 18.4 J/g [16]) which has the same aromatic content as in commercialized PBAT.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>( L_p (\text{Å}) )</th>
<th>( L_c (\text{Å}) )</th>
<th>( t (\text{Å}) )</th>
<th>( L_a (\text{Å}) )</th>
<th>( T_g ) (°C)</th>
<th>( T_c ) (°C)</th>
<th>( T_m ) (°C)</th>
<th>( \Delta H_c ) (J/g)</th>
<th>( \Delta H_m ) (J/g)</th>
<th>Ref.</th>
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<tbody>
<tr>
<td>PBS</td>
<td>100</td>
<td>30</td>
<td>10</td>
<td>60</td>
<td>-36.1</td>
<td>68.5</td>
<td>113.9</td>
<td>62.3</td>
<td>64.6</td>
<td>This study</td>
</tr>
<tr>
<td>PBSF10</td>
<td>103</td>
<td>30</td>
<td>10</td>
<td>63</td>
<td>-27.6</td>
<td>39.3</td>
<td>102.0</td>
<td>46.8</td>
<td>49.6</td>
<td>This study</td>
</tr>
<tr>
<td>PBS*</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>-40.9</td>
<td>76.6</td>
<td>114.0</td>
<td>75.9</td>
<td>74.8</td>
<td>[12]</td>
</tr>
<tr>
<td>PBSF10*</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>-25.0</td>
<td>53.1</td>
<td>104.0</td>
<td>65.2</td>
<td>61.9</td>
<td>[12]</td>
</tr>
</tbody>
</table>

\( \Delta H_c \) crystal long period; \( L_c \): thickness of the crystalline region; \( t \): thickness of the transition zone; \( L_a \): thickness of the amorphous region.
3.4. Isothermal crystallization and melting behavior

The isothermal melt crystallization of PBSF10 was conducted at crystallization temperature \( T_c \) ranging 57.5–82.5 °C, higher than the nonisothermal melt crystallization peak temperature (39.3 °C, see Fig. 3). The Avrami plots of relative crystallinity versus crystallization time are shown in Fig. 4. It can be seen that the crystallization kinetics was well described by Avrami equation (Eq. (3)). The Avrami index \( n \) varied in the range 2.10–2.87. The half crystallization time \( t_{1/2} \) was calculated with Eq. (4) from the crystallization rate constant \( k \). It is found that the total crystallization rate \( t_{1/2} \) decreased exponentially with increasing isothermal crystallization temperature in the experimental range, as shown in Fig. 5. The resulting empirical relationship between \( t_{1/2} \) and \( T_c \) is described in Eq. (5). The \( t_{1/2} \) value was 0.87 min at 57.5 °C, indicating high crystallization rate.

\[
\log[-\ln(1-X_t)] = \log k + n \log t \tag{3}
\]

\[
t_{1/2} = (\ln 2/k)^{1/n} \tag{4}
\]

\[
\ln(t_{1/2}^2) = 8.93 - 0.152 T_c \tag{5}
\]

After isothermal melt crystallization, the samples were heated at 10 °C/min to 150 °C to observe the melting behavior. In the heating scan (Fig. 6A), all samples exhibited three endothermal melting peaks, denoted as peaks I, II and III. With increasing \( T_c \), peak I kept very weak, peak II broadened and moved to higher temperature, and peak III diminished and shifted slightly toward higher temperature. The peaks II and III tended to merge at high \( T_c \). Similar multiple melting peaks were also observed in PBS [30,31] and some other polyesters [32]. Peak I is ascribed to melting of small and imperfect secondary crystals, peak II is attributed to melting of primary crystals formed during the crystallization at \( T_c \), and peak III is ascribed to melting of recrystallized ones. When the corresponding peak temperatures \( (T_{m,1}, T_{m,II}, T_{m,III}) \) were plotted versus \( T_c \) (Fig. 6B), it can be seen that all of them raise with \( T_c \) linearly in the experimental range, \( T_{m,I} \) keeps about 5.2 °C higher than \( T_c \), and the slope decreases in such an order \( T_{m,I} > T_{m,II} > T_{m,III} \). The less pronounced \( T_c \) dependence of \( T_{m,III} \) indicates peak III relates to more perfect crystals [33]. According to the well-known Hoffman-Week's equation \( (T_m = T_m^0(1-1/(2\beta)) + T_c/(2\beta)) \), in which \( \beta \) is the ratio of the thickness of the final crystallites \( L_c^* \) to that of the preliminary ones \( L_c^* \) [34], the equilibrium melting point \( (T_m^0) \) can be obtained as the intercept of the \( T_{m,III}-T_c \) line with the diagonal line \( (T_m = T_c) \). The \( T_m^0 \) of PBSF10 was estimated to be 122 °C. It is 15.5 °C lower than that of PBS (137.5 °C, 136.3 °C) [30,31].

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**Fig. 3.** DSC curves of PBS and PBSF10 copolyester.

**Fig. 4.** Avrami fitting of the isothermal melt crystallization of PBSF10.
3.5. Spherulite growth kinetics

The spherulite growth of PBSF10 was observed by POM in the $T_c$ range of 70–90 °C. It was seen from the POM micrographs (not shown) that the spherulite density decreased with increasing $T_c$. The spherulite size grew linearly with time until the spherulites contacted with each other. The spherulite growth rate ($G$) was calculated as the slope of spherulite radius-time curve. The $T_c$ dependence of the spherulite growth rate is visualized in Fig. 7. Clearly, the growth rate decreased with increasing $T_c$ from 70 °C to 90 °C because the supercooling degree, namely the thermodynamic driving force for spherulite growth, decreased accordingly.

$$\ln(t_{1/2}) = 8.93 - 0.152 T_c \quad (r=0.998)$$

$$t_{1/2} = 1.32 \times 10^{-4} \exp(0.152 T_c)$$

$$\ln(t_{1/2}) = 8.93 - 0.152 T_c \quad (r=0.998)$$

Fig. 5. $T_c$ dependence of the half crystallization time $t_{1/2}$ of PBSF10.

Fig. 6. (A) Heating scan (10 °C/min) DSC curves after isothermal melt crystallization at the indicated temperature and (B) Hoffman-Weeks plot of PSF10.

3.5. Spherulite growth kinetics

The spherulite growth of PBSF10 was observed by POM in the $T_c$ range of 70–90 °C. It was seen from the POM micrographs (not shown) that the spherulite density decreased with increasing $T_c$. The spherulite size grew linearly with time until the spherulites contacted with each other. The spherulite growth rate ($G$) was calculated as the slope of spherulite radius-time curve. The $T_c$ dependence of the spherulite growth rate is visualized in Fig. 7. Clearly, the growth rate decreased with increasing $T_c$ from 70 °C to 90 °C because the supercooling degree, namely the thermodynamic driving force for spherulite growth, decreased accordingly.

$$\ln G + U^* = \ln G_0 + \frac{K_g}{T_c \Delta T_f}$$

Fig. 7. (A) Growth of spherulite size with crystallization time at various temperature and (B) spherulite size growth rate of PBSF10 at various crystallization temperatures.
The dependence of spherulitic growth rate of PBSF10 was further analyzed with Lauritzen-Hoffman equation (Eq. (6)), where $G_0$ is a pre-exponential factor, $U^*$ is the transport activation energy, $T_\infty$ is a hypothetical temperature below which all viscous flow ceases, $K_g$ is a nucleation parameter, $\Delta T$ is the supercooling degree, and $f$ is a correction factor to account for the variation in the bulk enthalpy of fusion per unit volume with temperature, $f = 2T_c/(T_m + T_c)$. The universal values of $U^* = 1500$ cal/mol and $T_\infty = T_g - 30$ K were used in the calculation and the results are plotted in Fig. 7B. Quite good linear relationship was observed and no regime transition appeared in the experimental $T_c$ range. The slope of the curve gives a high value of $K_g$, $3.60 \times 10^5$ K$^2$.

$$\ln G = \frac{U^*}{RT} + \frac{K_g}{T}\Delta T$$

(6)

3.6. Tensile properties

Finally, the tensile properties of PBS and PBSF10 were also assessed and compared. As they are flexible crystalline plastics, elastic deformation followed by yielding and strain hardening were observed in stress-strain curves (Fig. 8). The tensile properties are listed in Table 3. Both of them have satisfactory tensile properties: modulus 370–430 MPa, strength at break 38–44 MPa and elongation at break 230–300%. In comparison with PBS, PBSF10 has lower tensile properties because of its lower extent of crystallinity. In comparison with our previous results, the PBS and PBSF10 samples in this study exhibited lower modulus but higher tensile strength and elongation at break because of their higher molecular weight and lower crystallinity. In comparison with PBSF45 which also has very high $M_w$ [16], the PBSF10 has much higher tensile modulus (372 MPa vs. 64 MPa), as seen in Table 3. The PBSF10 sample also shows higher tensile strength and modulus when compared with poly(butylene succinate-co-adipate) and poly(butylene succinate-co-terephthalate) with the same composition (PBSA10, PBST10) reported in literatures [23,26]. Besides, the $T_g$ of PBSF10 is higher than that of PBSA10 and PBST10 ($-27.6$ °C vs. $-39$ °C [27], $-37$ °C [23]) though they have almost the same $T_m$ (103 ± 2 °C [23,26–27]).

4. Conclusions

In this study, high molecular weight PBSF10 was synthesized and its crystal structure, crystallization-melting behavior and tensile properties were investigated. In comparison with PBS, PBSF10 has the same crystal structure with the same thicknesses of crystalline region and transition zone (3 nm and 1 nm), but larger thickness of amorphous region (6.3 nm vs. 6.0 nm), indicating that the BF unit is excluded from the crystalline region and located in the amorphous region. Therefore, PBSF10 exhibits less crystallizability than

Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_w$ (g/mol)</th>
<th>$T_m$ (°C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>$E$ (MPa)</th>
<th>$\sigma_b$ (MPa)</th>
<th>$\epsilon_b$ (%)</th>
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<tr>
<td>PBS</td>
<td>162,500</td>
<td>113.9</td>
<td>64.6</td>
<td>432 ± 22</td>
<td>43.6 ± 1.0</td>
<td>303 ± 15</td>
<td>This study</td>
</tr>
<tr>
<td>PBSF10</td>
<td>193,700</td>
<td>102.0</td>
<td>49.6</td>
<td>372 ± 20</td>
<td>38.0 ± 3.0</td>
<td>228 ± 6</td>
<td>This study</td>
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<tr>
<td>PBS$^*$</td>
<td>35,100</td>
<td>114.0</td>
<td>74.8</td>
<td>675 ± 5</td>
<td>30.6 ± 1.4</td>
<td>128 ± 14</td>
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<td>PBSF10$^*$</td>
<td>55,800</td>
<td>104.0</td>
<td>61.9</td>
<td>554 ± 30</td>
<td>21.4 ± 3.4</td>
<td>165 ± 41</td>
<td>Ref. [12]</td>
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<td>165,400</td>
<td>73.1</td>
<td>18.4</td>
<td>64 ± 1</td>
<td>56 ± 3</td>
<td>758 ± 17</td>
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<td>62</td>
<td>331</td>
<td>22</td>
<td>415</td>
<td>Ref. [23]</td>
</tr>
<tr>
<td>PBSA10$^*$</td>
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<td>105</td>
<td>59</td>
<td>–</td>
<td>18.3</td>
<td>402</td>
<td>Ref. [26]</td>
</tr>
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</table>

 PBSF10 is poly(butylene succinate-co-terephthalate) with 10 mol% butylene terephthalate unit.
 PBSA10 is poly(butylene succinate-co-adipate) with 10 mol% butylene adipate unit. The tensile properties of PBSA10 are obtained by interpolation method from the data of PBS and PBSF10 reported in Ref. [26].
PBS. But PBSF10 still exhibits rapid nonsothermal and isothermal crystallization. The half crystallization time was low as 0.9 min at 57.5 °C, and the nucleation parameter is as high as 3.60 × 10^3 K^2. The equilibrium melting temperature is estimated to be 122 °C. Because of high molecular weight and good crystallizability, the PBSF10 sample exhibited good tensile properties: modulus 370 MPa, strength at break 38 MPa and elongation at break 230%.

Acknowledgements

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