Non-isothermal crystallization and subsequent melting of biodegradable poly(butylene succinate-co-terephthalate) copolymers with different butylene terephthalate contents were investigated by differential scanning calorimetry measurements. Differential scanning calorimetry crystallization curves revealed that butylene terephthalate contents of poly(butylene succinate-co-terephthalate) copolymers had an identical effects on the onset, peak and final crystallization temperatures. Subsequent differential scanning calorimetry melting curves implied that both PBST-10 and PBST-70 copolymers had the narrow distribution of lamellar thickness, while the PBST-50 copolyester showed much wider distribution.

Key words: biodegradable, non-isothermal crystallization, poly(butylene succinate-co-terephthalate) copolymers, butylene terephthalate contents

Introduction

Recently, biodegradable polymers have increasingly attracted attention of researchers because of the serious environmental problems. Copolymerization of aromatic and aliphatic polymers is an effective way to obtain biodegradable polymers with balance of biodegradability and superior thermal and mechanical properties by adjusting the molar ratio of comonomers during synthesis process [1]. As a typical example, PBST copolymers developed in our previous research exhibited excellent mechanical, thermal and biodegradable properties [2-4]. There is little research on the non-isothermal crystallization behavior of poly(butylene succinate-co-terephthalate) (PBST) copolymers, so it is of great importance to study the non-isothermal crystallization kinetics of PBST copolymers.

In this paper, the non-isothermal crystallization and subsequent melting behaviors of PBST copolymers with different butylene terephthalate (BT) contents were investigated by differential scanning calorimetry (DSC) measurements, and the effects of BT comonomer contents on the non-isothermal crystallization behavior of the copolymers were analyzed.

* Corresponding author; e-mail: fxlee@dhu.edu.cn
Experimental section

Materials

PBST copolyesters were synthesized via direct esterification and polycondensation from the starting materials of terephthalic acid (TPA), succinic acid (SA) and 1,4-butanediol (BD). The feed molar ratios of TPA to SA were 30:70, 50:50 and 70:30 for PBST-30, PBST-50 and PBST-70. The detailed preparation of these copolyesters was described elsewhere [2].

DSC measurements

The non-isothermal crystallization and the following melting experiments of PBST films were carried out with the Pyris 6 DSC instrument. The samples were sealed in aluminum pans. Procedures were as follows: the samples were heated to 20 °C higher than the corresponding melting temperature of the copolyesters at 20 °C per minute and kept at that temperature for 3 min, then cooled down to room temperature at cooling rate of 5 °C per minute. After that, the new heating run was started with a heating rate of 10 °C per minute and the results were recorded.

Results and discussion

Figure 1 shows the DSC curves of PBST copolyesters with different BT contents non-isothermally crystallized at the cooling rate of 5 °C per minute. It can be clearly observed that there was only one crystallization peak and the position of this crystallization peak shifted to higher temperature as the BT content in the copolyesters increased. This indicated that the introduction of BT units increased the stereoregularity of poly(butylene succinate) (PBS) macromolecular chains.

Figure 2 sketches the relationship between the onset, peak and final crystallization temperatures and BT contents of PBST copolyesters. It can be seen that the slopes of the curves about these three crystallization temperatures against the BT content of PBST copolyesters were almost in accordance. This suggested that BT content of PBST copolyesters had the similar effects on these crystallization temperatures.

Figure 3 displays the subsequent DSC melting curves of PBST copolyesters with different BT contents non-isothermally crystallized at the cooling rate of 5 °C per minute. It can be observed that the position of melting peak possessed the similar tendency to that of crystallization peak with the BT content of these copolyesters. Furthermore, both the PBST-10 and PBST-70 copolyesters possessed sharp melting peaks, while the PBST-50 copolyester exhibited the broadest one. The width of the melting peak was relevant to the
distribution of the lamellar thickness and it meant that the PBST-50 had the widest distribution of the lamellar thickness which was the contribution of interactions between equal contents of BT and BS units.

The corresponding melting temperatures, enthalpy of melting and crystallinities during the melting process of PBST copolymers with different BT contents after non-isothermal crystallization are summarized in Table 1. The peak and final melting temperatures heightened with the increase of BT content of PBST copolymers. The reason why the onset melting temperatures were not referred to was that the melting peak was so broad not to tell the accurate onset temperatures. Crystallinity was a good demonstration for the perfection of the crystals in these copolymers. PBST-50 copolymer had the lowest crystallinity compared with PBST-10 and PBST-70 copolymers, which implied that it has less perfect crystal because the interactions between the equal content of BT to BS units in the copolyester.

Table 1. Thermal properties of PBST copolymers with different BT contents during the melting process after non-isothermally crystallized at the cooling rate of 5 °C per minute

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_m^p ) [°C]</th>
<th>( T_m^f ) [°C]</th>
<th>( \Delta H_f ) [Jg(^{-1})]</th>
<th>( X_c ) [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PBST-10</td>
<td>97.6</td>
<td>101.5</td>
<td>49</td>
<td>44.3</td>
</tr>
<tr>
<td>PBST-50</td>
<td>146</td>
<td>159.1</td>
<td>11.5</td>
<td>7.9</td>
</tr>
<tr>
<td>PBST-70</td>
<td>180.5</td>
<td>187.9</td>
<td>23</td>
<td>15.9</td>
</tr>
</tbody>
</table>

\( T_m^p \) – peak melting temperature, \( T_m^f \) – final melting temperature, \( \Delta H_f \) – enthalpy of melting, \( X_c \) – crystallinity

Conclusions

Non-isothermal crystallization and subsequent melting of biodegradable PBST copolymers with different BT contents were investigated by DSC measurements. The non-isothermal crystallization curves indicated that there was only one crystallization peak and the
position of this crystallization peak shifted to higher temperature as the BT content in the copolyesters increased. The similar tendency can be found in the melting curves of PBST copolyesters as the BT content increased. PBST-50 had the lowest crystallinity which implied that it has less perfect crystal.

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