Crystallization behaviour of cellulose acetate butylate/poly(butylene succinate)-co-(butylene carbonate) blends

Seung-Hwan Lee* and Siqun Wang
Tennessee Forest Products Center, 2506 Jacob Drive, University of Tennessee, Knoxville, TN 37996-4570, USA

Abstract: The kinetics of the isothermal crystallization process from the melt of pure poly(butylene succinate)-co-(butylene carbonate) (PBS-co-BC) and its blends with cellulose acetate butylate (CAB) (10–30 wt%) was studied by differential scanning calorimetry (DSC) and the well-known Avrami equation. In the blends, the overall crystallization rate of PBS-co-BC became slower with increasing CAB content. The equilibrium melting temperature (T\text{\text{\text{\text{\text{eq}}}}}m) of PBS-co-BC decreased with increasing CAB content, which was similar to that with other miscible crystalline/amorphous polymer blends. The slower crystallization kinetics of PBS-co-BC in the blends was explicable in terms of a diluent effect of the CAB component. By application of Turnbull–Fisher kinetic theory for polymer–diluent blend systems, the surface free energy (\sigma_e) of pure PBS-co-BC and of the blends was obtained, indicating that the blend with CAB resulted in a decrease in the surface free energy of folding of PBS-co-BC lamellar crystals.

Keywords: blend; crystallization; kinetics; cellulose acetate butylate; DSC

INTRODUCTION

With their advantageous biodegradability potential, the aliphatic polyesters have been actively studied as an alternative to some of the common synthetic polymers that cause environmental pollution problems.\textsuperscript{1–6} The aliphatic polyesters are believed to be able to degrade rather easily into less harmful structures under natural environmental conditions. However, the mechanical properties and thermal stability of these biodegradable aliphatic polyesters are not satisfactory for many industrial applications and they still have a small market that is only beginning to enter its growth stages. The market for biodegradable polymers has significant potential and if they were to capture a small portion of the global plastics market, it would become a significant industry.

Much research on physical or chemical modification of these aliphatic polyesters has been performed by means such as copolymerization or polymer blending to improve properties such as mechanical and thermal properties or to extend the fields of application.\textsuperscript{7–11} For example, Yong \textit{et al.} reported the influence of soft segment length on the properties of poly(butylene terephthalate)-co-(butylene succinate)-block-poly(ethylene glycol) segmented statistical copolymers with starting poly(ethylene glycol) (PEG) number-average molecular weight of 600, 1000 and 2000.\textsuperscript{12} Their research revealed that the increase in amorphous domains and the increase in molecular weight of poly(butylene succinate) (PBS) and PEG provide high elongation and good flexibility of copolymer chains. \textit{In vitro} degradation experiments showed that the partial substitution of aromatic segment poly(butylene terephthalate) with aliphatic PBS substantially accelerated the degradation rate, with enhanced safety of the degraded byproducts.

Teramoto \textit{et al.}\textsuperscript{13} have reported on graft copolymerization of cellulose acetate (CA) and poly(hydroxyalkanoate)s (PHA) and its characterization. They synthesized several different series of CA-graft-PHAs with a wide range of compositions by the graft copolymerization of lactic acid, L-lactide, (R,S)-\(\beta\)-butyrolactone, \(\delta\)-valerolactone and \(\varepsilon\)-caprolactone onto the residual hydroxyl positions of CA. The properties of the graft copolymer were changed depending on the composition of the graft chain.

Polymer blending with natural polymers (bio-based polymers) is also considered a useful way to control the properties without losing biodegradability.\textsuperscript{14–16} For example, Buchanan \textit{et al.}\textsuperscript{17–19} have reported on blends of biodegradable aliphatic polyesters and cellulose...
esters. In the CA/poly(ethylene succinate) blend, the blends containing more than 70 wt% CA were found to be miscible. Biodegradation experiments on the blends revealed that poly(ethylene succinate) decomposed relatively rapidly and that CA degraded slowly. In the case of poly(tetramethylene succinate) and poly(tetramethylene succinate)/cellulose acetate propionate (CAP) in the range of 10–40 wt% polyester, the blends had significantly higher tensile strengths, flexural moduli and heat-deflection temperatures, and greater hardness values than the corresponding CAP/dioctyl adipate blends. They also reported on a series of miscible blends consisting of CAP and poly(ethylene glutarate) or poly(tetramethylene glutarate) at a fixed CAP degree of substitution: when the content of polyester in the blend was increased, the rate of composting and the weight loss due to composting increased.

In our previous work, we have reported on the poly(butylene succinate)-co-(butylene carbonate) (PBS-co-BC)/cellulose acetate butyrate (CAB) miscible binary blend with single glass transition temperatures ($T_g$) over the entire composition range. PBS-co-BC is a high molecular weight aliphatic polyester-carbonate with properties that can be controlled by changing the ester and carbonate functional groups. CAB is one of the most useful cellulose esters derived from natural polymers and is commercially available. CAB is used in plastic film applications, automotive trims, tool handles and pen barrels. We found that CAB, an amorphous polymer, was clearly plasticized by PBS-co-BC as long as its addition was less than 40 wt%, whereas PBS-co-BC was confirmed to be crystallized in PBS-co-BC-rich blends and its crystallinity was affected by the introduction of CAB. Properties of the blends varied with the composition of each component.

In the present study, isothermal crystallization was carried out for PBS-co-BC-rich blends and Turnbull–Fisher kinetic theory for polymer–diluent blend systems was applied to explain the effect of CAB on the crystallization behaviour of PBS-co-BC.

**EXPERIMENTAL**

**Materials**

The CAB used for this experiment was CAB 40425-5000, commercially available from ACROS ORGANICS (New Jersey, USA). The butyryl content was 35–39 wt% and the acetyl content was 12–15 wt%. PBS-co-BC (S50 189, $M_w = 116 000$) was kindly supplied by the Mitsubishi Gas Chemical Co. In a previous report, it was found from analysis of the chemical composition of the PBS-co-BC by using $^{13}$C-NMR analysis that it contained a 1:20 molar ratio of carbonate to ester. Simply described, the ratio of the peak intensities (carbonate carbon at 157 ppm to ester carbonyl carbon at 174 ppm) was used to determine the molar composition of the ester and carbonate units in PBS-co-BC.

**Preparation of blends**

CAB and PBS-co-BC were first mixed in dry solid states followed by melt blending using a Labo Plastomill LPM 18–125 (Toyo Seiki Co. Ltd). The temperature, rotation rate and processing period were 200–240 °C, 90 rpm and 10 min, respectively. The blended materials were hot-pressed into sheets and allowed to age at room temperature. The temperature, duration period and pressure of the hot-press moulding were 150–200 °C, 30 s and 15.0 MPa, respectively.

**Differential scanning calorimetry**

DSC analysis was performed to study the crystallization behaviour of the blends using a Perkin-Elmer Diamond DSC. The apparatus was calibrated with an indium standard and the samples were placed in sealed aluminium cells. The samples were first heated from 20 to 200 °C at a heating rate of 10 °C min$^{-1}$ (first scan). After the samples were kept for 5 min at 200 °C to remove the thermal history, they were rapidly cooled to −60 °C at a rate of ~100 °C min$^{-1}$ and then the second scan was performed with a heating run at a rate of 10 °C min$^{-1}$ to 200 °C. The $T_g$ was estimated in the second heating scan, and the melting temperature and apparent enthalpy of fusion ($\Delta H_f$) were determined from the endothermal peaks in both the first and second heating scans.

For isothermal crystallization, another DSC experiment was performed on pure PBS-co-BC and the blends with 10–30 wt% CAB. After the first scan, the samples were kept for 5 minutes at 200 °C and quenched to a certain isothermal crystallization temperatures ($T_c$). After the isothermal crystallization was complete, the samples were cooled to 20 °C and then heated again to 200 °C to estimate melting temperatures.

**RESULTS AND DISCUSSION**

Figure 1 shows the composition dependence of the $T_g$ of PBS-co-BC-rich blends. With increasing CAB content, the $T_g$ value of PBS-co-BC increased. In our previous work, it was also found that in blends with PBS-co-BC content of less than 40 wt% the $T_g$ of CAB was shifted to lower temperatures regularly with increasing PBS-co-BC content. These results indicate that this blend system is at least miscible in the amorphous region.

Figure 2 shows the dependence of the melting temperature ($T_m$) and the heat of fusion ($\Delta H_f$) of PBS-co-BC on CAB content during the first and the second scan. In both scans, a decrease in the $T_m$ and $\Delta H_f$ with increasing CAB content was evident. In particular, at compositions containing 40 wt% or more of CAB in the second scan, it was no longer possible to detect a melting temperature. This was due to the slow crystallization of PBS-co-BC in the blend. As discussed in our previous paper, the crystallization rate and crystallinity of PBS-co-BC decrease rapidly with increasing CAB content. This decrease of $T_m$
and $\Delta H_f$ is well known as being characteristic of semicrystalline amorphous blends.

**Figure 1.** Dependence of $T_g$ on the composition of the blend.

**Figure 2.** Variation of melting temperature and heat of fusion with CAB content: (a) first scan; (b) second scan.

**Figure 3.** Hoffman–Weeks plots for isothermally crystallized PBS-co-BC and its blends with CAB.

**Isothermal crystallization behaviour**

For further studies of crystallization behaviour, the PBS-co-BC-rich blends with up to 30 wt% CAB were isothermally crystallized at various temperatures. Figure 3 shows the Hoffman–Weeks plots for isothermally crystallized PBS-co-BC and its blends with CAB, indicating the dependence of $T_m$ on $T_{ic}$. The melting temperature of all the samples increased with the crystallization temperature. At the same crystallization temperature, the melting temperature of all blends was lower than that of pure PBS-co-BC. The equilibrium melting temperature ($T_{eq}^m$) was obtained by using the following Hoffman–Weeks equation by extrapolation of $T_m$ versus $T_{ic}$ to the line $T_m = T_{ic}$:

$$T_m = \phi T_{ic} + (1 - \phi) T_{eq}^m$$

where $T_{eq}^m$ is the equilibrium melting temperature, $T_m$ is the melting temperature and $\phi$ is a stability parameter that is usually related to morphological factors concerning perfectness and size of the crystals. The stability parameter will be discussed in the last part of this study.

Values of $T_{eq}^m$ in pure PBS-co-BC and in 90/10, 80/20 and 70/30 blends with CAB were 135.5, 127.5, 109.6 and 98.0°C, respectively. The $T_{eq}^m$ values of PBS-co-polymesters such as PBS-co-(14 mol% ethylene succinate), PBS-co-(15 mol% hexamethylene succinate) and PBS-co-(butylene 2-methyl succinate) have been reported to be decreased by copolymerization, but the $T_{eq}^m$ value of pure PBS-co-BC was very close to those of melt-crystallized PBS. The value of $T_{eq}^m$ dramatically decreased with increasing CAB content, e.g. for the blend with 30 wt% CAB it was 37°C less than that of pure PBS-co-BC. These decreases in $T_{eq}^m$ may be due to the diluent effect of amorphous CAB molecules.
The kinetics of crystallization under isothermal conditions can be adequately discussed in terms of the Avrami equation. Fig 4 shows the crystallization isotherms of pure PBS-co-BC and the blend with 20 wt% CAB content at various temperatures. The degree of conversion, \( X(t) \), at time \( t \) is expressed by the following Avrami equation:

\[
X(t) = 1 - \exp(-Kt^n)
\]  

(2)

where \( t \) is time, \( K \) is the overall rate constant and \( n \) is the Avrami exponent, which is determined by the mode of crystal nucleation and the crystal growth geometry in the actual circumstances. The degree of conversion \( X(t) \) is defined as the ratio of the peak area at time \( t \) to the final area and can be calculated using the following equation:

\[
X(t) = \int_{t_0}^{t} \left( \frac{dH}{dt} \right) dt / \int_{t_0}^{t_{\infty}} \left( \frac{dH}{dt} \right) dt
\]  

(3)

where \( t_0 \) and \( t_{\infty} \) are the crystallization onset and end times, respectively. Equation (2) can be rewritten as follows:

\[
\log_{10}[-\ln(1-X(t))] = \log_{10} K + n \log_{10} t
\]  

(4)

Figure 5 shows the plots of \( \log_{10}[-\ln(1-X(t))] \) versus \( \log_{10} t \) for pure PBS-co-BC and for the blend with 20 wt% CAB. These plots gave a straight lines, whose slope was \( n \) and intercept on the ordinate was \( \log_{10} K \).

In addition, the \( t_{0.5} \), defined as the time taken for half of the crystallization to occur, can be used to develop the isothermal crystallization process. That is, the overall rate constant \( K \) is closely related to the reciprocal of the half-time of crystallization (\( t_{0.5}^{-1} \)):

\[
t_{0.5}^{-1} = \frac{K^{1/n}}{(\ln 2)^{1/n}}
\]  

(5)
It was found from Table 1 that as the crystallization one-, two- or three-dimensional growth, respectively, and the crystallization of pure PBS-co-BC lower than those of the blends did not show significant decreases even at 296°C. Polym Int 29

\[ K = K_0 \exp \left( \frac{-\Delta E}{RT_{ic}} \right) \] (6)

where \( K_0 \) is a constant related to the initial crystallization rate, \( R \) is the absolute gas constant and \( \Delta E \) is the activation energy of crystallization. The \( \Delta E \) was determined as the slope coefficient by plotting \((1/n)\ln K\) versus \(1/T_{ic}\), as shown in Fig. 6. The value of \( \Delta E \) for pure PBS-co-BC was found to be \(-174.06\,\text{kJ mol}^{-1}\) and \(-131.94, -61.08\) and \(-27.81\,\text{kJ mol}^{-1}\) for the 90/10, 80/20 and 70/30 blends, respectively. The obtained values were negative, which is due to the energy released during transforming the molten state into the crystalline state. The activation energies of the blends were lower than that of pure PBS-co-BC, and the values became smaller with increasing CAB content. From a thermodynamic aspect, it can be said that the crystallization of PBS-co-BC in the blends was delayed, releasing less energy than pure PBS-co-BC.

Furthermore, the overall rate constant obtained in this study at various \( T_{ic} \) values can be expressed by using the Turnbull–Fisher kinetic theory of isothermal crystallization in polymer–diluent systems.\(^{30}\) In this theory, it is expected that the crystallization rate decreases with decreasing concentration of crystalline fraction and increasing \( T_{ic} \). This was well fitted in the case of this study.

The overall rate constant \( K \) and the half-time of crystallization \( t_{0.5} \) are closely related to crystallization rate \( G \) as follows:\(^{31-36}\)

\[ G \propto t_{0.5}^{-1} = \frac{K^{1/n}}{(\ln 2)^{1/n}} \] (8)

According to this kinetic theory, the dependence of the crystal growth rate \( G \) on the crystallization
Temperature $T_{ic}$ is expressed by the following equation:$^{32,36,37}$

$$G = v_2 G_0 \exp \left( -\frac{\Delta E_D^*}{kT_{ic}} \right) \exp \left( -\frac{\Delta \Phi^*}{kT_{ic}} \right)$$ (9)

where $G_0$ is a pre-exponential factor generally assumed to be constant or proportional to $T_{ic}$, $\Delta E_D^*$ is the activation energy for the transport of crystallizing units across the molten liquid–solid interface, $\Delta \Phi^*$ is the free energy required to form a nucleus of critical size and $k$ is the Boltzmann constant. Here, the pre-exponential factor is multiplied by the volume fraction $v_2$ of the crystalline polymer because the rate of nucleation is proportional to the concentration of crystallizable units.

The activation energy $\Delta E_D^*$ can be calculated with the Williams–Landel–Ferry relation:$^{38}$

$$\frac{\Delta E_D^*}{kT_{ic}} = \frac{C_1}{R(C_2 + T_{ic} - T_g)}$$ (10)

where $C_1$ and $C_2$ are constants (generally assumed to be $1.724 \times 10^3 \text{J mol}^{-1}$ and 51.6 K, respectively), and $R$ is the absolute gas constant. $\Delta \Phi^*$ may be given as:$^{32,39}$

$$\frac{\Delta \Phi^*}{kT_{ic}} = \frac{K_g}{T_{ic} \Delta T} - \frac{2\sigma T_m^m \ln v_2}{b_0 \Delta H_u \Delta T}$$ (11)

with

$$K_g = \frac{Yb_0 \sigma \sigma_c T_m^m}{k \Delta H_u}$$ (12)

where $K_g$ is the nucleation constant for a given growth regime,$^{40,41}$ $\Delta T$ is the undercooling defined as $T_m^m - T_{ic}$, $\Delta T_1$ is the heat of fusion of completely crystalline component ($268 \times 10^3 \text{J m}^{-3}$ was adopted in this work),$^{42}$ $Y$ is a coefficient that depends on the regime of crystal growth, $\sigma$ and $\sigma_c$ are the lateral surface energy and the fold surface free energy, respectively, and $b_0$ is the layer thickness. Generally, the $Y$ value is 4 when the $T_{ic}$ values lie in regime I (lower $\Delta T$) and III (higher $\Delta T$), and is 2 for the regime II growth process (medium $\Delta T$).$^{40,41}$ In this study, it was assumed that the growth front was the (110) plane as for PBS ($b_0 = 0.45 \text{nm}$) and the mode of spherulite growth was regime II growth.$^{24,25,27,42,43}$

For the lateral surface energy of linear polymer crystals, the following relation holds:$^{44}$

$$\sigma = 0.1 b_0 \Delta H_u$$ (13)

By substituting Eqns (10)–(13) into Eqn (9), the latter can be rearranged as follows:$^{39,45}$

$$\alpha = \log_{10} A_0 - C \frac{T_m^m}{T_{ic} \Delta T}$$ (14)

where

$$\alpha = \left( \frac{1}{n} \right) \log_{10} K - \log_{10} v_2 + \frac{17240}{2.3R(51.6 + T_{ic} - T_g)} - \frac{0.2T_m^m \log_{10} v_2}{\Delta T}$$ (15)

$$C = \frac{K_g}{2.37T_{mc}^m} = \frac{Yb_0^2 \sigma_c}{23.0k}$$ (16)

As can be seen in Fig. 7, plots of $\alpha$ versus $T_m^m/(T_{ic} \Delta T)$ showed straight lines for pure PBS-co-BC and for its blends with CAB. The values of $K_g$ calculated from the slopes ($C$), and the surface free energy ($\sigma_c$) obtained from the values of $K_g$ are summarized in Table 2, along with the values of the stability parameter $\phi$ of the lamellar crystals calculated from Eqn (1). The surface free energy $\sigma_c$ decreased slightly with increasing CAB content, without showing significant differences among the $\sigma_c$ values. This means that the addition of CAB to PBS-co-BC resulted in only a small reduction in the surface free energy of folding of PBS-co-BC lamellar crystals. The nucleation factor $K_g$ represents the free energy necessary to form a nucleus of critical size. The values of $K_g$ decreased from that of pure PBS-co-BC with the addition of CAB, indicating that the nucleation process of PBS-co-BC is

![Figure 7. Plots of the quantity $\alpha$ versus $T_m^m/(T_{ic} \Delta T)$.](image)

Table 2. The Values of $\phi$, $K_g$ and $\sigma_c$ of pure PBS-BC and its blends with CAB

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\phi$</th>
<th>$K_g \times 10^5$ (k$^2$)</th>
<th>$\sigma_c \times 10^{-5}$ (J cm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure PBS-co-BC</td>
<td>0.72</td>
<td>3.57</td>
<td>2.98</td>
</tr>
<tr>
<td>Blend with 10 wt% CAB</td>
<td>0.56</td>
<td>3.37</td>
<td>2.87</td>
</tr>
<tr>
<td>Blend with 20 wt% CAB</td>
<td>0.36</td>
<td>2.73</td>
<td>2.44</td>
</tr>
<tr>
<td>Blend with 30 wt% CAB</td>
<td>0.22</td>
<td>2.38</td>
<td>2.19</td>
</tr>
</tbody>
</table>
influenced by the presence of CAB molecules acting as diluent. In particular, the $\phi$ value, which is related to morphological factors concerning perfectness and size of the crystals, decreased with increasing CAB content. These results indicate that the crystallization process of PBS–co–BC in the presence of CAB is more morphologically stable than that of PBS–co–BC itself.

CONCLUSIONS
From this DSC study of the melt crystallization behaviour of pure PBS–co–BC and its blends with CAB (10–30 wt%), the following information was obtained. The overall crystallization rate of PBS–co–BC became slower with increasing CAB content. The activation energy for isothermal crystallization decreased with increasing CAB content, indicating that the crystallization of PBS–co–BC in the blends released less energy than pure PBS–co–BC. The equilibrium melting temperatures of pure PBS–co–BC decreased with the addition of CAB, showing similar trends to those for other miscible crystalline/amorphous polymer blends. Turnbull–Fisher kinetic theory could successfully explain the slower crystallization kinetics of PBS–co–BC in the blends with a diluent effect of the CAB component. The addition of CAB into PBS–co–BC resulted in a small reduction in the surface free energy of folding of PBS–co–BC lamellar crystals. This result and the decreased stability parameter indicate that the crystallization process of PBS–co–BC in blends is more morphologically stable than pure PBS–co–BC.

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REFERENCES