

# Subsequent Melting Behavior of Poly(butylene succinate) in Its Miscible Blend with Poly(vinyl phenol) Crystallized Nonisothermally from the Melt

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**ABSTRACT:** Biodegradable crystalline poly(butylene succinate) (PBSU) are miscible with amorphous poly(vinyl phenol) (PVPh). Neat PBSU and PBSU blended with PVPh show complex melting behavior after nonisothermal melt crystallization at constant cooling rates. Both neat and blended PBSU can show one, two, or three melting peaks depending on the blend composition, cooling rate, and heating rate. A model

was proposed to explain the origin of the complex melting behavior of PBSU through conventional differential scanning calorimetry (DSC) and temperature-modulated differential scanning calorimetry (TMDSC) studies. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 104: 3637–3641, 2007

**Key words:** blends; melting behavior; DSC

## INTRODUCTION

Poly(butylene succinate) (PBSU) is a linear aliphatic biodegradable polyester with the chemical structure of  $-(\text{OCH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}-)_n$ . The crystal structure, crystallization, and melting behavior of PBSU have been reported.<sup>1–9</sup> Polymer blending is often used to modify the properties and extend the application field of polymeric materials. PBSU is miscible with some semicrystalline polymers, including poly(vinylidene fluoride), poly(vinylidene chloride-co-vinyl chloride), and poly(ethylene oxide).<sup>10–13</sup> PBSU is also found to be immiscible with some biodegradable polymers, including poly(hydroxybutyrate), poly(3-hydroxybutyrate-co-3-hydroxyvalerate), and poly( $\epsilon$ -caprolactone).<sup>14–16</sup> Poly(4-vinyl phenol) (PVPh) is an amorphous polymer with high glass transition temperature. In the previous works, we

studied the miscibility, morphology, and isothermal and nonisothermal melt crystallization kinetics of PBSU/PVPh blends.<sup>17–19</sup> PBSU and PVPh are completely miscible in an amorphous phase over the entire composition range as shown by the single composition-dependent glass transition temperature.<sup>17</sup>

Double or multiple melting endotherms are often found in semicrystalline polymers crystallized isothermally from the melt at selective crystallization temperature.<sup>5,13,20–22</sup> Liu summarized the possible origin of the double or multiple melting endotherms as follows: (1) melting, recrystallization, and remelting during the DSC heating process, (2) the presence of more than one crystal modifications (polymorphism), (3) variation in morphology (such as lamellar thickness, distribution, perfection, or stability), (4) physical aging or/and relaxation of the rigid amorphous fraction, (5) different molecular weight species, and so on.<sup>23</sup> Few works has dealt with the double or multiple melting endotherms of polymers crystallized nonisothermally from the melt at constant cooling rates.<sup>9,24</sup> However, semicrystalline polymers are usually processed nonisothermally from the melt. Therefore, much more attention should be paid to the nonisothermal crystallization and subsequent melting behavior of polymeric materials from the viewpoint of practical application.

Temperature-modulated differential scanning calorimetry (TMDSC) is a thermal analysis technique applying a sinusoidal temperature oscillation on a linear heating/cooling conventional DSC and makes

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the total heat flow to be separated into the heat capacity-related reversible and kinetic nonreversible components. The endothermic signals can thus be detected in both reversible and nonreversible scans, whereas the crystallization exotherms can only be found in the nonreversible signal. TMDSC is a very useful means for the separation of exotherms such as crystallization and recrystallization from glass transitions, reversible melting, or other heat capacity related events, indicating that TMDSC is a suitable candidate to be used to study the complex melting behavior of polymers.<sup>9,25,26</sup>

The subsequent melting behavior of PBSU/PVPh blends was investigated in this work using conventional DSC and TMDSC after they finished the nonisothermal crystallization at constant cooling rates from the melt to get a better understanding of the origin of the melting behavior of polymers crystallized nonisothermally.

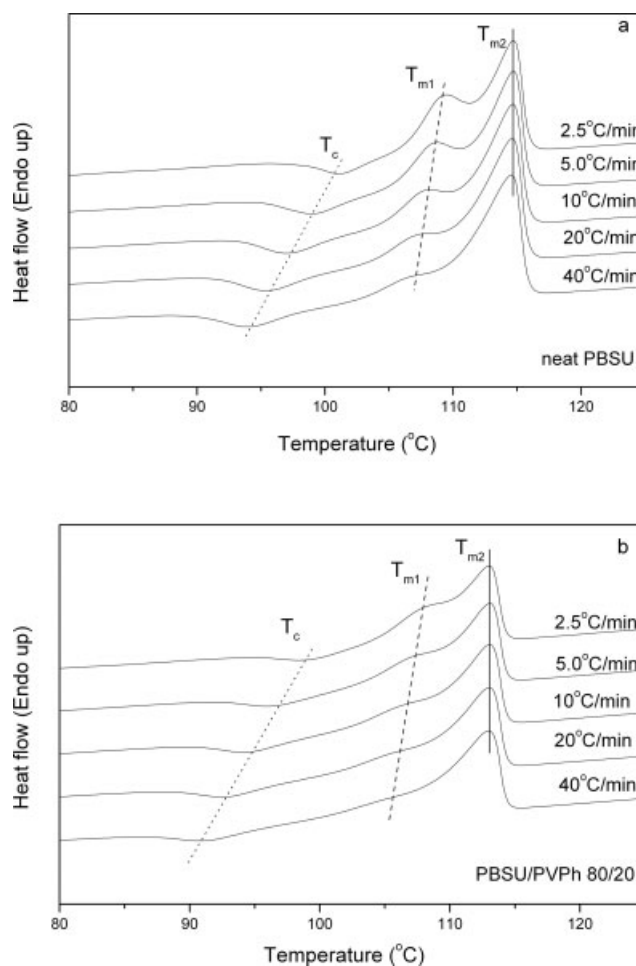
## EXPERIMENTAL

PBSU ( $M_w = 140,000$ ) and PVPh ( $M_w = 20,000$ ) was obtained from Showa High Polymer and Aldrich Company, respectively. PBSU/PVPh blends were prepared with mutual solvent *N,N*-dimethylformamide. The solution of both polymers (0.02 g/mL) was cast on a petri dish at room temperature. The solvent was allowed to evaporate in a controlled air stream for 1 day and the resulting films were further dried in vacuum at 50°C for 3 days. In this work, we only studied neat PBSU and PBSU blended with 20 wt % PVPh, that is, PBSU/PVPh 80/20, because PBSU did not crystallize or crystallized very slowly in the case of the weight fraction of PVPh greater than 40%.<sup>17</sup>

Nonisothermal crystallization and subsequent melting behavior were carried out using a Perkin-Elmer Diamond DSC. The samples were first melted at 150°C for 3 min to erase any thermal history of the samples first and then cooled at various constant cooling rates. After the completion of the nonisothermal crystallization, the samples were heated to the melt again to study the melting behavior at a heating rate of 10°C/min. The TA Q100 TMDSC was used for other measurements. For the TMDSC measurements, the heating was operated at 2°C/min with the oscillation amplitude of 0.5°C, and the oscillation period of 40 s throughout the investigation.

## RESULTS AND DISCUSSION

The subsequent melting behavior of PBSU/PVPh blends was investigated after they finished nonisothermal crystallization from the melt at a constant



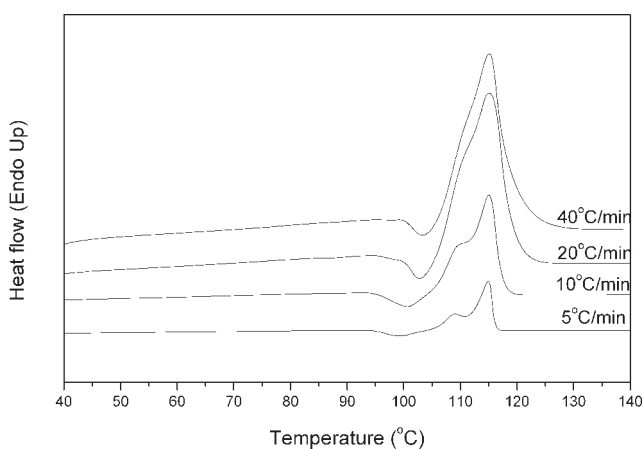
**Figure 1** Subsequent melting behavior of PBSU/PVPh blends crystallized nonisothermally at various cooling rates from the melt at a heating rate of 10°C/min; (a) neat PBSU and (b) PBSU/PVPh 80/20. The measurements were performed with PerkinElmer diamond DSC.

cooling rate. Figure 1 shows the subsequent melting behavior of PBSU/PVPh blends crystallized nonisothermally from the melt at the cooling rates ranging from 2.5 to 40°C/min. The heating rate was 10°C/min. PBSU/PVPh blends show complex melting behavior. One crystallization exotherm and two melting endotherms are found in the DSC traces upon heating to the melt for neat and blended PBSU. With increasing the cooling rate, the crystallization peak temperature ( $T_c$ ) shifts progressively to high temperature. For neat PBSU,  $T_c$  increases from around 94–101°C when the cooling rate increases from 2.5 to 40°C/min. For the PBSU blended with PVPh,  $T_c$  increases from around 91–99°C with increasing the cooling rate from 2.5 to 40°C/min. Blending with amorphous PVPh shifts  $T_c$  to low temperature at the same cooling rate. Two melting endotherms are observed for all the neat and blended PBSU samples despite the cooling rate. With increasing the cooling rate, the lower melting

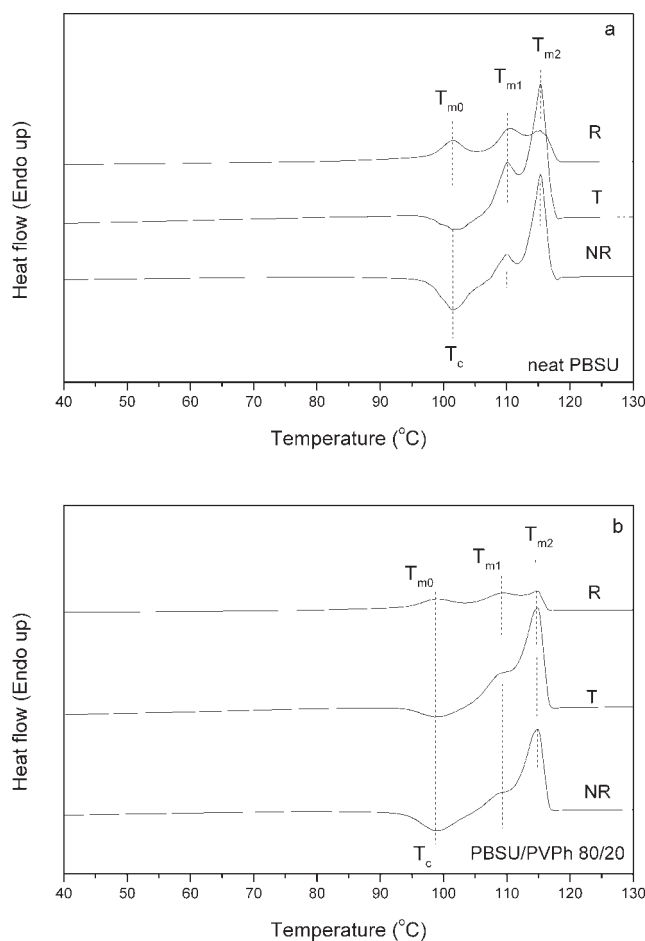
endothermic peak  $T_{m1}$  shifts to low temperature, while the higher melting endothermic peak  $T_{m2}$  is almost unchanged. Furthermore, the shape of the two melting endotherms is found to vary with the cooling rate. At the low cooling rate,  $T_{m1}$  shows a well-defined peak while it changes into a shoulder with increasing the cooling rate. With increasing the cooling rate,  $T_{m1}$  located at around 110°C diminishes gradually in area, and  $T_{m2}$  located at around 114°C increases gradually in area. Figure 1 also shows the blend composition effect on the melting behavior of PBSU/PVPh blends. At the same cooling rate,  $T_{m1}$  can show a well-defined melting peak for neat PBSU but a shoulder in the blend. Blending with PVPh not only affects the position of the two melting endotherms but also affects the shape and area of the two melting peaks. When compared with neat PBSU, the positions of the two melting endotherms shifted to low temperature range in the blends; furthermore, the area of  $T_{m1}$  also reduced in the blends.

The effect of the heating rate on the multiple melting behaviors of PBSU/PVPh blends was studied. Figure 2 shows the heating rate dependence of the melting behavior of neat PBSU crystallized from the melt at a cooling rate of 10°C/min as an example. With the increase of the heating rate,  $T_c$  and  $T_{m1}$  shift to high temperature range, while  $T_{m2}$  is almost unchanged. Furthermore, the shape of the two melting endotherms is found to vary with the heating rate. At the low heating rate,  $T_{m1}$  shows a well-defined peak, while it becomes a shoulder with increasing the heating rate. Finally, the two melting endotherms merge into a single peak as the heating rate of 40°C/min is used.

Figure 3 shows the TMDSC traces of PBSU/PVPh blends crystallized nonisothermally from the melt at



**Figure 2** Effect of the heating rate on the subsequent melting behavior of neat PBSU crystallized from the melt at a cooling rate of 10°C/min. The measurements were performed with TA Q100 TMDSC. The heating rates were shown in figure.

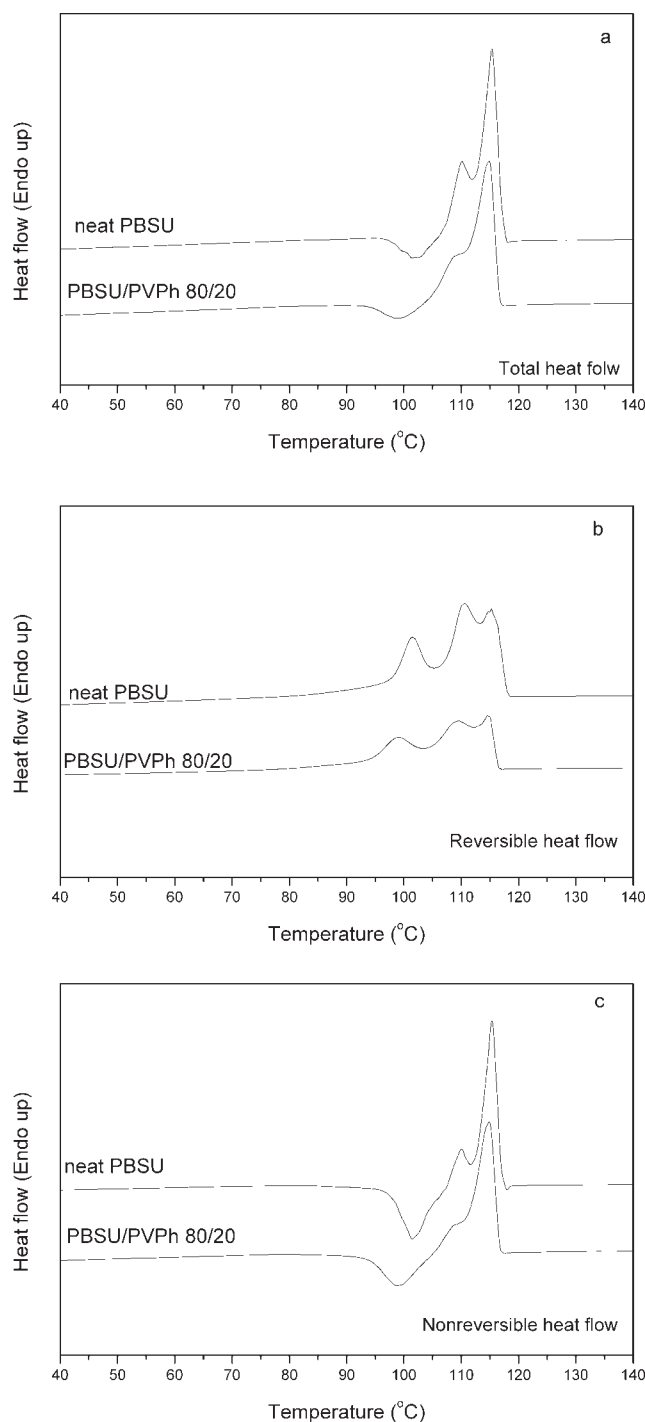


**Figure 3** TMDSC studies of the melting behavior of PBSU/PVPh blends after the nonisothermal melt crystallization at a cooling rate of 4°C/min; (a) neat PBSU and (b) PBSU/PVPh 80/20. In the TMDSC traces, the three curves from the top to the bottom are reversible heat flow ( $R$ ), total heat flow ( $T$ ) and nonreversible heat flow ( $NR$ ), respectively. The measurements were performed with TA Q100 TMDSC.

a cooling rate of 4°C/min. The heating rate of 2°C/min was used with the oscillation amplitude of 0.5°C and the oscillation period of 40 s for the TMDSC melting behavior study. The total heat flow can be separated into the reversible heat flow and the nonreversible heat flow. The total heat flow curves in Figure 3 are similar to those of the conventional DSC traces, showing one crystallization exotherm and two melting endotherms. However, three melting peaks can be found in the reversible heat flow curves for neat and blended PBSU. They are at around 101.5, 110.1, and 115.4°C for neat PBSU, respectively. For the blended PBSU, they are at around 99, 109.5, and 114.6°C, respectively. The melting peaks at around 110 and 115°C correspond to  $T_{m1}$  and  $T_{m2}$  as in the conventional DSC curves. It is very interesting that a new melting peak  $T_{m0}$  at around 100°C can be found in the reversible heat flow curves for neat and blended PBSU. To show the effect of blend composi-

tion on the complex melting behavior of PBSU/PVPh blends more clearly, we redraw Figure 3 into Figure 4 to compare the melting behavior of neat and blended PBSU. From Figure 4, it is easier to see that blending with PVPh not only shifts  $T_c$ ,  $T_{m0}$ ,  $T_{m1}$ , and  $T_{m2}$  to low temperature range but also affects the shape and area of the above-mentioned parameters, indicating that blending with PVPh suppresses the crystallization of PBSU and has an apparent effect on the melting behavior.

PBSU/PVPh blends can show one, two, or three melting peaks depending on the experimental conditions from the above-mentioned results. In the following section, we will discuss the origin of the complex melting behavior of PBSU/PVPh blends. It is clear that the complex melting behavior of PBSU/PVPh blends crystallized nonisothermally from the melt must be affected by the following factors, including the crystallization condition, that is, the cooling rate, the blend composition, and the heating rate. As to the melting behavior of neat PBSU, Im and coworkers reported that the multiple melting behavior of PBSU crystallized isothermally from the melt using DSC and wide angle X-ray diffraction (WAXD), and found that there was no crystal modification change through the WAXD measurement for PBSU crystallized at different temperatures.<sup>5</sup> Satou and coworkers found that PBSU showed double-melting endotherms upon crystallizing nonisothermally from the melt at a constant cooling rate for three different molecular weight samples, which was ascribed to the recrystallization and melting mechanism.<sup>27</sup> On the basis of the above-mentioned results, we propose that there are two kinds of PBSU crystallites with different thermal stability, which were formed during the cold crystallization process from the melt at a constant cooling rate for PBSU/PVPh blends. The two kinds of PBSU crystallites have the same crystal structure but with different thermal stability probably because of the difference in the crystal size and crystal thickness, so they have different melting point temperatures. Their melting corresponds to  $T_{m0}$  and  $T_{m1}$  as seen in Figure 3. The crystallites with low thermal stability corresponding to  $T_{m0}$  at 100°C melt first and then recrystallized upon heating to melt. The crystallization exotherm  $T_c$  found both in the conventional DSC and TMDSC traces corresponds to the recrystallization of the melt of the crystallites with low thermal stability. The crystallites with high thermal stability corresponds to the melting endotherm  $T_{m1}$  at around 110°C in the DSC traces upon heating to the melt, while the final melting endotherm  $T_{m2}$  at around 115°C corresponds to the melting of the crystallites formed through the recrystallization and reorganization of the crystallites with high thermal stability during the DSC heating scan.



**Figure 4** TMDSC studies of the melting behavior of PBSU/PVPh blends; (a) total heat flow, (b) reversible heat flow, and (c) nonreversible heat flows. The measurements were performed with TA Q100 TMDSC.

Through this proposed model, the complex melting behavior of PBSU/PVPh blends can be explained reasonably. As seen in Figure 1, both  $T_c$  and  $T_{m1}$  shift to high temperature range progressively while  $T_{m2}$  is almost unchanged with the increase of the cooling rate. Increasing the cooling rate indicates that PBSU/PVPh blends do not have enough time to

crystallize during the nonisothermal melt crystallization, so the crystallites will melt at low temperature range and the melting peaks will shift to low temperature range with the cooling rate.  $T_{m1}$  shows a well-defined melting peak at the low cooling rate, and becomes a shoulder gradually with increasing the cooling rate.  $T_{m0}$  cannot be observed in Figure 1 because of the fast heating rate of 10°C/min used in conventional DSC; however, it indeed appears in the TMDSC curves in Figure 3 when the heating rate is as low as 2°C/min.  $T_{m2}$  originates from the melting of the crystallites from the recrystallization and reorganization of  $T_{m1}$  upon heating to the melt in DSC; therefore, the cooling rate used in the study does not have a significant effect on the position of  $T_{m2}$ , but have a clear effect on its shape and area.

On the other hand, blending with amorphous PVPh suppressed the crystallization of PBSU in the blend when compared with that of neat PBSU, again indicating that the thermal stability of the formed crystallites in the blend is not so high as that of neat PBSU. Therefore,  $T_c$ ,  $T_{m0}$ ,  $T_{m1}$ , and  $T_{m2}$  of blended PBSU are all lower than those of neat PBSU as in Figures 1, 3, and 4.

Figure 2 shows that  $T_c$  and  $T_{m1}$  shift to high temperature range with increasing the heating rate and  $T_{m2}$  remains almost unchanged. Increasing the heating rate indicates that the crystallites do not have enough time to recrystallize and reorganize during the heating process to the melt; therefore,  $T_c$  and  $T_{m1}$  will shift to high temperature range with the heating rate because of the above-mentioned reason and the lag effect of DSC instrument. Furthermore, the recrystallization and reorganization of the crystallites of  $T_{m1}$  to  $T_{m2}$  is also inhibited with the heating rate. So  $T_{m1}$  shows a well-defined melting peak at low heating rate, and becomes a shoulder with the increase of the heating rate, and finally merges with  $T_{m2}$  showing a single melting peak at the heating rate of 40°C/min.

The melting and recrystallization occur simultaneously during the DSC heating, so the melting and the crystallization may superpose each other significantly in some cases. As a result,  $T_{m0}$  cannot be detected by the conventional DSC, while it is really found in the TMDSC traces. Furthermore, the crystallization exotherm of the crystallites of  $T_{m1}$  to  $T_{m2}$  cannot be detected even through TMDSC. It is probably due to the very closeness between the two melting endotherms. The difference between  $T_{m1}$  and  $T_{m2}$  is only around 4°C. The difference of  $T_{m0}$  and  $T_{m1}$  is around 10°C; therefore, the crystallization exotherm  $T_c$  can be detected both in the conventional DSC and TMDSC traces.

## CONCLUSIONS

PBSU/PVPh blends show complex melting behavior after nonisothermal melt crystallization at constant cooling rates. PBSU/PVPh blends can show one, two, or three melting endothermic peaks depending on the blend composition, cooling rate, and heating rate. A model was proposed to explain the origin of the complex melting behavior of PBSU/PVPh blends.  $T_{m0}$  and  $T_{m1}$  correspond to the melting of the crystallites with different thermal stability formed during the nonisothermal crystallization from the melt.  $T_{m2}$  corresponds to the melting of the crystallites resulting from the recrystallization and reorganization of the crystallites formed before the DSC scan. TMDSC experiments give direct evidences to support the proposed model.

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