# Nonisothermal Crystallization Kinetics of Biodegradable Poly(butylene succinate)/Poly(vinyl phenol) Blend

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**ABSTRACT:** Nonisothermal melt crystallization kinetics of biodegradable PBSU/PVPh blend was investigated with differential scanning calorimetry (DSC) from the viewpoint of practical application. PBSU/PVPh blends were cooled from the melt at various cooling rates ranging from 2.5 to 40°C/min. The crystallization peak temperature decreased with increasing the cooling rate for both neat and blended PBSU. Furthermore, the crystallization peak temperature of PBSU in the blend was lower than that of neat PBSU at a given cooling rate. Two methods, namely the Avrami equation and the Tobin method, were used to describe the nonisothermal crystallization of PBSU/PVPh blend. It was found that the Avrami equation was more suitable to predict the nonisothermal crystallization of PBSU/PVPh blend than the Tobin method. The effects of cooling rate and blend composition on the crystallization behavior of PBSU were studied in detail. It was found that the crystallization rate decreased with decreasing the cooling rate for both neat and blended PBSU. However, the crystallization of PBSU blended with PVPh was retarded compared with that of neat PBSU at the same cooling rate. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 972–978, 2007

**Key words:** blends; crystallization; DSC

## INTRODUCTION

Biodegradable polymers have attracted much more attention in the last two decades. PBSU is biodegradable polyester with the chemical structure of $(—OCH_2CH_2CH_2CH_2O_2CCH_2CH_2CO—)_n$. The crystal structure, crystallization, and melting behavior of PBSU have been reported in literature.[1–9] Polymer blending is often used to modify the properties of PBSU and extend its application field. PBSU was miscible with some semicrystalline polymers, including poly(vinylidene fluoride), poly(vinylidene chloride-co-vinyl chloride), and poly(ethylene oxide).[10–13] On the other hand, PBSU was immiscible with some biodegradable polymers, including poly(hydroxybutyrate), poly(3-hydroxybutyrate-co-3-hydroxyvalerate), and poly(ε-caprolactone).[14–16]

PVPh is an amorphous polymer with high glass transition temperature. PVPh is miscible in many polymers, and the miscibility of polymer blends containing PVPh usually arises from the hydrogen bonding interaction between the hydroxyl group of PVPh and other groups of the partners, such as the carbonyl group.[17–21] In previous work, we reported the miscibility, crystallization, and morphology of PBSU/PVPh blends. PBSU and PVPh were completely miscible in the amorphous phase over the entire composition range as shown by the single composition dependent glass transition temperature. The negative and composition dependent polymer–polymer interaction parameter indicated that PBSU/PVPh blends were thermodynamically miscible in the melt.[21]

The crystalline structure and morphology of semicrystalline polymers are influenced greatly by the thermal history. It is well-known that crystallinity plays an important role in the physical properties and biodegradability of biodegradable polymers. Therefore, much more attention should be paid to the crystallization kinetics study, because it affects not only the crystalline structure and morphology of semicrystalline polymers but also the final physical properties and biodegradability of the biodegradable polymers. The isothermal crystallization of PBSU/PVPh blends were studied in detail with DSC, OM, wide-angle X-ray diffraction (WAXD), and small-angle X-ray scattering (SAXS).[22] It was found that blending with PVPh did not change the crystallization mechanism of PBSU, but reduced the crystallization rate compared with that of neat PBSU at the same crystallization temperature. The crystallization

rate decreased with increasing crystallization temperature, while the crystallization mechanism did not change for both neat and blended PBSU irrespective of crystallization temperature.

It is essential to study the nonisothermal crystallization kinetics from the viewpoint of practical application, because most polymer processing operations are carried out under nonisothermal conditions. In this work, we reported our results on the nonisothermal crystallization kinetics of PBSU/PVPh blend cooled from the melt at various cooling rates by DSC. It is expected that these results will be helpful for a better understanding of the relationship between structure and properties of biodegradable polymer blends from the viewpoint of practical process.

## EXPERIMENTAL

PBSU ($M_w = 140{,}000$) and PVPh ($M_w = 20{,}000$) were obtained from Showa High Polymer Co. 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, i.e., 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%.[21] The glass-transition temperature and equilibrium melting point temperature of neat PBSU were −33.7 and 138.8°C, respectively, while those of PBSU blended with 20% PVPh were −24 and 132.9°C, respectively.[21,22]

Nonisothermal crystallization studies were carried out with a PerkinElmer Diamond DSC. Samples weight varied about 4–6 mg, and all operations were performed under nitrogen. The samples were first heated to 150°C, held for 5 min to destroy any thermal history, and then cooled at various cooling rates ranging from −2.5 to −40°C/min. The exothermal curves of heat flow as a function of temperature were recorded and analyzed.

## RESULTS AND DISCUSSION

### Nonisothermal melt crystallization of PBSU/PVPh blend

Polymer crystallization has been of great interest for several decades from both the scientific and the industrial viewpoints. Crystallization studies are usually limited to idealized conditions for simplicity, where the external conditions are constant. However, the external conditions change continuously in real
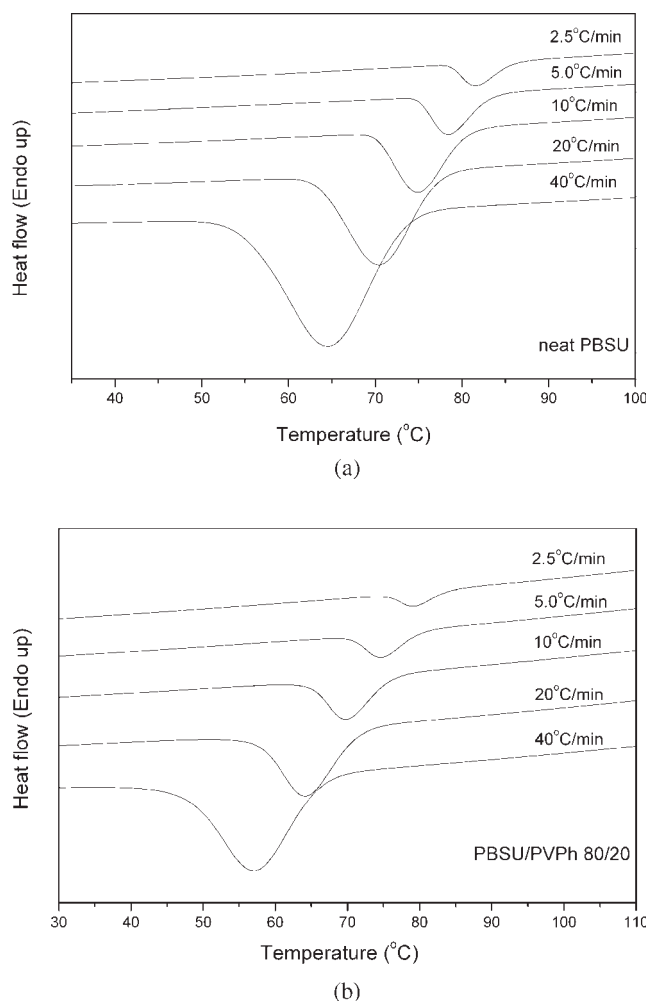


(a)



(b)

**Figure 1** DSC traces of PBSU/PVPh blend cooled from the melt at various cooling rates; (a) neat PBSU and (b) PBSU/PVPh 80/20.

situations, resulting in that the study of nonisothermal crystallization is more complex than that of isothermal crystallization. Compared with the successful studies of isothermal crystallization by the Avrami equation and the secondary nucleation crystal growth theories,[23–26] only a few methods have been proposed to study the nonisothermal crystallization from the melt on the basis of the modifications of the Avrami equation, including the Ozawa, Ziabicki, Nakamura, Tobin models, and so on.[27] Di Lorenzo has recently reviewed the basic hypotheses of various models of nonisothermal crystallization of polymers and their relative drawbacks.[27]

As described in the experimental section, the nonisothermal crystallization kinetics of PBSU/PVPh blend, i.e., neat PBSU and PBSU/PVPh 80/20, were studied with DSC. Figure 1 shows the DSC traces of neat and blended PBSU cooled from the melt at various cooling rates. The well-defined crystallization exotherms shifted to lower temperature range with increasing the cooling rate for both neat and
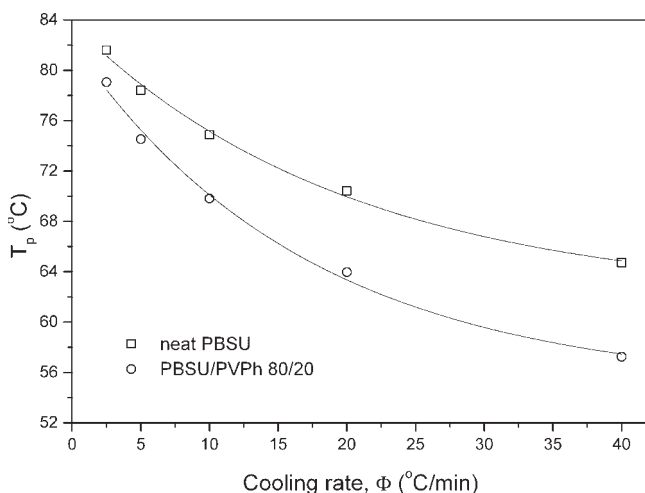
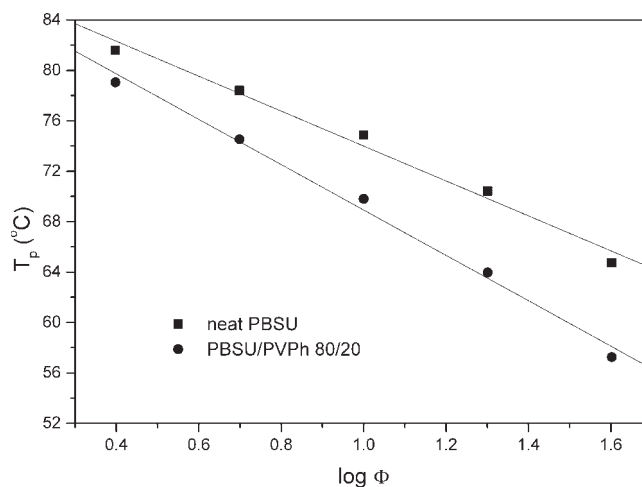**Figure 2** Plots of crystallization peak temperature $T_p$ as a function of cooling rate for PBSU/PVPh blend.



**Figure 3** Plots of crystallization peak temperature $T_p$ against log Φ for PBSU/PVPh blend.

blended PBSU. At the same cooling rate, the exothermic curve of blended PBSU shifted to lower temperature range compared with that of neat PBSU, indicating that the crystallization of PBSU was retarded in the blends. It is interesting to study the effects of the cooling rate and the addition of amorphous PVPh component on the variation of crystallization peak temperature ($T_p$) of PBSU/PVPh blend. Figure 2 summarizes the variation of $T_p$ against the cooling rate (Φ) for neat and blended PBSU. It can be seen that $T_p$ decreased with the increase of the cooling rate for both neat and blended PBSU. At the same cooling rate, $T_p$ of blended PBSU was lower than that of neat PBSU. Moreover, the difference of $T_p$ between neat and blended PBSU became more significant with the increase of the cooling rate. Such results could be attributed to the following reasons. The time for PBSU to crystallize at high crystallization temperature was not long enough with increasing the cooling rate, so $T_p$ shifted to low crystallization temperature range. Similarly, blending with PVPh reduced the crystallizability of PBSU; therefore, $T_p$ of blended PBSU shifted to low temperature range compared with that of neat PBSU. The fact that $T_p$ difference became more significant could be explained as follows. Blending PVPh reduced the crystallizability of PBSU in the blend compared with neat PBSU. At any cooling rates, the $T_p$ of blended PBSU should be lower than that of neat PBSU. The crystallization of PBSU was also influenced by the cooling rate. Increasing the cooling rate may suppress the crystallization. At low cooling rate, both neat and blended PBSU had enough crystallization time to crystallize and the supercooling required for the crystallization was small; therefore, the $T_p$ difference is small. However, at high cooling rates, the blended PBSU did not have enough crystallization

time and needed larger supercooling to crystallize since the crystallizability of PBSU in the blends was suppressed compared with neat PBSU. The larger supercooling required for the blended PBSU to crystallize at high cooling rates resulted in the big $T_p$ difference.

Furthermore, $T_p$ displays a linear relation as a function of log Φ for PBSU/PVPh blend as shown in Figure 3. The slope of the plot for neat PBSU was lower than that of blended PBSU, indicating again that the crystallization of PBSU was influenced more significantly in the blend with the increase of the cooling rate. Similar results were also reported for the nonisothermal melt crystallization of polypropylene.[28]

Crystallization enthalpy is also an important parameter in studying the nonisothermal crystallization of polymers. Figure 4 shows the variation of crystal-
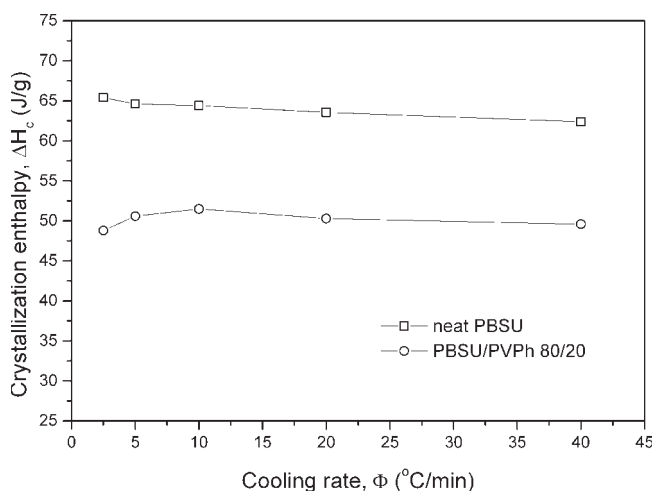


**Figure 4** Plots of crystallization enthalpies against cooling rate for PBSU/PVPh blend.
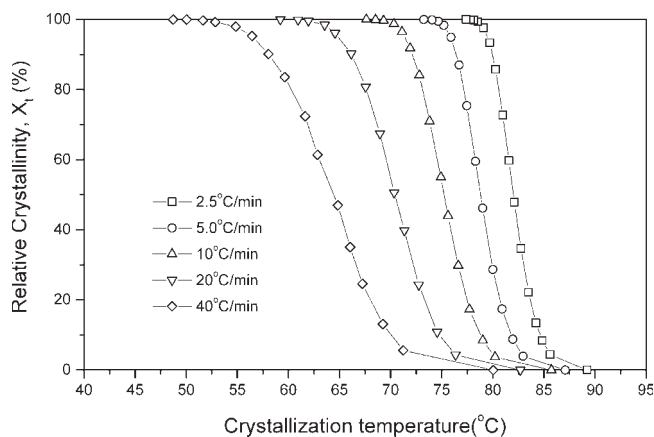
**Figure 5** Plots of relative crystallinity against crystallization temperature for neat PBSU during nonisothermal melt crystallization.

lization enthalpy as a function of the cooling rate for PBSU/PVPh blend. The values of the crystallization enthalpy of neat PBSU are around 65 J/g and almost unchanged irrespective of the cooling rate, while those of blended PBSU are around 50 J/g. All the aforementioned results indicate that the cooling rate does not exert a significant influence on the final crystallinity of PBSU/PVPh blend despite the high or the low cooling rate used. On the basis of the heat fusion of 100% crystalline PBSU (200 J/g)[6] and the blend composition, the degrees of crystallinity of neat and blended were estimated to be around 32% after the nonisothermal crystallization from the melt at various cooling rate.

Integration of the exothermic peaks during the nonisothermal crystallization shown in Figure 1 gave the relative crystallinity as a function of temperature. Figure 5 shows the plots of relative crystallinity versus crystallization temperature for neat PBSU as an example. The plots shifted to the low temperature range with increasing the cooling rate. During the nonisothermal crystallization from the melt at a constant cooling rate, the relationship between the crystallization time $t$ and the crystallization temperature $T$ can be described as

$$t = \frac{T_o - T}{\Phi} \tag{1}$$

where $\Phi$ was the cooling rate, and $T_o$ was the onset temperature of crystallization. Using eq. (1), the plot of relative crystallinity as a function of crystallization could be transformed into the plot of relative crystallinity as a function of crystallization time. Figure 6 shows the relative crystallinity as a function of crystallization time for PBSU/PVPh 80/20. The crystallization time became shorter with the increase of the cooling rate.

Two methods, namely Avrami[23–25] and Tobin methods,[29–31] were employed to investigate the kinetics of nonisothermal crystallization of PBSU/PVPh blend. The well-known Avrami equation is often used to analyze the isothermal crystallization kinetics; it assumes that the relative degree of crystallinity development with crystallization time $t$ is

$$X_t = 1 - \exp(-k_a t^{n_a}) \tag{2}$$

where $n_a$ is the Avrami exponent depending on the nature of nucleation and growth geometry of the crystals, and $k_a$ is a composite rate constant involving both nucleation and growth rate parameters.[23–25]

The Avrami equation has also been applied directly to describe the nonisothermal crystallization of polymers, although it is often used to study the isothermal crystallization behavior of polymers.[32–34] Using eq. (2) in its double logarithmic form, and plotting $\log(-\ln(1 - X_t))$ against $\log t$ for each cooling rate as shown in Figure 7, a series of straight lines were obtained, from which the values of $n_a$ and $k_a$ were obtained and listed in Table I. It should be noted that negative deviation from linearity were found for high $X_t$ values in the case of low cooling rates, indicating the underestimation of secondary crystallization. The values of $n_a$ varied between 3.6 and 4.6 for PBSU/PVPh blend within the cooling rates of 2.5 to 40°C/min. On the other hand, the values of $k_a$ increased with the cooling rate for PBSU/PVPh blends. The value of $k_a$ for neat PBSU was higher than that of blended PBSU at the same cooling rate, indicating that the addition of amorphous PVPh component reduced the crystallization rate of PBSU in the blend.

However, it must be emphasized that in the nonisothermal crystallization the values of $n_a$ and $k_a$ do not have the same physical meaning as in the
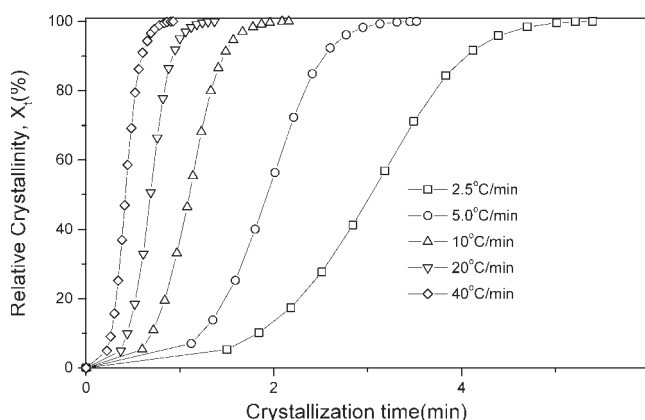


**Figure 6** Plots of relative crystallinity against crystallization time for PBSU/PVPh 80/20 during nonisothermal melt crystallization.
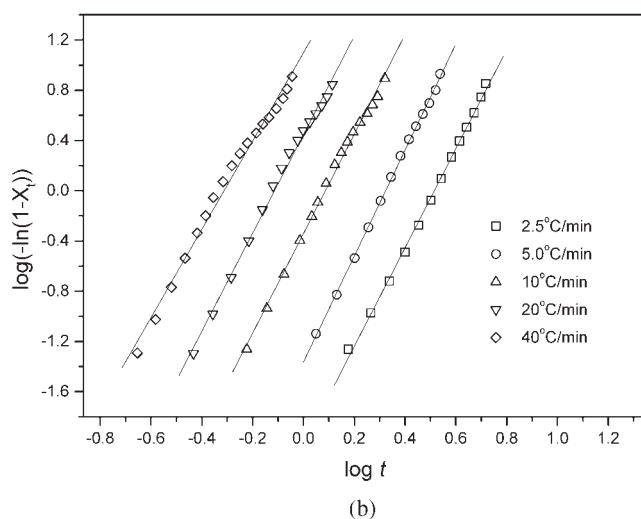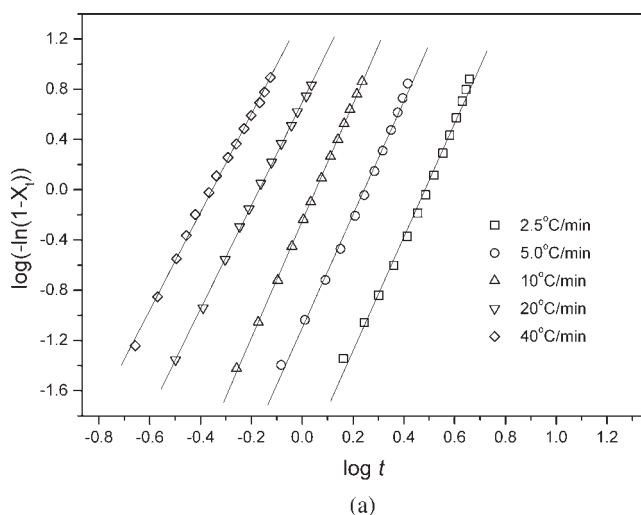
**Figure 7** Avrami plots of PBSU/PVPh blend during nonisothermal melt crystallization; (a) neat PBSU and (b) PBSU/PVPh 80/20.

isothermal crystallization due to the fact that under nonisothermal condition the temperature changes continuously. This must affect the rates of both nuclei formation and spherulite growth since they are both

temperature dependent. Although the physical meaning of $n_a$ and $k_a$ cannot be related in a simple way to the isothermal case, the direct application of the Avrami equation do provide further insight into the kinetics of nonisothermal crystallization. Considering the nonisothermal character of the investigated process, Jeziorny suggested that the value of rate parameter $k_c$ should be used, which was corrected by the cooling rate $\Phi$ factor as $\log k_c = \log k_a/\Phi$.[35] The meaning of $k_c$ was also the crystallization rate constant depending on nucleation and growth rate as $k_a$ in the Avrami equation. The obtained values of $k_c$ were listed in Table I, too, for PBSU/PVPh blend. The variation trend of the values of $k_c$ was similar to that of $k_a$ for PBSU/PVPh blend.

The nonisothermal crystallization kinetics of PBSU/PVPh blend were also studied by the Tobin methods, which suggested a theory of phase transformation kinetics with growth site impingement to describe the nonisothermal crystallization process of polymers.[29–31] According to this approach, the equation of phase transition is

$$X_t = \frac{k_t t^{n_t}}{1 + k_t t^{n_t}} \tag{3}$$

where $X_t$ is the relative crystallinity as a function of time, $k_t$ is the Tobin crystallization rate constant, and $n_t$ is the Tobin exponent. Equation (3) could be rewritten as follows to calculate the Tobin crystallization kinetics parameters.

$$\log(X_t/(1 - X_t)) = \log k_t + n_t \log t \tag{4}$$

Figure 8 shows the Tobin plots for PBSU/PVPh blend, from which $n_t$ and $k_t$ were obtained and listed in Table I, too. It must be noted that positive deviation from linearity were found for high $X_t$ values, especially in the case of high cooling rates, probably indicating the overestimation of impingement. The values of $n_t$ varied between 5.1 and 5.9 for PBSU/PVPh blend. On the other hand, the values of $k_t$ increased with the cooling rate for both neat and

**TABLE I**
**Nonisothermal Crystallization Kinetics Parameters from the Avrami Method and the Tobin Method for Neat and Blended PBSU**

|  | $\Phi$ (°C/min) | $n_a$ | $k_a$ | $k_c$ (min$^{-n_a}$) | $n_t$ | $k_t$ (min$^{-n_t}$) |
|---|---|---|---|---|---|---|
| PBSU | 2.5 | 4.5 | $6.52 \times 10^{-3}$ | 0.133 | 5.2 | $4.71 \times 10^{-3}$ |
|  | 5.0 | 4.5 | $7.95 \times 10^{-2}$ | 0.602 | 5.4 | $8.38 \times 10^{-2}$ |
|  | 10 | 4.6 | $5.63 \times 10^{-1}$ | 0.944 | 5.6 | $8.74 \times 10^{-1}$ |
|  | 20 | 4.1 | 4.98 | 1.083 | 5.5 | $1.78 \times 10^{1}$ |
|  | 40 | 3.9 | $2.42 \times 10^{1}$ | 1.082 | 5.5 | $1.87 \times 10^{2}$ |
| PBSU/PVPh 80/20 | 2.5 | 3.9 | $9.42 \times 10^{-3}$ | 0.154 | 5.1 | $4.69 \times 10^{-3}$ |
|  | 5.0 | 4.2 | $4.34 \times 10^{-2}$ | 0.534 | 5.9 | $2.70 \times 10^{-2}$ |
|  | 10 | 4.0 | $4.57 \times 10^{-1}$ | 0.924 | 5.6 | $7.54 \times 10^{-1}$ |
|  | 20 | 3.9 | 2.81 | 1.053 | 5.6 | $1.09 \times 10^{1}$ |
|  | 40 | 3.6 | $1.25 \times 10^{1}$ | 1.065 | 5.3 | $1.17 \times 10^{2}$ |

blended PBSU. The values of $k_t$ for blended PBSU were lower than those of neat PBSU at the same cooling rate, indicating that the crystallization of PBSU was retarded in its blend with amorphous PVPh component.

It was interesting to compare the results obtained from the Avrami method and the Tobin approach. It was clear that the values of Avrami exponent $n_a$ were always smaller than those of the Tobin exponent $n_t$ at the same cooling rate. By taking the average of the difference between the two values for the PBSU/PVPh blend, it could be concluded that $n_t \approx n_a + 1.4$. Similar results were also found for poly(ethylene succinate) and syndiotactic polypropylene (s-PP).[34,36]

To test the efficiency of both methods in describing the nonisothermal crystallization process of PBSU/PVPh blend, the relative crystallinity $X_t$ was reconstructed as a function of crystallization time for each
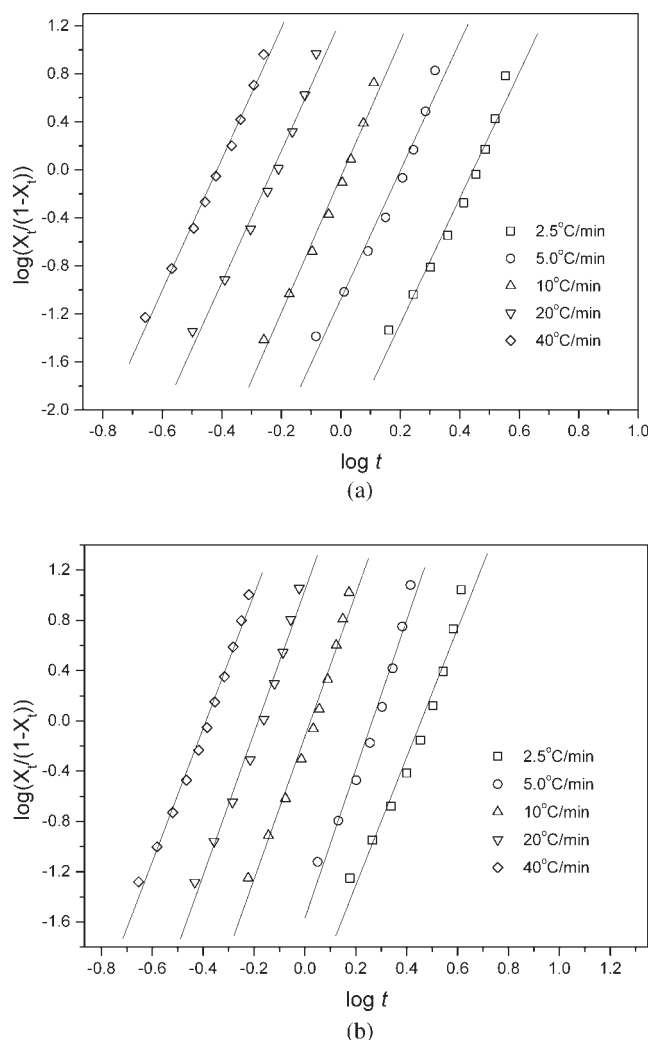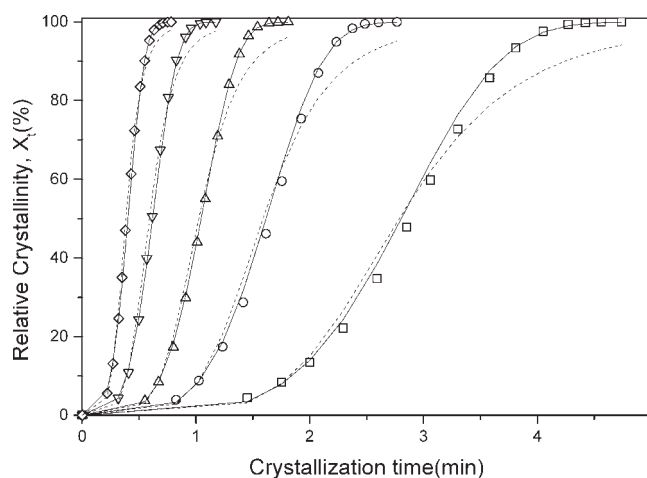
**Figure 9** Model predictions based on the Avrami and the Tobin equations are shown as solid and dashed lines, respectively, to fit the experimental relative crystallinity as a function of crystallization time for various cooling rates (°C/min): (□) 2.5, (○) 5, (△) 10, (▽) 20 and (◇) 40.

cooling rate using the mathematical eqs. (2) and (3). On the basis of the kinetics parameters listed in Table I, the reconstructed $X_t$ was calculated and shown in Figure 9 for neat PBSU as an example, where the Avrami prediction was shown as solid lines, and the Tobin prediction was shown in dashed lines. It is clear that both methods could provide a good fit to the experimental data for the majority of $X_t$. However, the Tobin method always gave the low values compared with the experimental data in the higher $X_t$ range ($X_t \geq 70\%$), especially for the low cooling rates. The reason was perhaps due to the overemphasis of the impingement effect. Similar results were also found for poly(ethylene succinate) and s-PP. Compared with the Tobin method, the Avrami model could fit almost the whole range of $X_t$ well.

## CONCLUSIONS

Nonisothermal melt crystallization kinetics of biodegradable crystalline/amorphous PBSU/PVPh blend was investigated with DSC. The effects of the addition of amorphous component PVPh and cooling rates on the nonisothermal crystallization kinetics of PBSU were studied in detail. The crystallization peak temperature decreased with increasing cooling rate for both neat and blended PBSU. Furthermore, the crystallization peak temperature of PBSU in the blend was lower than that of neat PBSU at a given cooling rate. The Avrami equation and the Tobin method were employed to describe the nonisothermal crystallization kinetics of PBSU/PVPh blend from the melt. The Avrami equation was found to be more suitable to predict the whole nonisothermal

**Figure 8** Tobin plots of PBSU/PVPh blend during nonisothermal melt crystallization; (a) neat PBSU and (b) PBSU/PVPh 80/20.

crystallization process of PBSU/PVPh blend than the Tobin method. It was concluded that the crystallization of PBSU in the blend was retarded compared with that of neat PBSU at the same cooling rate. Meanwhile, the crystallization rate decreased with decreasing the cooling rate for both neat and blended PBSU.

## References

1. Chatani, Y.; Hasegawa, R.; Tadokoro, H. Polymer Prepr Jpn 1971, 20, 420.
2. Ihn, K. J.; Yoo, E. S.; Im, S. S. Macromolecules 1995, 28, 2460.
3. Ichikawa, Y.; Suzuki, J.; Washiyama, J.; Moteki, Y.; Noguchi, K.; Okuyama, K. Polymer 1994, 35, 3338.
4. Ichikawa, Y.; Kondo, H.; Igarashi, Y.; Noguchi, K.; Okuyama, K.; Washiyama, J. Polymer 2000, 41, 4719.
5. Yoo, E. S.; Im, S. S. J Polym Sci Polym Phys 1999, 37, 1357.
6. Miyata, T.; Masuko, T. Polymer 1998, 39, 1399.
7. Gan, Z.; Abe, H.; Kurokawa, H.; Doi, Y. Biomacromolecules 2001, 2, 605.
8. Qiu, Z.; Fujinami, S.; Komura, M.; Nakajima, K.; Ikehara, T.; Nishi, T. Polym J 2004, 36, 642.
9. Qiu, Z.; Komura, M.; Ikehara, T.; Nishi, T. Polymer 2003, 44, 7781.
10. Lee, J. C.; Tazawa, H.; Ikehara, T.; Nishi, T. Polymer J 1998, 30, 327.
11. Lee, J. C.; Tazawa, H.; Ikehara, T.; Nishi, T. Polymer J 1998, 30, 780.
12. Qiu, Z.; Ikehara, T.; Nishi, T. Polymer 2003, 44, 2799.
13. Qiu, Z.; Ikehara, T.; Nishi, T. Polymer 2003, 44, 3095.
14. Qiu, Z.; Ikehara, T.; Nishi, T. Polymer 2003, 44, 2503.
15. Qiu, Z.; Ikehara, T.; Nishi, T. Polymer 2003, 44, 7519.
16. Qiu, Z.; Komura, M.; Ikehara, T.; Nishi, T. Polymer 2004, 44, 7749.
17. Pedrosa, P.; Pomposo, J. A.; Calahorra, E.; Cortazar, M. Polymer 1995, 36, 3889.
18. Huang, Y. P.; Kuo, J. F.; Woo, E. M. Polymer Int 2001, 51, 55.
19. Iriondo, P.; Iruin, J. J.; Fernandez-Berridi, M. J. Polymer 1995, 36, 3235.
20. Zhang, L.; Goh, S. H.; Lee, S. Y. J Appl Polym Sci 1999, 74, 383.
21. Qiu, Z.; Komura, M.; Ikehara, T.; Nishi, T. Polymer 2003, 44, 8111.
22. Qiu, Z.; Yang, W. T. Polymer 2006, 47, 6429.
23. Avrami, M. J Chem Phys 1939, 7, 1103.
24. Avrami, M. J Chem Phys 1940, 8, 212.
25. Avrami, M. J Chem Phys 1941, 9, 177.
26. Hoffman, J. D.; Davis, G. T.; Lauritzen, J. I. Treatise on Solid State Chemistry, Vol 3; New York: Plenum Press; 1976. Chapter 7.
27. Di Lorenzo, M. L.; Silvestre, C. Prog Polym Sci 1999, 24, 917.
28. Caze, C.; Devaux, E.; Crespy, A.; Cavrot, J. P. Polymer 1997, 38, 497.
29. Tobin, M. C. J Polym Sci Polym Phys Ed 1974, 12, 399.
30. Tobin, M. C. J Polym Sci Polym Phys Ed 1976, 14, 2253.
31. Tobin, M. C. J Polym Sci Polym Phys Ed 1977, 15, 2269.
32. Cebe, P. Polym Compos 1988, 9, 271.
33. de Juana, R.; Jauregui, A.; Calahorra, E.; Cortázar, M. Polymer 1996, 37, 3339.
34. Qiu, Z.; Ikehara, T.; Nishi, T. Polymer 2003, 44, 5429.
35. Jeziorny, A. Polymer 1978, 19, 1142.
36. Supaphol, P. J Appl Polym Sci 2000, 78, 338.