Nonisothermal Crystallization Kinetics of *In Situ* Polyamide-6 Blended with Poly(phenylene oxide)

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ABSTRACT: Blends of Polyamide-6/Poly(phenylene oxide) (PA-6/PPO) were prepared by *in situ* polymerization, in which the reactive compatibilizer SP was added. Based on two kinds of kinetic equation of nonisothermal crystallization proposed by Ozawa and Liu, the influences of PPO, the cooling rate, and the compatibilizer on crystallization process of PA-6 were investigated. At a given cooling rate, the presence of PPO reduces the overall crystallization rate of PA-6; for a fixed PPO level, the time of crystallization completed becomes shorter when the cooling rate is higher; the addition of SP impedes the development of crystal growth. Scanning electronic microscope (SEM) results fortified the above conclusion. According to the analysis result of experiment data, it shows that the Ozawa equation does not adequately describe the nonisothermal crystallization behavior of PA-6/PPO blends, whereas the Liu approach can be well applied in this studied system. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 767–775, 1999

Key words: crystallization; nonisothermal; PA-6; PPO

INTRODUCTION

At present, blends of PA-6/PPO are the engineering thermoplastics of high consumption due to their special physical and mechanical properties, such as excellent chemical resistance, high-dimensional stability, and good thermal properties. This has been widely applied in mechanics, electronic applications, and automobile package materials.¹ But because PPO is an amorphous polymer and PA-6 is a crystalline material, the two components of the blend are immiscible, and may appear to phase separate during the melting mixing process. Thus, it causes the blend to exhibit poor mechanical properties. It is generally believed that the key factors that affect the properties of blends are dispersion quality and the adhesion degree between the two phases.^{2, 3} To im-

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prove the compatibility between the two phases, our laboratory adopted a reactive blending technique, in situ polymerization, and the addition of a reactive compatibilizer SP, which is a type of bisphenol A epoxide. The epoxy functional groups of the SP compatibilizer can react with both the amine and carboxylic end groups of PA-6 and the hydroxyl end group of PPO at an interface to form various copolymers. These in situ-formed grafted copolymers tend to concentrate along the interface between PA-6 and PPO as an effective compatibilizer. In our previous work, the mechanical properties and the morphology of in situ PA-6/ PPO blends have been studied.⁴ These results indicate that the reaction between functional units that exists in polymer blends during the polymerization process can improve the interface interaction between the two components, in the meantime, the addition of SP can reduce the size of dispersed phase of the blends markedly. The morphology of incompatible polymer blends in the presence of the *in situ*-formed copolymers during

the reactive processing becomes a very fine structure due to the reduction of interfacial tension between the dispersed phase and the matrix.

The final properties of blends of PA-6/PPO in an engineering application are critically depended on the degree of crystalinity and the nature of crystalline morphology, which in turn, rely on the processing condition, because most practical process such as industrial synthesis, extrusion, molding, and melt spinning of synthetic fibers frequently occur under situations closed to nonisothermal conditions.^{5,6} Compared to the isothermal crystallization experiment, the nonisothermal crystallization investigation is of considerable practical significance.

It is well known that the Avrami equation has been widely used in the study of polymer crystallization in isothermal conditions because the Avrami parameters provide information both on the nucleation and growth of the crystal.⁷ To elucidate the mechanism of nonisothermal crystallization, several different data-analyzing methods based on the Avrami equation were produced. Among these mathematics treatments, more widely applied were those proposed by Mandelkern,⁸ Ziabicki,⁹ Jeziorny,¹⁰ and Ozawa.¹¹ For example, the Ozawa equation has been well used to describe the nonisothermal crystallization behavior of PET,¹¹ PP,¹² PPS,¹³ but for PBT,¹⁴ PE,¹² and PEEK,¹⁵ the Ozawa analysis failed to characterize the crystallization behavior. Recently a new approach was proposed by Liu, derived by combining Avrami and Ozawa equations to study the nonisothermal crystallization kinetics of a polymer. It has been successfully applied to the PEO/PBHE¹⁶ and PEEKK¹⁷ systems, but it is also difficult to show that this method is suitable for all systems. In fact, all these mathematics treatments have a common drawback, i.e., each only applying to limited systems. Despite the above limit, these treatments can still provide useful information regarding the mechanism and rates of crystallization.

In this article, the nonisothermal crystallization behavior of PA-6/PPO blends was investigated by means of a differential scanning calorimeter and scanning electronic microscope. Based on the experimental results, the effects of PPO, cooling rate, and SP on PA-6 crystallization behavior were investigated. Furthermore, the applicability of the Ozawa equation and the Liu analysis to this studied system was discussed.

EXPERIMENTAL

Materials

Blends of PA-6/PPO were prepared from the homogeneous system ε -Caprolactam/PPO above the melting point of PA-6 via hydrolytic ring-opening polymerization. During the polymerization process, the reactive compatibilizer (SP) was added. PPO was provided by GE plastics, SP was made by us, which is a kind of bisphenol A epoxide. ε -Caprolactan was obtained through redistilliation, and 6-amino-caproic acid was provided by Beijing Chemistry Company. The different PA-6/ PPO blends compositions (PA-6/PPO/SP wt/wt/ wt) were pure PA-6, 95/5/0, 95/5/0.25, 95/5/0.5, 90/10/0, and 90/10/0.5.

Differential Scanning Calorimeter

The overall nonisothermal crystallization kinetics of molten blends was analyzed by a differential scanning calorimeter (Perkin-Elmer DSC 7). The samples were heated from room temperature to 553 K, and after 10 min at that temperature they were cooled at various constant cooling rates: 10, 15, 20, 25, and 30°C/min. The heat of the crystallization as a function of performance time was recorded.

Melting point and heat of fusion of PA-6/PPO blends were also measured by a Perkin-Elmer DSC 7. Samples were heated from room temperature to 553 K, and then rapidly cooled to room temperature to erase the thermal history of the samples. A second run was carried out at the heating rate of 10°C/min. All these operations were carried out under a nitrogen purge, and the samples were dried in a vacuum at 120°C for 24 h before measuring. Sample weights were about 7–8 mg.

SEM Observation

Samples were merged in liquid nitrogen and then fractured at the primed notch. The fractured areas of samples were gilded with gold before testing. An Hitachi S-530 scanning electronic microscope was used to study the morphology of the samples.

RESULTS AND DISCUSSION

Figure 1 shows the crystallization exotherms for the 95/5 PA-6/PPO blend at various cooling rates.



Figure 1 DSC crystallization traces for the 95/5/0 PA-6/PPO/SP blend at various cooling rates.

It is obvious that the crystallization peak is moved down to lower temperatures as the cooling rate is increased, which can be explained by the fact that there must enough time to activate nuclei at different cooling rates, i.e., the nuclei are activated at lower temperature as the cooling rate is increased.¹⁸

Meanwhile the temperature, at which the maximum of the peaks occurs, T_{cmax} decreases with increased cooling rate. The undercooling degree, $T_m - T_{c\max}$, where T_m is the equilibrium melting temperatures of PA-6/PPO blends (which were respectively measured by means of DSC at the same heating rate). The dependence of the undercooling degree on the cooling rate is shown in Figure 2. From this plot, it can be seen for a given composition that the undercooling degree increases at higher cooling rates, which also can be explained by the fact that the lower time scale was afforded to the polymer to crystallize as the cooling rate increased, therefore requiring a higher undercooling degree to initiate crystallization.¹⁹

Following the heat flow's relationship with the temperature at a fixed component, the relative degree of crystallinity can be calculated:

$$X_{(T)} = \int_{T_0}^{T} (dH/dt) \ dt / \int_{T_0}^{T_{\infty}} (dH/dt) \ dt \qquad (1)$$

where T_0 and T_{∞} are the onset and end crystallization temperatures, respectively. The relative degree of crystalinity $X_{(T)}$ as a function of temperature for the 95/5 PA-6/PPO blend at different cooling rates is illustrated in Figure 3. During the nonisothermal crystallization process, the time and the temperature exhibit the following relationship:

$$t = |(T_0 - T)/R|$$
(2)

where T_0 is initial temperature when the crystallization begins (t = 0), T is the temperature at time t, and R is the cooling rate. According to Figure 3 and eq. (2), the half-crystallization time, $t_{1/2}$ for different components at various cooling rates can be obtained. Figure 4 shows how the $t_{1/2}$ depends on the cooling rate for blends of PA-6/ PPO; the value of $t_{1/2}$ is clearly decreased as the cooling rate is increased. In general, the overall crystallization rate is determined by both the nucleation and the growth of crystal. Although at a high temperature range close to the melting point of materials the crystallization rate mainly depends on the nucleation, in such a temperature range the nucleation rate increases with decreasing temperature. In this studied system, the crystallization temperature is in the range of 433-473 K, which is much closer to the melting point of PA-6/PPO blends. (The melting point of pure



Figure 2 Variation of undercooling degree vs. cooling rate for blends of PA- 6/PPO.

PA-6, 95/5/0 PA-6/PPO/SP, and 90/10/0 PA-6/ PPO/SP are 493.3, 493.5, and 488.5 K.)

As also can be seen in Figure 4, for a given cooling rate, the values of $t_{1/2}$ increase with the presence of PPO; furthermore, as the content of PPO increases, the values of $t_{1/2}$ become larger. It is well known that $t_{1/2}$ can be used to characterize the crystallization rate under isothermal conditions: the higher the value of $t_{1/2}$, the lower the

crystallization rate. For nonisothermal crystallization, $t_{1/2}$ can also be used to illustrate the crystallization rates.¹⁶ The trend in Figure 4 shows the presence of PPO reduces the overall crystallization rate of PA-6/PPO blends, which were expected behaviors. On one side, the presence of amorphous PPO diluted the crystalline polymer PA-6 chains at the crystal growth front; on the other side, the presence of PPO increased the T_g



Figure 3 Relative degree of crystallinity as a function of temperature for the 95/5/0 PA-6/PPO/SP blend at various cooling rates.



Figure 4 Variation of the half-crystallization time $t_{1/2}$ as a function of the PA-6/PPO blend composition at different cooling rates.

of the blend, consequently reducing the mobility of crystalline chains (PPO, $T_g = 493$ K, PA-6, $T_g = 323$ K),¹⁸ which has been proven by DMA in our previous work.⁴

Ozawa has extended the Avrami equation, originally valid for isothermal crystallization, to nonisothermal condition of a controlling constant cooling rate. Assuming that nonisothermal crystallization is the result of infinite isothermal processes, and the mathematics analysis proposed by Evans is appropriate,²⁰ the following equation has been derived:

$$\log\{-\ln[1 - X_{(T)}]\} = \log K_{(T)} - n \log R \quad (3)$$

where $X_{(T)}$ is the fraction of material crystallized at temperature T, R is the cooling rate, $K_{(T)}$ is the cooling function, and n is the Ozawa exponent that depends on the nucleation type and the growth dimension. Plotting log $\{-\ln[1 - X_{(T)}]\}$ against logR at a given temperature, if the Ozawa method is valid, a series of parallel straight lines should be obtained, and $K_{(T)}$ and n can be determined from the intercept and slope, respectively.

Figure 5 shows the plot of $\log \{-\ln[1 - X_{(T)}]\}$ vs. log *R* for the 95/5/0 PA-6/PPO/SP blend. Clearly, these straight lines do not exhibit a parallel relationship, which makes it very difficult to determine the constant value of *n*. The values of *n* obtained through the linear treatment of these scattering dots increased with a raised temperature; this trend is illustrated in Figure 6. It is impossible to predict the nucleation mechanisms occurring during nonisothermal crystallization from a wide range of n values.

Three main factors can be contributed to explain the inapplicability of the Ozawa equation: the Ozawa analysis does not take into consideration secondary crystallization processes, such as PE, PEEK, or PEEKK, in which a large portion of the crystallization is attributed to secondary processes; the Ozawa exponent may change with the crystallization temperature, the cooling rate, and the transformed volume function; at a given temperature, during the plotting log $\{-\ln[1 - X_{(T)}]\}$ against log R, it is very difficult to find more than two or three points; getting a straight line in such a case appears to be a little incorrect.

To the same sample, the crystallization temperatures are distinct at various cooling rates, when plotting log $\{-\ln[1 - X_{(T)}]\}$ against log R at different crystallization temperatures; if the range of cooling rate is broader, the parallel relationship of the above plot is poor, it is indeed difficult for the Ozawa equation to reflect the practical crystallization process. Recently a new convenient approach for the nonisothermal crystallization was proposed by Liu,^{16,17} derived by combining the Avrami equation with the Ozawa equation. Under no-isothermal conditions the crystallinity is related to both the cooling rate R and the crystallization time t. At a fixed crystal-



Figure 5 Ozawa plot of $\log\{-\ln[1 - X_{(T)}]\}$ vs. $\log R$ for the 95/5/0 PA-6/PPO/SP blend.

(4)

linity, the relationship between R and t can be derived by combining the Avrami equation and the Ozawa equation as follows:

 $Log\{-ln[1 - X_{(T)}]\} = log Z_t + n log t$

$$\operatorname{Log} Z_t + n \, \log t = \log K_{(T)} - m \, \log R \qquad (6)$$

Equation 6 can be rewritten as follows:

$$\log R = \log F_{(T)} - a \log t \tag{7}$$

$$\log\{-\ln[1 - X_{(T)}]\} = \log K_{(T)} + m \log R \quad (5)$$

Combining eqs. (4) and (5):

where the parameter $F_{(T)} = [K_{(T)} / Z_T]^{1/m}$ refers to the value of cooling rate, which has to be chosen at a unit crystallization time when the measured



Figure 6 Variation of Ozawa exponent vs. temperature for the PA-6/PPO blend.



Figure 7 Plot of log R vs. log tfor different relative degree of crystallinity for the 95/5/0 PA-6/PPO/SP blend.

system amounts to a certain degree of crystallinity: a is the ratio the Avrami exponent n to the Ozawa exponent, i.e., a = n/m. It can be seen that $F_{(T)}$ has a definite physical and practical meaning. Plotting $\log R$ vs. $\log t$ should obtain a straight line; the $F_{(T)}$ and a can be determined from the intercept and slope of the line. The $\log F_{(T)}$ has been plotted for a given temperature against $\log R$, as illustrated for the 95/5/0 PA-6/PPO/SP blend in Figure 7. Table I lists the values of parameter $F_{(T)}$ and a at different relative degrees of crystallinity for the pure nylon PA-6/PPO series blends. It can be seen that the values of a are almost constant at a fixed PPO composition and the values of $F_{(T)}$ systematically increase with raising the relative degree of crystallinity; meanwhile, these increase as the amount of PPO in the blend increase, indicating the increase of amorphous PPO reduces the overall crystallization rate. The higher the values of $F_{(T)}$, the lower the crystallization rate; these phenomena can be attributed again to the previous two factors, and is well in accordance with the conclusion derived by referring to $t_{1/2}$.

From Table I we can also find that the presence of SP increases the values of $F_{(T)}$ for a given composition (95/5 PA-6/PPO), and the increase in the amount of SP increases the values of $F_{(T)}$, which indicates the addition of a compatibilizer reduces the overall crystallization rate. On one hand, the nucleation agent SP may accelerate the development of crystal growth. On the other hand, the presence of SP can improve the compatibility between PA-6 and PPO. SEM micrographs of the fracture surface of 95/5 PA-6/PPO blends

Table IValue of $F_{(T)}$ and a of Blends of PA-6/PPO at Various Compositions

PA-6/PPO/SP	$X_{(T)}$ (%)	$F_{(T)}$	a
	40	1.56	1.56
100/0/0 95/5/0 90/10/0 95/5/0.25 95/5/0.5	50	1.82	1.50
	60	2.47	1.46
	75	3.50	1.44
	40	2.79	1.59
	50	3.10	1.70
	60	4.06	1.64
	75	5.37	1.65
	40	3.81	1.49
	50	5.06	1.43
	60	5.96	1.43
	75	7.72	1.43
	40	4.13	1.47
	50	5.37	1.42
	60	6.35	1.39
	75	8.24	1.39
	40	4.48	1.34
	50	5.58	1.29
	60	6.59	1.30
	75	8.23	1.30



(A)



(B)



(C)

Figure 8 Morphology of the 95/5 PA-6/PPO series blends: (A) 95/5/0 PA-6/PPO/SP blend; (B) 95/5/0.25 PA-6/PPO/SP blend; (C) 95/5/0.5 PA-6/PPO/SP blend.

are shown in Figure 8. The large dispersed and spherical PPO particles can be easily identified from the uncompatibilized blend (95/5/0 PA-6/ PPO/SP) in Figure 8(A). With increasing the amount of SP, the configuration of PPO particles become small and finely dispersed, resulting in fine and stable morphology, which can be observed in Figure 8(B) (95/5/0.25 PA-6/PPO/SP) and Figure 8(C) (95/5/0.5 PA-6/PPO/SP). Consequently, the dispersed PPO particles more effectively impede the mobility of orderly crystalline PA-6 chains, and step up the growth of crystals of PA-6. Comparing the effects of these two aspects, the latter is more important.

CONCLUSION

The results of experiment data were analyzed by using Ozawa and Liu equations with the DSC technique. The presence of PPO impedes the growth of cystals of PA-6, and reduces the overall crystallization rate. Meanwhile, because the compatibilizer (SP) improved the compatibility of PA-6 and PPO, the addition of SP steps up the development of crystallinity, which was also proven by SEM results.

The Ozawa equation failed to describe the nonisothermal crystallization behavior of the PA-6/PPO blend probably because of the inapplicability of some of the inherent assumption in this type of analysis, such as secondary crystallization. The Ozawa exponent was related to the cooling rate and crystallization temperature. Liu's approach, combined by Avrami and Ozawa equations, was applied to study the nonisothermal crystallization process. The experiment results analyzed shows agreement with this new equation. It also suggested that the compatibility between the components for a certain system could be observed by DSC. But the imperfect aspect of this method is that it does not provide some information about the dimension of crystal growth because the values of a (the ratio of the Avrami exponent n to the Ozawa exponent m) are not easily compared.

REFERENCES

- Hobbs, S. Y.; Dekkers, M. E. J. J Mater Sci 1989, 24, 1316.
- 2. Folkes, M. J.; Hope, P. S. In Polymer Blends and Alloys; Blackie: London, 1993.
- 3. Utracki, L. A. In Polymer Alloys and Blends; Hanser: New York, 1989.
- 4. Si, M.; Ou, Y. J Polym Sci Part B Polym Phys, submitted.
- 5. Tamor, Z.; Gogos, C. G. In Principles of Polymer Processing; John Wiley & Sons: New York, 1979.

- Ziabicki, A. In Fundmentals of Fiber Formation; Wiley: London, 1976.
- 7. Avrami, M. J Chem Phys 1940, 8, 212.
- 8. Mandelkern, L. In Crystallization of Polymers; McGraw-Hill: New York, 1964.
- 9. Ziabicki, A. Appl Polym Symp 1967, 6, 1.
- 10. Jeziorny, A. Polymer 1978, 19, 1142.
- 11. Ozawa, T. Polymer 1971, 12, 150.
- 12. Eder, M.; Ulochowicz, A. Polymer 1983, 24, 1593.
- 13. Pratt, C. F.; Hobbs, S. V. Polymer 1976, 17, 12.
- Hammami, A.; Squriell, J.; Mehrotra, A. K. Polym Eng Sci 1995, 35, 797.
- 15. Cebe, P.; Hong, S. D. Polymer 1986, 27, 1183.
- Liu, J. P.; Mo, Z. S.; Qi, Y. C.; Zhang, H. F.; Chen, D. L. Acta Polym Sinica (Chin) 1993, 1, 1.
- Liu, T. X.; Mo, Z. S.; Wang, S. G.; Zhang, H. F. Polym Eng Sci 1997, 37, 568.
- de Juana, R.; Jauregui, A.; Calahorra, E.; Cortazar, M. Polymer 1997, 37, 3339.
- Srinivas, S.; Babu, J. R.; Riffle, J. S.; Wilkes, G. L. Polym Eng Sci 1997, 37, 506.
- 20. Evans, U. R. Trans Farady Soc 1945, 41, 365.