Nonisothermal Crystallization Behavior of Glass-Bead-Filled Polypropylene

Qiang Yuan,[1,2] Wei Jiang,[1] Lijia An,[1] R. D. K. Misra[2]

[1]State Key Laboratory of Polymer Physics and Chemistry, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, People's Republic of China
[2]Center for Structural and Functional Materials and Department of Chemical Engineering, University of Louisiana at Lafayette, Louisiana 70504-4130

ABSTRACT: The effects of the glass-bead content and size on the nonisothermal crystallization behavior of polypropylene (PP)/glass-bead blends were studied with differential scanning calorimetry. The degree of crystallinity decreased with the addition of glass bead, and the crystallization temperature of the blends was marginally higher than that of pure PP at various cooling rates. Furthermore, the half-time for crystallization decreased with an increase in the glass-bead content or particle size, implying the nucleating role of the glass beads. The nonisothermal crystallization data were analyzed with the methods of Avrami, Ozawa, and Mo. The validity of various kinetic models for the nonisothermal crystallization process of PP/glass-bead blends was examined. The approach developed by Mo successfully described the nonisothermal crystallization behavior of PP and PP/glass-bead blends. Finally, the activation energy for the nonisothermal crystallization of pure PP and PP/glass-bead blends based on the Kissinger method was evaluated. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 102: 2026–2033, 2006

Key words: blends; crystallization; poly(propylene) (PP)

INTRODUCTION

Polypropylene (PP) is a semicrystalline, thermoplastic, polymeric material that is widely used because of its attractive combination of good processability, mechanical properties, and chemical resistance. However, its inadequate stiffness and brittleness limit its applications to some extent. Compounding with inorganic particles is a simple, effective, and economical method for improving the mechanical and thermal properties of PP. In recent years, some studies on the structure and properties of inorganic-particle-filled polymer blends have been conducted.[1–6] Glass beads are cost-effective fillers and enable us to reinforce the polymer matrix. In our previous work, we observed that glass beads could be used to toughen polyethylene and PP.[2,6]

Crystallinity is a key factor that determines the mechanical and thermal properties of a polymer, and a number of researchers have dealt with this aspect. Gaymans et al.[7] studied the effect of crystallinity on the fracture behavior of PP. Liang et al.[8] studied the effects of the glass-bead content and size on the crystallization and melting behavior of glass-bead-filled low-density polyethylene (LDPE) composites. Kenny et al.[9] investigated the effects of different kinds of fibers on the crystallization of isotactic PP and observed that the fibers significantly affected the crystallization rate and crystallization peak temperature of the composites. The crystallization behavior of PP/liquid-crystalline polyester blends was studied by Shank et al.[10] The relation between the inorganic-particle size and content and the crystallization behavior of PP has been determined.[11–20]

Although the effects of additives on the crystallization behavior of PP have been reported for some cases, the majority have been studied under isothermal conditions. The study of the nonisothermal crystallization of composites and polymer blends is of practical significance because processing techniques generally are performed under nonisothermal conditions. In comparison with isothermal crystallization, the study of nonisothermal crystallization widens the knowledge of the crystallization behavior of poly-

mers. The influence of the addition of various types of fillers (micro- or nanosize) on the nonisothermal crystallization process of thermoplastics has been studied by several researchers.[21–26] For instance, Leelapornpisit et al.[21] carried out a study on the crystallization behavior of single-walled carbon nanotube (SWNT) reinforced PP. They indicated that the SWNTs displayed a distinct nucleating effect on the PP crystallization, favoring the α-crystalline form rather than the β form. An analysis of the kinetics of crystallization showed a significant increase in the activation energy (ΔE) with the incorporation of SWNTs. Xu et al.[25] studied the nonisothermal crystallization kinetics of PP and PP/organic-montmorillonite nanocomposites with differential scanning calorimetry (DSC). The results indicated that PP/montmorillonite nanocomposites could be conveniently processed in a manner similar to that used for neat PP, and the addition of organomontmorillonite accelerated the overall nonisothermal crystallization process. Similarly, Karayannidis et al.[26] recently examined the effect of the silica content on the isothermal and nonisothermal crystallization kinetics of PP/surface-treated SiO_2 nanocomposites. Liang and coworkers noted that the size of the glass bead influenced the drop-weight dart impact fracture behavior of PP/glass-bead composites[27] and the viscoelasticity of polyethylene/glass-bead composites.[28] Recently, Yuan et al.[29] also observed that the size of the glass bead and heat treatment affected the crystallization behavior of glass-bead-filled PP. Thus, changes in the crystallization behavior are of significant importance in determining the ultimate properties.

In the work described here, the nonisothermal crystallization kinetics as a function of the filler content and size of neat and PP/glass-bead blends prepared by melt compounding were studied by DSC. The kinetics were subsequently analyzed with a different theoretical approach[30–32] for nonisothermal crystallization. Finally, the ΔE value describing the nonisothermal crystallization process was calculated with the Kissinger method.[33]

EXPERIMENTAL

Materials

PP with a melt flow index of 3.3 g/10 min (ASTM D 1238) was produced by Liaoyang Petrochemical Fiber Co. (Liaoyang, People's Republic of China). Its weight-average molecular weight (M_w) was 3.72×10^5, its number-average molecular weight (M_n) was 6.90×10^4, its molecular weight distribution (M_w/M_n) was 5.4, and its density was 0.9 g/cm^3. The filler glass beads were produced by Potters Industries (Texas, United States). Their properties are listed in Table I. The surface of the glass beads was treated with a silane coupling agent.

TABLE I
Properties of the Filler Glass Beads

Number	Name	Diameter (μm)			Mean (μm)	Bulk density (kg/cm^3)	
		10%	50%	90%		Untapped	Tapped
GB1	6000	1.4	3.7	8	4	913.14	1441.80
GB2	3000	13	32	61	35	1281.60	1585.98
GB3	2530	30	64	103	66	1457.82	1569.96

Preparation of the samples

PP pellets and glass-bead blends with different glass-bead contents were mixed in an internal batch mixer with a capacity of 55 cm^3 (Rheocoder XSS-300 Shanghai, China) at 468 K for 4 min. The roller speed used for blending was 40 rpm. The temperature, mixing time, and roller speed were the same for all the blends.

DSC

DSC measurements were performed with a Perkin-Elmer Diamond DSC calorimeter equipped with a 2P intracooler (Massachusetts). Each specimen was first held at 473 K for 5 min to erase the previous thermomechanical history and to obtain a completely relaxed melt. Then, the melt was cooled to room temperature to crystallize at selected cooling rates of 1, 2.5, 5, 10, and 20 K/min. Lastly, the samples were heated again to 473 K at a rate of 10 K/min. Both heating and cooling were carried out in a nitrogen environment.

RESULTS AND DISCUSSION

Figure 1 shows representative DSC scans of PP and glass-bead-filled PP blends on cooling from 473 K at various cooling rates. From Figure 1, the crystallization temperature (T_c) of PP and its blends, defined as the temperature at the crystalline peak, can be determined. Also, the degree of crystallinity (X_c) can be calculated from the enthalpy of fusion (ΔH_m; during the second heating) with eq. (1):

$$X_c(\%) = \frac{\Delta H_m}{(1 - \phi)\Delta H_m^o} \times 100 \quad (1)$$

where $\Delta H_m^o = 209$ J/g is the enthalpy of fusion for 100 wt % crystalline PP[34] and ϕ is the weight percentage of the glass beads in the blends. The values of X_c and T_c are listed in Table II. The results indicate that the addition of glass beads to PP leads to a decrease in the crystallinity accompanied by a small but consistent increase in the peak T_c value at various cooling rates. However, for particles of various sizes, the trend of T_c with the glass-bead content is different. For the PP/GB1 and PP/GB2 blends, T_c increases with the glass-bead content, but for PP/GB3 blends, T_c decreases with
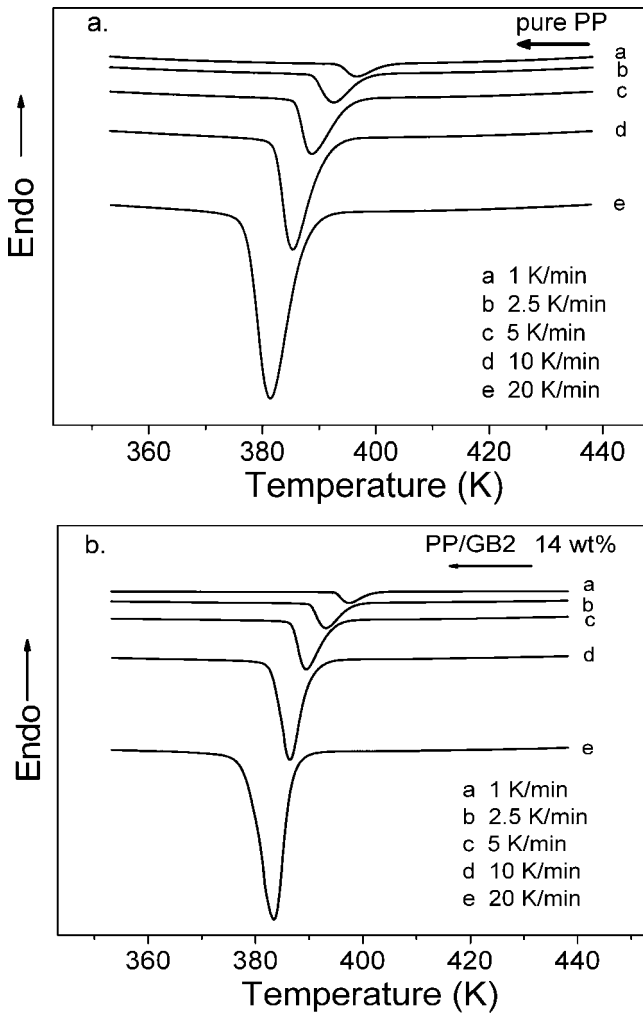
Figure 1 DSC traces of (a) pure PP and (b) PP/GB2 (14 wt % glass beads) at various cooling rates.

the glass-bead content. The increase in T_c of PP in PP/GB1 and PP/GB2 with the addition of glass beads can be attributed to the nucleating effect of glass beads, and the nucleating effect is influenced by the size of the particles, as evident from the T_c variation. More importantly, the data suggest that there is an optimum size for the filler to exhibit effective nucleating ability, which is related to the surface area. The smaller the surface area is, the smaller the nucleating ability is of the filler. For this reason, T_c decreases with the glass-bead content for PP/GB3. Liang et al.[8] obtained a similar increasing trend for T_c in LDPE/glass-bead composites. The crystallinity decrease can be ascribed to the lowered mobility of the polymer chains in the PP matrix, which results from the presence of glass-bead particles. The presence of these dispersed particles makes large crystalline domains difficult to form in the restricted space. Figure 2 (only the plots of the samples with 14 wt % glass beads are presented; the same applies to Figs. 3–6) shows the relationship between the relative degree of crystallinity (X_t) and the temperature

for the PP/glass-bead blends at various cooling rates. X_t, as a function of T_c, can be estimated with eq. (2):

$$X_t = \frac{\int_{T_o}^{T} (dH_c/dT)dT}{\int_{T_o}^{T_\infty} (dH_c/dT)dT} \qquad (2)$$

where T_o and T_∞ are the onset and end crystallization temperatures, respectively, and dH_c is the enthalpy of crystallization released during infinitesimal temperature range dT. At different cooling rates, the temperature parameters in Figure 2 can be converted into a timescale with eq. (3):

$$t = (T_o - T)/\lambda \qquad (3)$$

where T is the temperature at crystallization time t and λ is the cooling rate. Figure 3 shows plots of X_t as a function of time. Increasing the cooling rate reduces the time for the completion of crystalliza-

TABLE II
ΔH_m, T_c, X_c, and $t_{0.5}$ Values for PP and PP/Glass-Bead Blends at Various Cooling Rates

| Material	Cooling rate (K/min)	ΔH_m (J/g)	T_c (K)	X_c (%)	$t_{0.5}$ (min)
PP	1	123.1	396.7	58.9	8.85
	2.5	111.0	392.5	53.1	4.65
	5	104.9	388.7	50.2	2.45
	10	100.9	385.3	48.3	1.27
	20	95.1	381.4	45.5	0.62
PP/GB1 (14 wt % glass beads)	1	101.2	398.6	48.4	7.52
	2.5	95.3	393.9	45.6	3.89
	5	89.5	389.9	42.8	2.18
	10	88.4	386.4	42.3	1.16
	20	87.2	383.1	41.7	0.70
PP/GB2 (14 wt % glass beads)	1	103.7	397.4	49.6	6.78
	2.5	98.2	393.1	47.0	3.57
	5	93.8	389.5	44.9	2.05
	10	90.9	386.5	43.5	1.15
	20	91.8	383.4	43.9	0.61
PP/GB3 (14 wt % glass beads)	1	104.7	399.1	50.1	6.74
	2.5	98.4	394.9	47.1	2.71
	5	93.6	391.3	44.8	1.71
	10	90.5	388.4	43.3	0.94
	20	92.8	385.2	44.4	0.59
PP/GB1 (48 wt % glass beads)	1	92.4	403.7	44.2	7.38
	2.5	86.5	398.8	41.4	3.70
	5	82.8	395.1	39.6	1.89
	10	84.6	392.0	40.4	1.18
	20	84.2	387.8	40.3	0.66
PP/GB2 (48 wt % glass beads)	1	117.2	397.8	56.1	7.32
	2.5	109.5	393.9	52.4	3.38
	5	105.8	390.5	50.6	1.75
	10	84.6	387.2	40.5	1.13
	20	76.9	384.1	36.8	0.60
PP/GB3 (48 wt % glass beads)	1	113.5	397.8	54.3	6.91
	2.5	107.6	393.6	51.5	3.33
	5	105.8	390.2	50.6	2.03
	10	99.7	387.4	47.7	1.04
	20	95.7	384.1	45.8	0.39
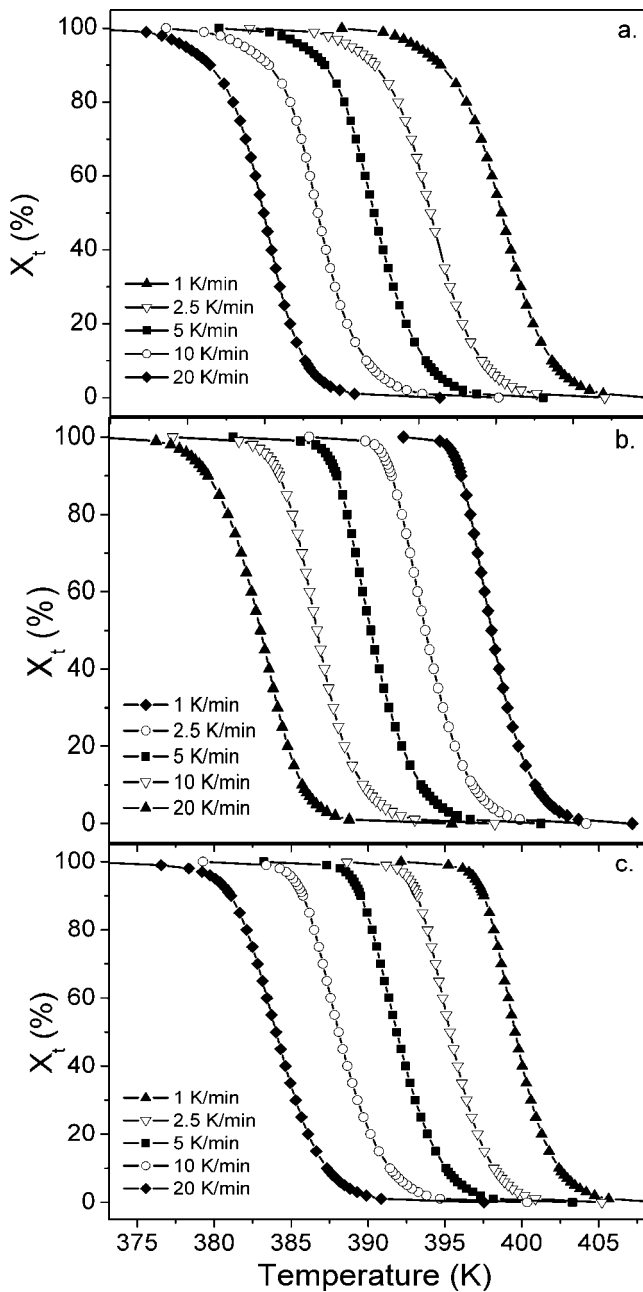
Figure 2 Variation of X_t with the temperature for the nonisothermal crystallization of (a) PP/GB1, (b) PP/GB2, and (c) PP/GB3 blends filled with 14 wt % glass beads.

tion. From Figure 3, an important parameter that can be derived is the half-time of crystallization ($t_{0.5}$), which is the time from the onset of crystallization to the time at which X_t is 50%; it is listed in Table II. It is apparent that the value of $t_{0.5}$ for different PP/glass-bead blends at various cooling rates is lower than that of neat PP. This can be explained as follows. Glass-bead particles act as heterogeneous nucleating agents to facilitate crystallization, and the higher the glass-bead content is, the greater the nucleating effect is. Consequently, $t_{0.5}$ for crystalliza-

tion tends to decrease with increasing glass-bead content for the same particle size. In addition, $t_{0.5}$ for PP/glass-bead blends tends to decrease with increasing particle size at the same glass-bead content. This suggests that the greater the glass-bead size is, the stronger the nucleating ability is. In addition to $t_{0.5}$, other parameters, such as the kinetic rate coefficient, are commonly used to characterize the nonisothermal crystallization kinetics of polymers. The most common approach used to analyze the isothermal crystallization kinetics is the Avrami equation [eq. (4)],
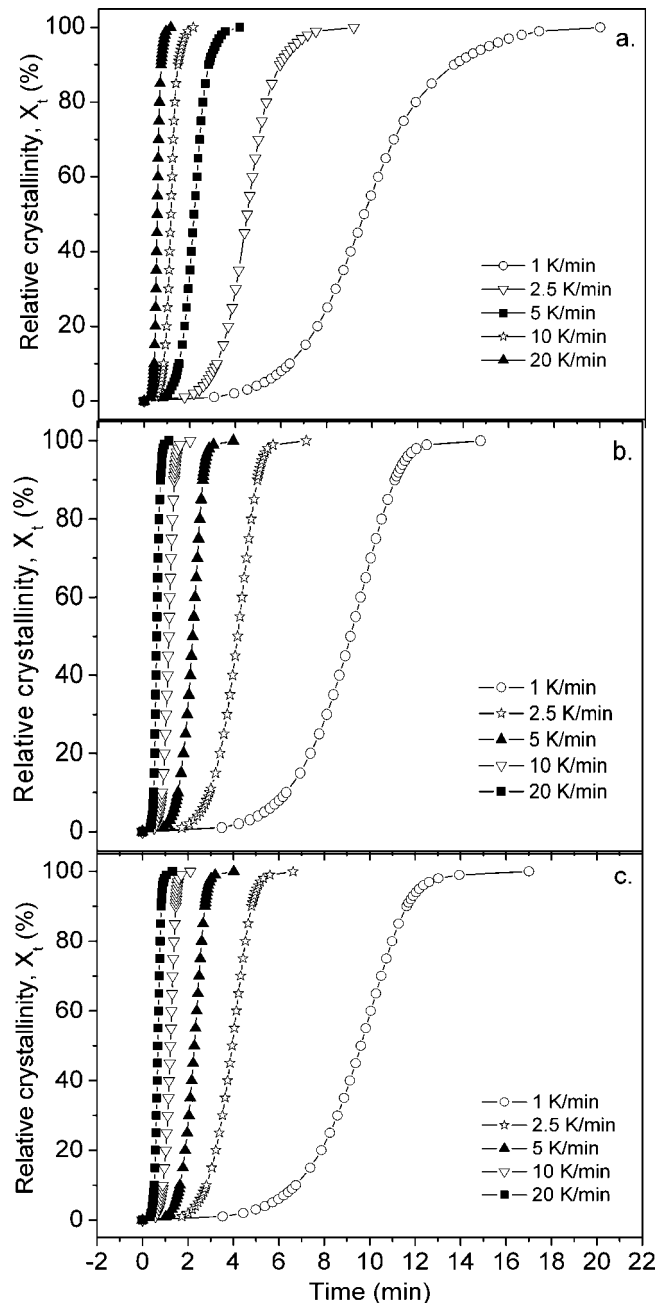

Figure 3 Variation of X_t with time for the nonisothermal crystallization of (a) PP/GB1, (b) PP/GB2, and (c) PP/GB3 blends filled with 14 wt % glass beads.
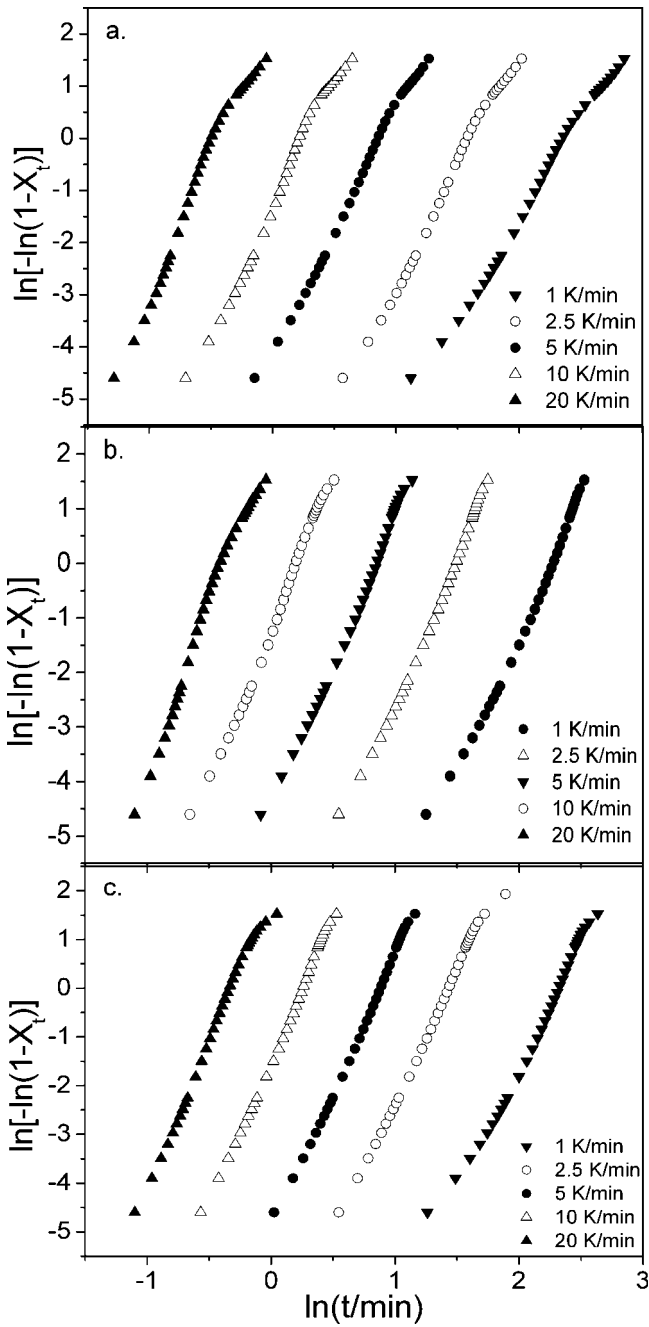
Figure 4 Plots of $\ln[-\ln(1-X_t)]$ versus $\ln t$ for the crystallization of (a) PP/GB1, (b) PP/GB2, and (c) PP/GB3 blends filled with 14 wt % glass beads at various cooling rates.

which assumes that X_t develops with crystallization time t. The logarithmic form of eq. (4) is eq. (5):

$$X(t) = 1 - \exp(-kt^n) \qquad (4)$$

$$\ln[-\ln(1 - X(t))] = \ln k + n \ln(t) \qquad (5)$$

where $X(t)$, k, t, n are the relative crystallinity, rate constant, crystallization time, and Avrami exponent, respectively.[30]

Figure 4 shows plots of $\ln[-\ln(1 - X_t)]$ versus $\ln t$ for PP/glass-bead blends at various cooling rates. Each plot has a linear portion in the early stage of crystallization and is followed by a gentle deviation at a longer time.

When eq. (5) is applied to nonisothermal crystallization, parameters k and n have different physical meanings because the temperature changes instantly in the nonisothermal crystallization. Because of the nonisothermal character of the process, λ is the factor that needs to be considered. On the basis of the
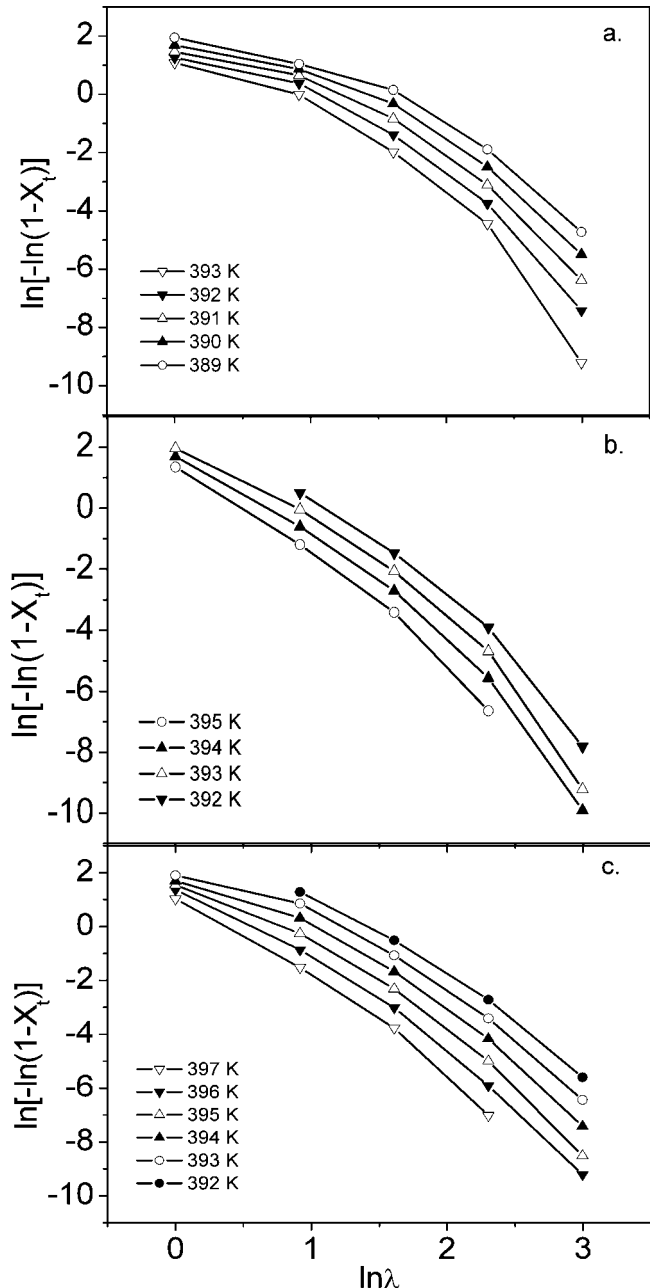

Figure 5 Ozawa plots of $\ln[-\ln(1 - X_t)]$ versus $\ln \lambda$ for the crystallization of (1) PP/GB1, (2) PP/GB2, and (3) PP/GB3 blends filled with 14 wt % glass beads.
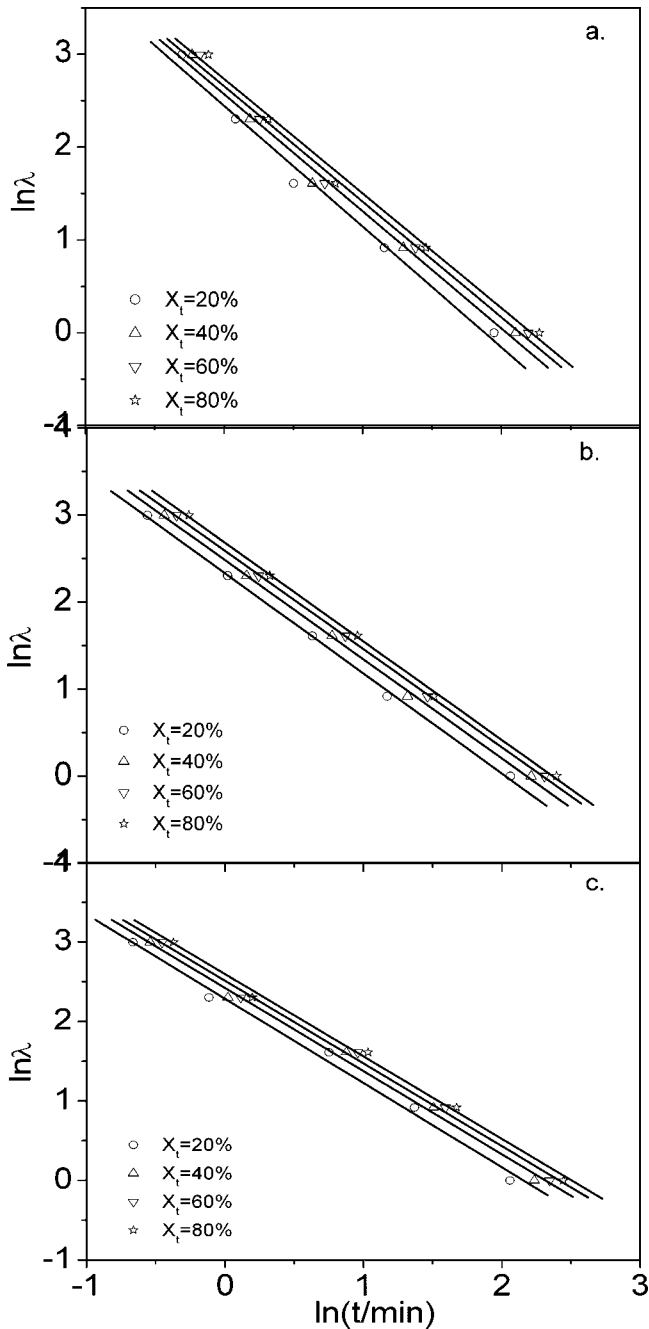
Figure 6 Plots of ln λ versus ln t for (a) PP/GB1, (b) PP/GB2, and (c) PP/GB3 blends filled with 14 wt % glass beads.

mathematical derivation of Evans, Ozawa[31] modified the Avrami equation by incorporating the λ factor:

$$1 - X(t) = \exp[-K(T)/\lambda^m] \qquad (6)$$

where $K(T)$ and m are the Ozawa crystallization rate constant and exponent, respectively. Equation (6) in the logarithmic form can be written as follows:

$$\ln[-\ln(1 - X(T))] = \ln K(T) - m \ln(\lambda) \qquad (7)$$

In Figure 5, plots based on the nonisothermal crystallization data of PP and PP/glass-bead blends for a series of temperatures are presented. In our study, the Ozawa equation fails to describe the nonisothermal crystallization of blends because the plots do not yield straight lines. The Ozawa equation ignores secondary crystallization. A modified method was proposed by Mo et al.[32] to describe the nonisothermal crystallization by combining the Avrami equation [eq. (5)] and Ozawa equation [eq. (7)]. The modified equation is

$$\ln \lambda = \ln F(T) - \alpha \ln t \qquad (8)$$

where kinetic parameter $F(T) = [K(T)/k]^{1/m}$ refers to the cooling rate that needs to be selected within a unit of crystallization time when the measured system amounts to a certain degree of crystallinity and α is the ratio of Avrami exponent n to Ozawa exponent m (n/m). Thus, at a given degree of crystallinity, from the plot of ln λ versus ln t (Fig. 6), the values of α and $F(T)$ can be obtained by the fitting of the linear slopes and the determination of the intercepts of the lines, respectively. The results are listed in Table III. α for PP varies from 1.19 to 1.25 and for PP/glass-bead blends varies from 1.03 to 1.30. The value of $F(T)$ systematically increases with an increase in the relative crystallinity for PP and PP/glass-bead blends. Thus, at a unit of the crystallization time, a higher cooling rate should be used to obtain a higher degree of crystallinity. In addition, the value of $F(T)$ of PP/glass-bead blends is smaller than that of pure PP at a certain X_t value. Moreover, it decreases with an increase in the glass-bead content or filler size; that is, it amounts to the same X_t value. PP/glass-bead blends require a lower cooling rate, and this suggests that the blends crystallize at a faster rate than pure PP. This is in accordance with the aforementioned results for $t_{0.5}$. The combination method of Mo et al. [eq. (8)] is successful in describing the nonisothermal process of PP and PP/glass-bead blends.

It is well known that the crystallization of polymers is controlled by two factors: the dynamic factor, which is related to the ΔE value for the transport of crystalline units across the phase, and the static factor, which is related to the free energy barrier for nucleation. ΔE for nonisothermal crystallization can be evaluated with the Kissinger method:

$$\frac{d[\ln(\lambda/T_p^2)]}{d(1/T_p)} = -\frac{\Delta E}{R} \qquad (9)$$

where T_p and R are the peak temperature and universal gas constant, respectively.[33] Figure 7 shows plots based on the Kissinger method, and the slopes of the least-square lines drawn through these plots equal $\Delta E/R$, enabling the determination of ΔE. The results for ΔE are listed in Table III. It appears that

TABLE III
Nonisothermal Crystallization Kinetic Parameters for PP and PP/Glass-Bead Blends with Different X_t Values by a Combination of the Avrami–Ozawa Equation and ΔE Values Based on the Kissinger Method

Material	X_t	α	$F(T)$	Regression coefficient	ΔE (kJ/mol)
PP	0.2	1.25	11.36	0.9991	−252.05
	0.4	1.22	13.60	0.9994	
	0.6	1.21	15.49	0.9993	
	0.8	1.19	16.95	0.9994	
PP/GB1 (14 wt % glass beads)	0.2	1.08	11.29	0.9989	−250.04
	0.4	1.06	13.07	0.9994	
	0.6	1.05	14.30	0.9993	
	0.8	1.03	15.49	0.9996	
PP/GB2 (14 wt % glass beads)	0.2	1.15	10.28	0.9998	−275.80
	0.4	1.11	11.84	0.9999	
	0.6	1.11	13.33	0.9998	
	0.8	1.13	14.59	0.9993	
PP/GB3 (14 wt % glass beads)	0.2	1.15	9.87	0.9989	−282.72
	0.4	1.14	11.25	0.9995	
	0.6	1.13	12.30	0.9999	
	0.8	1.13	13.46	0.9996	
PP/GB1 (48 wt % glass beads)	0.2	1.06	9.68	0.9960	−258.16
	0.4	1.05	11.25	0.9970	
	0.6	1.04	12.43	0.9976	
	0.8	1.04	14.59	0.9980	
PP/GB2 (48 wt % glass beads)	0.2	1.30	9.49	0.9938	−281.42
	0.4	1.26	10.91	0.9954	
	0.6	1.24	12.06	0.9961	
	0.8	1.24	13.46	0.9964	
PP/GB3 (48 wt % glass beads)	0.2	1.05	9.39	0.9994	−285.77
	0.4	1.04	10.59	0.9993	
	0.6	1.03	11.47	0.9993	
	0.8	1.03	12.43	0.9993	

the absolute value of ΔE tends to increase with the addition of glass beads or an increase in the glass-bead size. From eq. (9), we know that the Kissinger method[33] can be used to calculate ΔE for the entire crystallization process on the basis of the relationship between T_c and cooling rates obtained from the nonisothermal crystallization data.

The observation that T_c of all glass-bead-reinforced PP is greater than that of neat PP and that $t_{0.5}$ of all glass-bead-reinforced PP is lower than that of neat PP implies that crystal nucleation occurs faster because of the nucleating effect of glass beads. The crystallization process can be divided into two parts: nucleation and growth. In this study, the fact that the absolute value of ΔE increases with the addition of glass beads or an increase in the glass-bead size leads us to suggest that the experimentally determined ΔE value is largely related to the growth process rather than the initiation of the nucleation process.

On the other hand, the observation of smaller values of $t_{0.5}$ and $F(T)$ for PP/glass beads compared with those of the neat polymer suggests that glass beads do act as nucleating agents. However, ΔE of

PP/glass-bead blends is higher and is contrary to the expectations of half-time data. We believe that this behavior is a result of a weak attraction between the filler and polymer segments. A similar behavior was recently reported by Mitchell and Krishnamoorti[35] in their study on poly(ε-caprolactone)-functionalized SWNT nanocomposite systems. Also, our recent viscosity measurements have shown that the addition of glass beads increases the effective viscosity of the polymer matrix. It is our opinion that the increase in the viscosity of PP prevents the formation of large crystalline domains, thereby increasing ΔE.
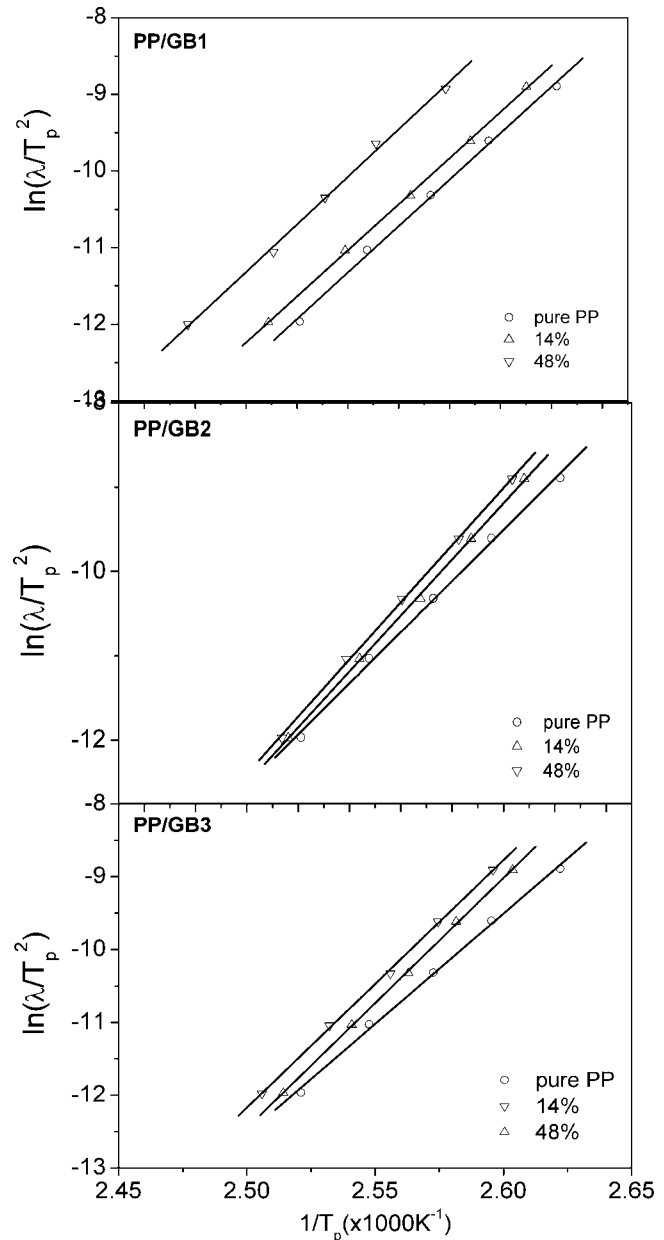

Figure 7 Determination of ΔE for the nonisothermal crystallization process of PP and PP/glass-bead blends based on the Kissinger method: (a) PP/GB1, (b) PP/GB2, and (c) PP/GB3.

CONCLUSIONS

The nonisothermal crystallization behavior of neat PP and glass-bead-filled PP were studied with DSC. The results revealed that the addition of glass beads to PP resulted in a decrease in $t_{0.5}$ at various cooling rates. This was ascribed to the nucleating effect of glass-bead particles. Several models, based on the Avrami, Ozawa, and modified Avrami–Ozawa equations, were used to analyze the nonisothermal crystallization behavior. Both the Avrami and Ozawa equations failed to provide an adequate description of the nonisothermal crystallization of PP and PP/glass-bead blends. However, the method developed by Mo et al.[32] successfully described the nonisothermal crystallization behavior of PP and PP/glass-bead blends. Finally, ΔE for the nonisothermal crystallization of PP and PP/glass-bead blends was determined with the Kissinger method. The results showed that the addition of glass beads to PP had a significant influence on ΔE; this could probably be attributed to a weak attraction between the glass bead and the polymer segments.

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