

Nonisothermal Crystallization of PP/Nano-SiO₂ Composites

Jiasheng Qian,^{1,2} Pingsheng He,¹ Kangming Nie²

¹Department of Polymer Science and Engineering, University of Science & Technology of China, Hefei 230026, Anhui, China

²School of Chemistry and Chemical Engineering, Anhui University, Hefei 230039, Anhui, China

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ABSTRACT: The kinetics of nonisothermal crystallization of polypropylene (PP) containing nanoparticles of silicon dioxide (SiO₂) were investigated by differential scanning calorimetry (DSC) at various cooling rates. Several different analysis methods were used to describe the process of nonisothermal crystallization. The results showed that the Ozawa equation and Mo's treatment could describe the nonisothermal crystallization of the composites very well. The nano-SiO₂ particles have a remarkable heterogeneous nucleation effect in the PP matrix. The rate of crystallization

of PP/nano-SiO₂ is higher than that of pure PP. By using a method proposed by Kissinger, activation energies have been evaluated to be 262.1, 226.5, 249.5, and 250.1 kJ/mol for nonisothermal crystallization of pure PP and PP/nano-SiO₂ composites with various SiO₂ loadings of 1, 3, and 5%, respectively. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 1013–1019, 2004

Key words: silicon oxide; polypropylene; nanocomposite; crystallization; DSC

INTRODUCTION

The resin-based nanocomposites are a new class of materials where nanoscale particles (inorganic clay or any other particles) are finely dispersed on a resin matrix. They have been reported to exhibit markedly improved properties as compared to the pure polymers or conventional particle composites.^{1–5} The increasing properties include their strength, modulus, heat resistance, and barrier properties, etc. with only low loadings of the inorganic component as compared to resin-based composites filled with normal fillers.

Polypropylene (PP) is a common polymer with interesting characteristics, which make it a high consumption polymer. However, its toughness, weather resistance, and weather aging are not good enough, which have limited its application in many high-tech fields. One measure for improving the disadvantage is to mix the resin with nanofiller to form the composite.^{6–8} Nanofillers are different from the traditional fillers; the performances of polymer matrix could be markedly improved at very low loadings (1–10 wt %) of the nanofiller as compared to conventional filled polymers, which require a high loading of the order of 20–50 wt %. Various resin-based nanocomposites,

such as PP/nano-CaP,⁸ nylon-6/clay,⁹ PP/nano-CaCO₃,¹⁰ polystyrene/Al₂O₃,¹¹ etc., were investigated. A considerable improvement in the properties of polymers was observed; for example, Liu¹² prepared PP/clay nanocomposites by grafting-melt intercalation, and results show that 27% improvement in tensile strength and 42% increase in tensile modulus are obtained in PP/clay nanocomposite with 5 wt % clay content compared with PP. Shi¹³ and coworkers studied the PP/SiO₂ nanocomposites; compared with PP, the Izod impact strength, flexural modulus, and tensile strength of PP/SiO₂ nanocomposites with SiO₂ loadings of 2% increased by 90, 23, and 5%, respectively. In this presentation, we investigated the composite of PP with nanoscale silicon oxide (SiO₂) filler.

PP is a semicrystalline polymer. Its isothermal and nonisothermal crystallization behavior has been investigated by many researchers.^{14–17} The isothermal crystallization conditions are rarely met during the practice processing and it is desirable to study the crystallization of composite under nonisothermal conditions.

The crystallization behavior of PP mixed with nanofiller has been reported by several authors.^{5–8} Sautjana⁷ prepared PP/nano-CaP composites by a new route based on matrix-mediated control of growth and morphology and investigated the structure development and isothermal crystallization behavior of the composites. The result shows that the ultimate spherulite size of PP/nano-CaP composite is related to the filler size, and the nucleating efficiency was found to be dependent on the particle size as inverse exponential power law. Yang et al.¹⁸ investigated the effects of

Correspondence to: H. Pingsheng (hpsm@ustc.edu.cn).

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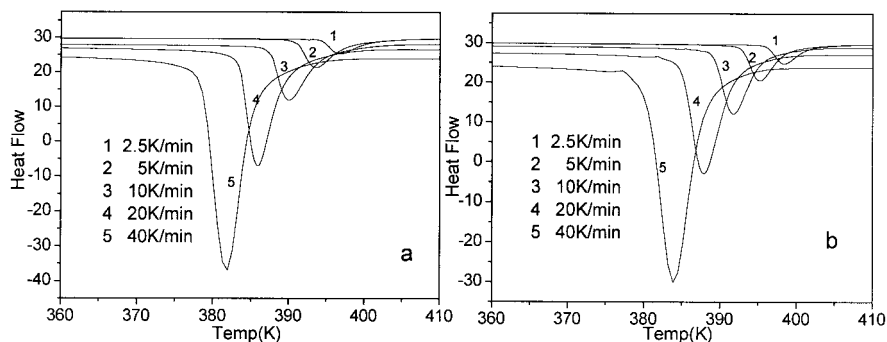


Figure 1 DSC thermograms of nonisothermal cold crystallization for plain PP (a) and PP/nano-SiO₂ composite with 3% nano-SiO₂ loading (by weight) (b).

superfine CaCO₃ on the crystallization behavior of PP. The crystallization rate of PP/CaCO₃ composites is 1.5–2.0 times higher than that of neat PP. The content and size of CaCO₃ affect remarkably the crystallization behavior of the composite. In our previous work,^{3,4} we successfully prepared polypropylene/montmorillonite (PP/MONT) nanocomposites and polyoxymethylene/montmorillonite (POM/MONT) nanocomposites and studied the nonisothermal crystallization of the nanocomposite based on the Avrami analysis modified by Jeziorny and a method developed by Mo's group. In this presentation, we report the crystallization behavior of PP/nano-SiO₂ composite. Several nonisothermal crystallization kinetic equations were employed to deal with the nonisothermal crystallization data. The kinetic parameters such as the Ozawa exponent and the activation energies were estimated from differential scanning calorimetry (DSC) crystallization exotherms for pure PP and PP/nano-SiO₂ composites.

EXPERIMENTAL

Materials

The nano-SiO₂ filler with a size of 16 nm was supported by the Zhoushan Mingri Nano-materials Co. (China). Having been dried in 383 K for 4 h, the surface of SiO₂ filler was covered by KH560 silane coupling agent (Nanjing Shuguang Chemical Co.) before use. Polypropylene (500P) used was a product made in Saudi Arabia (at Al Jubail Polypropylene Plant) with a melt index of 4 g/10 min.

Preparation of PP/nano-SiO₂ composite

The PP and nano-SiO₂ filler covered with silane coupling agent were mixed in a roller mill at 428–438 K for 10–15 min. The shear rate was $7.0 \times 10^2 \text{ s}^{-1}$. The resulting sheet was compression molded at 453 K for 5 min into a plate with a thickness of 2 mm and kept in a room waiting for use.

Nonisothermal DSC analysis

The nonisothermal crystallization of PP/nano-SiO₂ composite in cooling mode from the molten temperature (melt crystallization) was carried out on a Perkin–Elmer Pyris-1 DSC in nitrogen atmosphere. The temperature and energy readings were calibrated with indium at each cooling rate used in the measurement. The sample of 7–10 mg was heated up first to 453 K rapidly and kept in the cell for 5 min to eliminate the thermal history of the sample and destroy any nuclei that might act as seed crystals. Then, the sample was cooled down to 293 K at five different cooling rates of 2.5, 5, 10, 20, and 40 K/min, respectively. The exothermic crystallization peak was recorded as a function of temperature, and the change of enthalpy was recorded at the same time.

RESULTS AND DISCUSSION

Crystallization behavior of PP/nano-SiO₂ composite

The crystallization exotherms of pristine PP and PP/nano-SiO₂ composite at five cooling rates of 2.5, 5, 10, 20, and 40 K/min are shown in Figure 1. Some useful crystallization kinetic parameters can be read directly from the exotherm curves. They are the peak temperature, T_p , the relative degree of crystallinity X_t , starting crystallization temperature T_{on} , and crystallization enthalpy ΔH_c , respectively, as shown in Table I. The effect of the different cooling rates is observed from these exotherm curves. The faster the cooling rate, the lower the temperature range at which the crystallization occurs. At a slower cooling rate, there is sufficient time to activate nuclei; therefore, the crystallization can be growing at a higher temperature. On the contrary, at faster cooling rates, the activation of nuclei occurs at a lower temperature. Consequently, crystallization nucleates at higher temperatures when the polymer samples are cooled at a slower scanning rate. The peak temperature T_p shifts to a lower temperature with an increasing cooling rate for both origin PP and

TABLE I
Values of the T_{peak} , $t_{1/2}$, ΔH_c and T_{onset} at Various Cooling Rates ϕ

Samples	ϕ (K/min)	T_{peak} (K)	T_{onset} (K)	$t_{1/2}$ (min)	ΔH (J/g)
Origin PP	40	381.9	386.9	0.388	88.2
	20	385.8	390.5	0.865	89.9
	10	390.0	394.7	1.55	94.9
	5	393.5	398.2	2.94	96.9
	2.5	396.7	401.2	5.12	96.8
PP/SiO ₂ (1%)	40	383.2	387.6	0.347	88.1
	20	386.3	391.6	0.755	90.6
	10	390.1	398.4	1.50	93.1
	5	394.2	401.8	2.81	95.1
	2.5	397.6	404.5	5.04	96.5
PP/SiO ₂ (3%)	40	383.9	388.1	0.305	84.9
	20	388.0	392.1	0.641	88.7
	10	391.8	395.7	1.10	89.7
	5	395.2	398.9	2.50	93.9
	2.5	398.4	401.9	4.18	93.7
PP/SiO ₂ (5%)	40	386.2	390.6	0.252	82.1
	20	390.6	394.2	0.542	83.5
	10	394.2	397.6	0.977	86.6
	5	397.7	400.9	1.85	88.0
	2.5	400.9	403.9	3.51	89.9

PP/nano-SiO₂ composites; for a given cooling rate, T_p of PP/nano-SiO₂ composites was slightly higher than that of origin PP, indicating that the addition of nano-SiO₂ into PP increased the rate of crystallization of PP. The crystallization enthalpy ΔH_c has the same variation tendency as the cooling rate increases but shifts to lower when content of SiO₂ in composites increases. This means that the crystallization of PP/nano-SiO₂ composites become more imperfect than plain PP. The nanoparticles of SiO₂ have a remarkable heterogeneous nucleation effect on PP matrix.

Nonisothermal crystallization kinetics of PP/nano-SiO₂ composite

The relative degree of crystallization, X_t , is defined as

$$X_t = \int_{T_0}^T (dH_c/dT)dT / \int_{T_0}^{T_\infty} (dH_c/dT)dT \quad (1)$$

where T_0 and $T_{(\text{infinity})}$ are the onset and end of crystallization temperatures, respectively. Figure 2 shows the relative degree of crystallinity X_t as a function of temperature T , for pure PP and PP/nano-SiO₂ composites at various cooling rates. All these curves have the same sigmoidal shape, implying that the lag effect of the cooling rate on crystallization is observed only. Using the equation $t = (T_0 - T)/\phi$ (where T is the temperature at crystallization time t and ϕ is the cooling rate), Figure 2 with the horizontal axis in temperature scale could be converted into Figure 3 with the horizontal axis in time scale. It can be seen from Figure 3 that the faster the cooling rate, the shorter the time for completing the crystallization. The half-time $t_{1/2}$ of nonisothermal crystallization of pure PP and PP/nano-SiO₂ composites can be also obtained from Figure 3; data are listed in Table I. The results showed that the order of $t_{1/2}$ decreases with the increasing cooling rates for both pure PP and PP/nano-SiO₂ com-

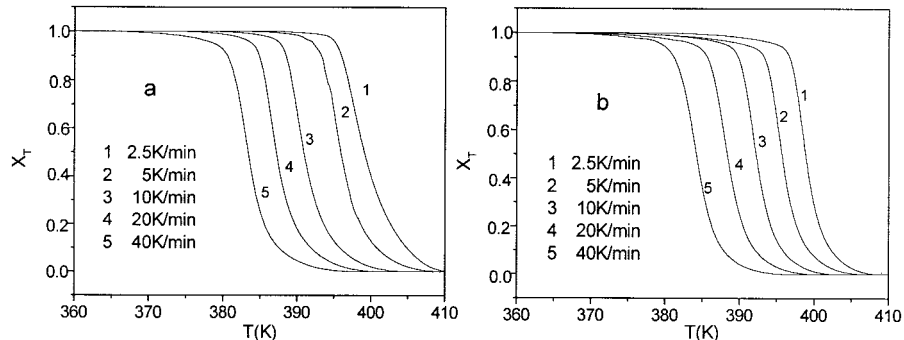


Figure 2 Plots of X_t versus T for crystallization of plain PP (a) and PP/nano-SiO₂ composite with 3% nano-SiO₂ loading (by weight) (b).

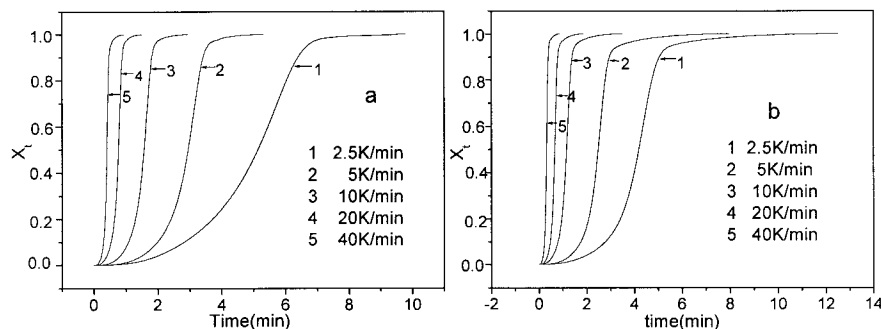


Figure 3 Plots of X_t versus t for crystallization of plain PP (a) and PP/nano-SiO₂ composite with 3% nano-SiO₂ loading (by weight) (b).

posites. However, the $t_{1/2}$ values of PP/nano-SiO₂ composites are lower than that of the original PP at a given cooling rate. The SiO₂ nanoparticles accelerate the crystallization process of pure PP.

Several available methods for describing the crystallization kinetics are based on the Avrami equation^{19,20}

$$1 - X_t = \exp(-Z_t t^n) \quad (2)$$

where the X_t is a relative degree of crystallinity and a function of crystallization temperature T ; n is a mechanism constant depending on the type of nucleation and growth process parameters; and Z_t is a complicated rate constant involving both nucleation and growth rate parameters.

Having assumed that nonisothermal crystallization process is the result of infinite small isothermal crystallization steps, Ozawa²¹ modified the Avrami equation by incorporating a heating/cooling factor. The following equations have been derived

$$1 - X_t = \exp[-K(T)/\phi^m] \quad (3)$$

or its double-logarithmic form

$$\ln[-\ln(1 - X_t)] = \ln K(T) - m \ln \phi \quad (4)$$

where $K(T)$ is the function of cooling rate, and m is the Ozawa exponent depending on the dimension of crystal growth. Doing the experiments at different cooling rates and plotting $\ln[-\ln(1 - X_t)]$ against $\ln \phi$ at a given temperature, a straight line should be obtained if Ozawa method is valid. Thus, the m and $K(T)$ can be obtained from the slope and intercept of the plot, respectively.

The plot of $\ln[-\ln(1 - X_t)] - \ln \phi$ for plain PP and PP/nano-SiO₂ composites is shown in Figure 4, according to Ozawa's eq. 4. A series of almost parallel lines for various temperatures are obtained, indicating that the Ozawa equation is suitable to describe the nonisothermal crystallization behavior of the PP and PP/nano-SiO₂ composites investigated. As reported by Eder and Wlochowicz,²² the Ozawa equation is valid for PP, although it is not valid for PE. The exponent m and parameter $K(T)$ in the Ozawa equation obtained at different temperatures are listed in Table II. It can be seen from Table II that the m value decreases with decreasing temperature for original PP and PP/nano-SiO₂ composites, but the m value of PP/nano-SiO₂ composite is higher than that of original PP at a given cooling rate except for PP/nano-SiO₂ composite with SiO₂ loading of 1% by weight. More specifically, m values are various for PP with or with-

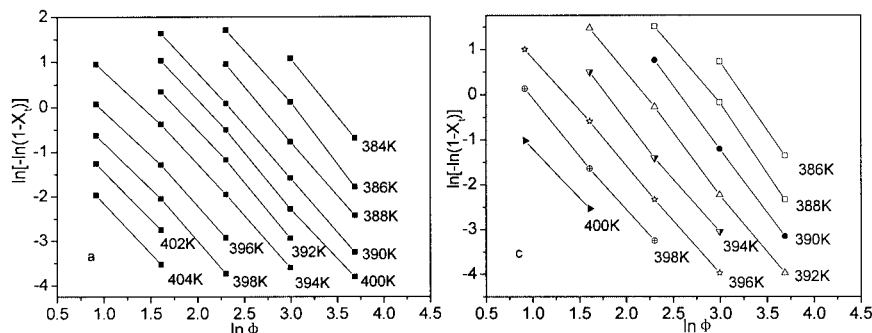


Figure 4 Ozawa Plots of $\ln[-\ln(1 - X_t)]$ versus $\ln \phi$ for crystallization of plain PP (a) and PP/nano-SiO₂ composite with 3% nano-SiO₂ loading (by weight) (b).

TABLE II
Ozawa Exponent m , Parameter K of Nonisothermal Crystallization of PP and PP/nano-SiO₂

Temperature (K)	Original PP		PP/nano-SiO ₂ (1%)		PP/nano-SiO ₂ (3%)		PP/nano-SiO ₂ (5%)	
	m	$K(T)$	m	$K(T)$	m	$K(T)$	m	$K(T)$
384	—	—	2.14	1339	—	—	—	—
386	2.51	1919	1.97	420.	3.00	16984	3.07	36318
388	2.45	735.	2.08	299.	2.77	2864	3.36	54180
390	2.29	190.	1.87	92.8	2.83	1436	4.00	162767
392	2.32	118.	1.83	46.1	2.64	308	3.84	24345
394	2.11	34.8	1.71	18.4	2.56	96.56	3.07	788
396	2.15	18.9	1.71	9.58	2.40	25.06	3.41	590.
398	2.12	8.33	1.60	4.22	2.44	10.4	3.17	95.6
400	2.23	4.39	1.60	2.25	2.18	2.64	3.39	39.3
402	2.00	1.70	1.58	1.12	—	—	3.27	6.82
404	2.24	1.08	—	—	—	—	—	—
Average \bar{m}	2.24	—	1.81	—	2.60	—	3.40	—

out SiO₂ fillers; for example, they range from 2.0 to 2.51 for original PP and from 1.58 to 2.14, 2.18 to 3.00, and 3.07 to 4.00 for PP/nano-SiO₂ composites with SiO₂ loadings of 1, 3, and 5%, respectively. The fact that trend of the m value decreases with a decrease of temperature has been also reported for other polymers by Chiu.^{23,24} This result suggests that the nucleation of polypropylene might be a thermal-to-thermal type during the cooling process. The nucleation is then followed by a three-dimensional to a two-dimensional mixed crystal growth. The $K(T)$ value, on the contrary, decreases with increasing temperature and increases with increasing nano-SiO₂ loading. The definition of $K(T)$ has been detailed by Ozawa²¹ and it is bulk crystallization rate related. The result shows that the crystallization rate increases when the temperature decreases in the supercooling region for both plain PP and PP/nano-SiO₂ composites. The crystallization rate of the PP/nano-SiO₂ composite is higher than that of plain PP. This result is the same as reported by Chiu^{23,24} for origin PP and its blends.

A method proposed by Mo's group^{25,26} is also used to describe the nonisothermal crystallization of the

PP/nano-SiO₂ composite. For the nonisothermal crystallization process, physical variables concerning the process are relative to the degree of crystallization X_t , cooling rate ϕ , and crystallization temperature T . By combining Ozawa and Avrami equations, Mo's group developed the following equations:

$$\ln Z_t + n \ln t = \ln K(T) - m \ln \phi \quad (5)$$

or

$$\ln \phi = \ln F(T) - a \ln t \quad (6)$$

where $F(T) = [K(T)/Z_t]^{1/m}$ and $a = n/m$, the ratio of the Avrami exponent n and Ozawa exponent m . $F(T)$ refers to the value of the cooling rate chosen at unit crystallization time, when the system has a defined degree of crystallinity. According to eq. (6), the plots $\ln \phi$ versus $\ln t$ give a straight line, for a given relative degree of crystallinity, as shown in Figure 5. Thus $\ln F(T)$ and a can be obtained from the intercept and the slope in Figure 5 and the list in Table III. The $F(T)$ systematically increases with increasing of relative de-

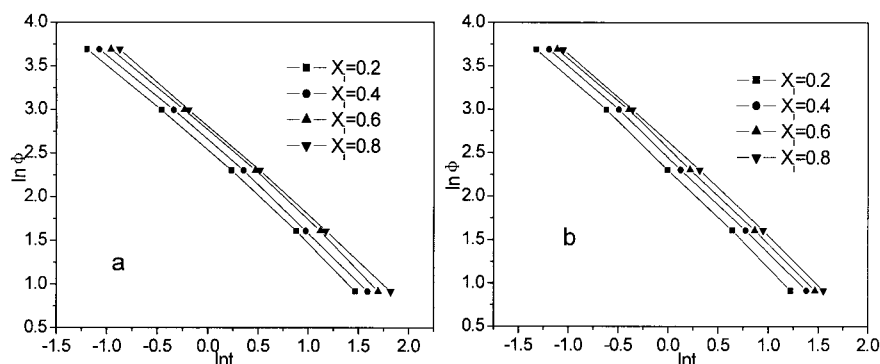


Figure 5 Plots of $\ln \phi$ versus $\ln t$ for crystallization of plain PP (a) and PP/nano-SiO₂ composite with 3% nano-SiO₂ loading (by weight) (b).

TABLE III
Nonisothermal Crystallization Kinetic Parameters
at Different Degrees of Crystallinity

Sample	X_i (%)	$F(T)$	a	ΔE (kJ/mol)
Plain PP	20	12.1	1.04	262.1
	40	13.7	1.04	
	60	15.5	1.04	
	80	16.5	1.03	
PP/nano-SiO ₂ (1%)	20	10.6	1.07	226.5
	40	13.7	1.07	
	60	15.2	1.07	
	80	18.2	1.10	
PP/nano-SiO ₂ (3%)	20	8.85	1.09	249.5
	40	11.4	1.08	
	60	12.6	1.08	
	80	13.5	1.06	
PP/nano-SiO ₂ (5%)	20	7.86	1.04	250.1
	40	9.20	1.06	
	60	10.3	1.10	
	80	11.0	1.10	

gree of crystallinity, and the a values decrease with increasing relative degree of crystallinity. The $F(T)$ value of plain PP is larger than that of PP/nano-SiO₂ composites, and a values of plain PP are lower than that of PP/nano-SiO₂ composites if their relative degrees of crystallinity are same. The a varies from 1.03 to 1.04 and from 1.04 to 1.10 for plain PP and PP/nano-SiO₂ composites, respectively. It is clear that this method is successful in describing the nonisothermal process of plain PP and PP/nano-SiO₂ composites as did PP/MONT composites³ and POM/MONT composites.⁴ The result is the same as Ozawa analysis.

In addition, the approach often used for estimation of activation energy at different cooling rates was proposed by Kissinger,²⁷ based on the following equation:

$$d[\ln(\phi/T_p^2)]/d(1/T_p) = -\Delta E/R \quad (7)$$

where R is the universal gas constant and ΔE is the activation energy for crystallization. Having plotted

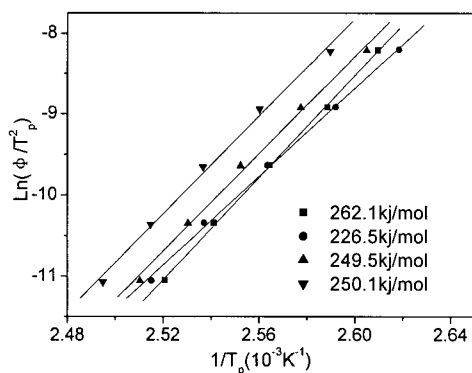


Figure 6 Plots of $\ln(\phi/T_p^2)$ versus $1/T_p$ for plain PP and PP/nano-SiO₂ composites.

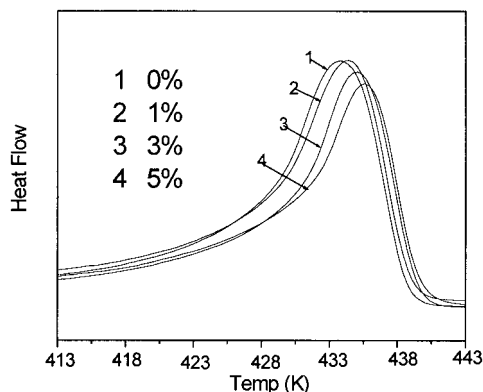


Figure 7 Melt DSC thermograms (20 K/min) of plain PP and PP/nano-SiO₂ composites with 1, 3, and 5% nano-SiO₂ loading (by weight).

$\ln(\phi/T_p^2)$ versus $1/T_p$, a straight line can be obtained. These lines of plain PP and PP/nano-SiO₂ composites with nano-SiO₂ loading of 1, 3, and 5% by weight are shown in Figure 6. Thus, the activation energies ΔE of nonisothermal melt crystallization can be estimated from the slope of the lines, and they are 262.1, 226.5, 249.5, and 250.1 kJ/mol for plain PP and PP/nano-SiO₂ composites with SiO₂ (wt) of 1, 3, and 5%, respectively. The ΔE of nonisothermal melt crystallization of plain PP is higher than that of PP/nano-SiO₂ composites, and the ΔE of nonisothermal cooling crystallization of PP/nano-SiO₂ composites increases with increasing nano-SiO₂ loading on PP resin-matrix. Figure 7 shows the melt DSC thermograms (20 K/min) of the PP/nano-SiO₂ composites with various nano-SiO₂ loading after melt crystallization at the same cooling rate. The peak temperatures increase with increasing of nano-SiO₂ loading, indicating that nano-SiO₂ particles improved the heat resistance of composite.

CONCLUSION

Nonisothermal crystallization of PP/nano-SiO₂ composites shows different rate-dependent characteristics. The Ozawa equation and Mo's treatment were successful for describing the nonisothermal crystallization process of PP/nano-SiO₂ composites. The nano-SiO₂ particles act as effective nucleating agents for PP. The crystallization behavior of PP filled nano-SiO₂ particles exhibits much lower induction period, higher crystallization rate, and smaller half-time $t_{1/2}$ value as compared to neat PP. By using the method proposed by Kissinger, activation energies have been evaluated to be 166.3, 206.2, 251.1, and 266.0 kJ/mol for nonisothermal crystallization of neat PP and PP/nano-SiO₂ composites with the nano-SiO₂ loading of 1, 3, and 5% by weight, respectively. The change of trend of activation energies is same as the change of crystallization enthalpy of neat PP and nano-SiO₂ composites.

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References

1. Ma, J.; Qi, Z.; Hu, Y. *J Appl Polym Sci* 2001, 82, 3611.
2. Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; Okada, A. *Macromolecules* 1997, 30, 6333.
3. Xu, W. B.; Ge, M. L.; He, P. S. *J Appl Polym Sci* 2001, 82 (12), 2281.
4. Xu, W. B.; Ge, M. L.; He, P. S. *J Polym Sci, Part B: Polym Phys* 2002, 40 (5), 408.
5. Stricher, F.; Bruch, M.; Mülhaupt, R. *Polymer* 1997, 38(21), 5347.
6. Wu, W.; Qian, Q.; Pu, W.; Yuan, J. *Chin Plast* 2002, 16 (1), 23.
7. Rong, M.; Zhang, M.; Zheng, Y.; Zeng, H. *Acta Mater Compos Sinica* 2002, 19 (1), 1.
8. Saujanya, C.; Radhakrishnan, S. *Polymer* 2001, 42, 6723.
9. Okada, A.; Kawasumi, M.; Usuki, A.; Kojima, Y.; Kurauchi, T.; Karmigaito, O. *Mater Res Soc Proc* 1990, 171, 45.
10. Ren, X.; Bei, L.; Wang, G.; Zhang, B. *Chin Plastics* 2000, 14 (1), 22.
11. Xiaoang, C.; Wen, D.; Pi, Z. *Polym Mater Sci Eng* 1994, 4, 69 (in Chinese).
12. Liu, X.; Wu, Q. *Polymer* 2001, 42, 10013.
13. Shi, P.; Jin, G.; Wu, H.; Qu, J.; He, H. *Chin Plastics* 2002, 16 (1), 37.
14. Alonso, M.; Velasco, J. I.; de Saja, J. A. *Eur Polym J* 1997, 33 (3), 255.
15. Bogoeva-Gaceva, G.; Janevski, A.; Grozdanov, A. *J Appl Polym Sci* 1998, 67, 395.
16. Mubarak, Y.; Harkin-Jones, E. M. A.; Martin P. J. Ahmad M. *Polymer* 2001, 42, 3171.
17. Supaphol, P. *J Appl Polym Sci* 2000, 78, 338.
18. Yang, J.; Liu, W.; Chen, G.; Liu, J. *Acta Polym Sinica* 2001, 3, 383.
19. Di Lorenzo, M. L.; Silvestre, C. *Prog Polym Sci* 1999, 24, 917.
20. Sajkiewicz, P.; Carpaneto, L.; Wasiak, A. *Polymer* 2001, 42, 5365.
21. Ozawa, T. *Polymer* 1971, 12, 150.
22. Eder, M.; Wlochowicz, A. *Polymer* 1983, 24, 1593.
23. Chiu, F.; Fu, Q.; Shih, H. *J. Polym. Sci, Part B: Polym Phys* 2002, 40, 325.
24. Chiu, F.; Peng, C.; Fu, Q. *Polym Eng Sci* 2000, 40, 2397.
25. Liu, T.; Mo, Z. S.; Wang, S.; Zhang H. *Polym Eng Sci* 1997, 37, 568.
26. An, Y.; Li, L.; Do, L.; Mo, Z.; Feng, Z. *J. Polym Sci, Part B: Polym Phys* 1999, 37, 443.
27. Kissinger, H. E. *J Res Natl Stds* 1956, 57, 217.