

Crystallization Behaviors of Polypropylene/Montmorillonite Nanocomposites

JISHENG MA, SHIMIN ZHANG, ZONGNENG QI, GE LI, YOULIANG HU

State Key Laboratory of Engineering Plastics (SKLEP), Center for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100080, China

Received 18 January 2001; accepted 17 April 2001

ABSTRACT: The isothermal crystallization kinetics of polypropylene/montmorillonite (PP/MMT) nanocomposites synthesized via intercalation polymerization were investigated by using differential scanning calorimeter and polarizing optical microscope (POM). The crystallinity of the nanocomposites decreased with the increase of the montmorillonite content, indicating that the MMT layers dispersed in the PP matrices confined the PP chains and hindered the crystallization of the PP chains. The POM photographs showed that the spherulites of the PP/MMT nanocomposites were greatly decreased in size as MMT was introduced. On the other hand, the crystallization rate increased dramatically with the increasing of MMT content. The interfacial free-energy per unit area perpendicular to PP chains in PP/MMT nanocomposites decreased with increasing MMT content, suggesting that the MMT layers acted as heterogeneous nuclei in the nucleation of crystallization. The nucleus density increased with the increasing of MMT content, leading to a positive effect on the crystallization. © 2002 John Wiley & Sons, Inc. *J Appl Polym Sci* 83: 1978–1985, 2002

Key words: crystallization kinetics; nanocomposites; montmorillonite; polypropylene

INTRODUCTION

The recent interest in polymer/clay nanocomposites stems from the dramatic improvement in their thermal and mechanical properties that can be produced by adding just a small fraction of clay to a polymer matrix.¹ However, the procedure of preparing polymer/clay nanocomposites was successfully applicable to only polar polymers and not to nonpolar ones such as polypropylene (PP).² Because of the industrial importance of PP, a few works on the PP/clay nanocomposite were reported but with not very positive results. Hasegawa et al.³ reported a PP/clay nanocomposite prepared by melt intercalative compounding by

using a functional oligomer as compatibilizer; but introduction of the oligomer showed a negative effect on the properties of the nanocomposites. Oya et al. reported the PP/clay nanocomposites prepared through a complex procedure consisting of three steps,^{4–5} but their mechanical properties were not improved as they expected.⁵ Most recently, we successfully synthesized the PP/clay nanocomposites via intercalation polymerization.⁶ The PP chains grown up on the montmorillonite (MMT) layers by the initiation of Ziegler–Natta catalyst loaded on the MMT and MMT-exfoliated PP/clay nanocomposite were obtained. The storage modulus of the nanocomposites increased by three times that of pure PP at a temperature higher than T_g . The decomposition temperature and HDT all increased greatly.

It is well known that the properties of PP depend significantly on its crystallization behaviors.

Correspondence to: Z. Qi (qizn@mail.icas.ac.cn).

Journal of Applied Polymer Science, Vol. 83, 1978–1985 (2002)
© 2002 John Wiley & Sons, Inc.
DOI 10.1002/app.10127

Therefore, the properties of the PP/clay nanocomposite should also be dependent on its crystallization behaviors. Up to now, only a few studies have been reported on the crystallization behaviors of polymer/clay nanocomposites, such as nylon-6/clay⁷ and PET/clay.⁸ Because PP is a semicrystalline polymer, it is substantially important to study the crystallization behavior of PP/clay nanocomposites. However, no work on crystallization of PP/clay nanocomposites has been found in our literature survey, as only a few works on the nanocomposite itself have been reported.

The investigation on the crystallization kinetics is widely used to characterize the crystalline properties of polymers. The Avrami equation and Hoffman theory have been commonly employed to analyze the isothermal crystallization kinetics of PP. In the present study, we use them to study the isothermal crystallization kinetics of PP/clay nanocomposites. The parameters in Avrami equations and surface free energy (σ_e) are evaluated and, therefore, the amount of crystal nuclei and the mode of crystal growth are determined.

EXPERIMENTAL

Preparation of Pure PP and PP/MMT Nanocomposites

MMT (Tianjing Organo-clay Factory, P.R. China), one of the smectite-type clays, was used to prepare PP/clay nanocomposites. The nanocomposites, PP/MMT1 (MMT content 2.5 wt %), PP/MMT2 (4.6 wt %), and PP/MMT3 (8.1 wt %), were synthesized via intercalation polymerization.⁶ The pure PP was also prepared by using the Ziegler–Natta catalysts in conventional form under the same polymerization condition, as a counterpart reference of the nanocomposites.

Thermal Analysis

The crystallization behaviors of PP/MMT nanocomposites were investigated by means of differential scanning calorimetry (DSC) by using a Perkin–Elmer DSC-7 differential scanning calorimeter with samples weights of 4–6 mg. All operations were carried out under a nitrogen environment. Before the data gathering, the samples were heated to 210°C and held in the molten state for 10 min to eliminate the influence of thermal history. The sample melts were then subsequently quenched at a rate of 80°C/min to reach

a given crystallization temperature. The exothermal flow was recorded at the following selected crystallization temperatures: 125, 126, 127, 128, 129, and 130°C.

Polarized Optical Microscopy (POM)

Polarized optical microscopic photographs were obtained by using a German Leica DMLP microscope. The samples were sandwiched between microscope coverslips, melted at 210°C for 10 min, and then set to the crystallization temperature for complete crystallization.

RESULTS AND DISCUSSION

Effect of Temperature and MMT Content on Crystallization

To analyze the effect of temperature on the crystallization of the PP/MMT nanocomposites, the DSC crystallization isotherms at different crystallization temperatures were obtained. As an example, the crystallization isotherms of PP/MMT3 are graphically presented in Figure 1. As can be seen, the time to reach the maximum crystallization rate increases as the crystallization temperature increases. Figure 2 shows the DSC crystallization isotherm curves of pure PP and PP/MMT nanocomposites at 128°C. The peaks of PP/MMT nanocomposites are all sharper than that of pure PP. That is to say, the presence of the MMT narrowed the width of the crystalline peak (i.e., decreased the crystallization time remarkably of the PP chains). Therefore, it can be concluded that the introduction of the MMT increased the crystallization rate of PP chains.

The presence of MMT layers acts as heterogeneous nuclei of PP crystallization. Because the clay layers are exfoliated, the number of the heterogeneous nuclei in PP/MMT is much larger than that in pure PP. Therefore, the crystallization of PP/MMT proceeds mainly via heterogeneous nucleation, whereas pure PP proceeds via both heterogeneous and homogeneous nucleation mechanisms.^{9–10} Because homogeneous nucleation starts spontaneously by chain aggregation below the melting point, it requires a longer time, whereas heterogeneous nuclei form simultaneously as soon as the sample reaches the crystallization temperature. Thus, the time to reach the maximum crystallization rate in pure PP was longer than that of PP/MMT. The greater the

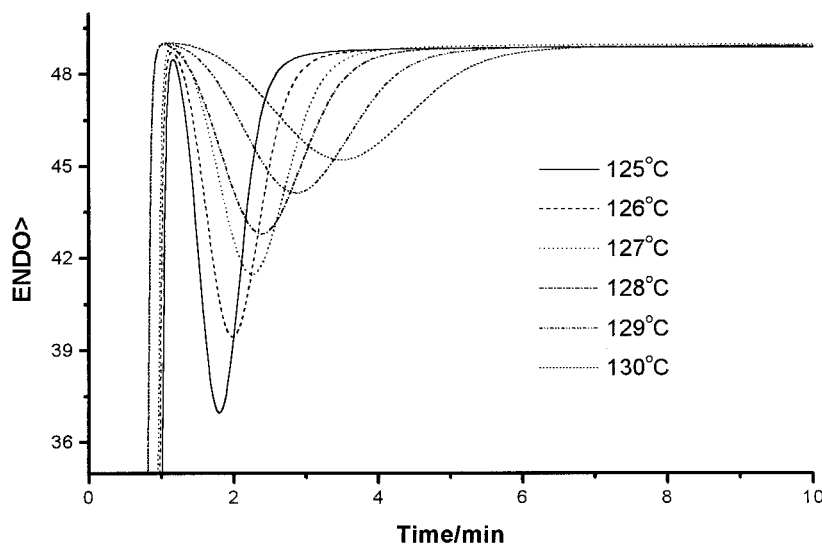


Figure 1 Heat flow versus time during isothermal crystallization of PP/MMT with MMT content of 4.6 wt %.

MMT content, the greater the number of nuclei. Therefore, the time to reach the maximum crystallization rate decreased with increasing MMT content in PP/MMT nanocomposites. The result indicated that the MMT layers dispersed in PP matrices had a dramatically heterophase nucleation effect on the crystallization.

Effect of MMT Content on Equilibrium Melting Temperature and Crystalline Degree

To determine the equilibrium melting temperature (T_m^0) of PP and PP/MMT nanocomposites, the

pure PP and PP/MMT were isothermally crystallized at various temperatures between 123 and 132°C after premelting at 210°C for 10 min. After crystallization at a predetermined temperature (T_c), the samples were reheated to reach the melting state at a rate of 10°C/min so that the melting temperature (T_m) is determined. T_m^0 was obtained using a Hoffman–Weeks plot by plotting T_c versus T_m and observing the intersection of this line with a line having a slope equal to unity ($T_c = T_m$). The result is shown in Table I. It can be seen that the T_m^0 increases with the increase of MMT content, suggesting that the crystalline in

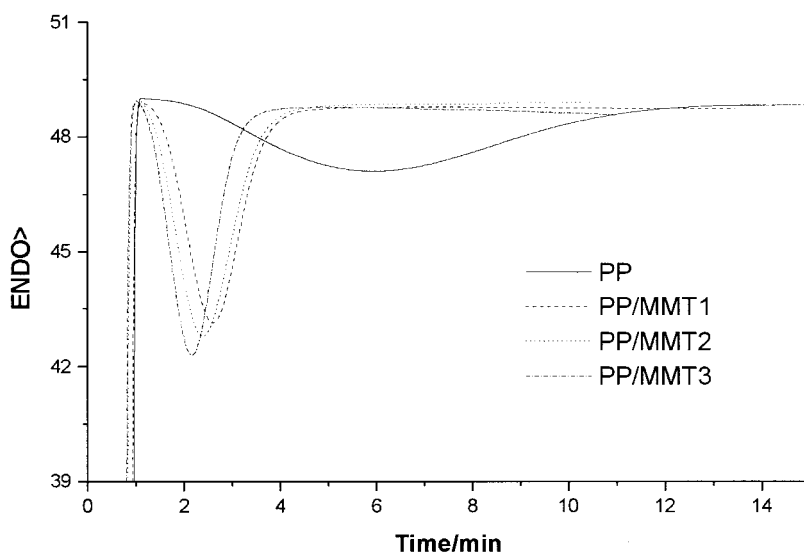


Figure 2 Heat flow versus time during isothermal crystallization ($T_c = 128^\circ\text{C}$) of PP/MMT content at with different MMT contents.

Table I T_m° of Pure PP and PP/MMT Nanocomposites

	PP	PP/MMT1	PP/MMT2	PP/MMT3
T_m° (°C)	208.7	213.4	217.6	220.1

PP/MMT nanocomposites is even more perfect than that of pure PP. This phenomenon must result from the nucleation effect of the MMT in the nanocomposites.

Figure 3 shows the relationship between the crystallization degree and supercooling temperature in the function of MMT content in PP/MMT nanocomposites. It shows that the relative crystallization degree decreases with the increasing MMT content, even though the supercooling temperature increases slightly with the MMT content. Generally, the relative crystallization degree increases with the increasing supercooling temperature. However, in the PP/MMT nanocomposite, the nanoscale clay layers hinder the motion of macromolecular chains of polypropylene. Some PP chains intercalated between the MMT layers might not crystallize so that the crystallization degree decreased with the increasing MMT content in spite of the increase of supercooling temperature. Therefore, the crystallization of the PP/MMT nanocomposites was less temperature dependent than that of pure PP for the dramatic nucleation of MMT layers.

As can be seen in Figure 3, the relative crystallization degree is affected more dramatically by MMT content than the supercooling temperature, suggesting that the nanoscale MMT layers affect the crystallization in two opposite ways. On the one hand, the interaction between the MMT layers and PP chains decreased the number of crystalline PP chains. On the other hand, the nucleation of MMT resulted in more perfect crystallization structure. The nucleation of MMT would increase relative crystallization degree slightly because only a small portion of MMT had an effect on the nucleation,¹¹⁻¹² whereas most MMT layers restricted the motion of the PP chains because the PP chains were grown up on the MMT layers.⁶ The restricted chains might not crystallize. Therefore, the relative crystallization degree decreases with the increasing MMT content in the PP/MMT nanocomposites.

Morphology of the PP Spherulites

Figure 4 shows the POM photographs of the PP/MMT nanocomposites as well as that of the pure PP. The pure PP [Fig. 4(a)] reveals common spherulitic structure with a diameter of the spherulite of 200 μm or more. With the introduction of 4.6 wt % MMT [PP/MMT2, Fig. 4(b)], the dimension of the PP spherulite in the nanocomposite reduces to 60 μm or less, whereas the right-angled intersection is still evident and clear. When the MMT content increases to 8.1 wt %

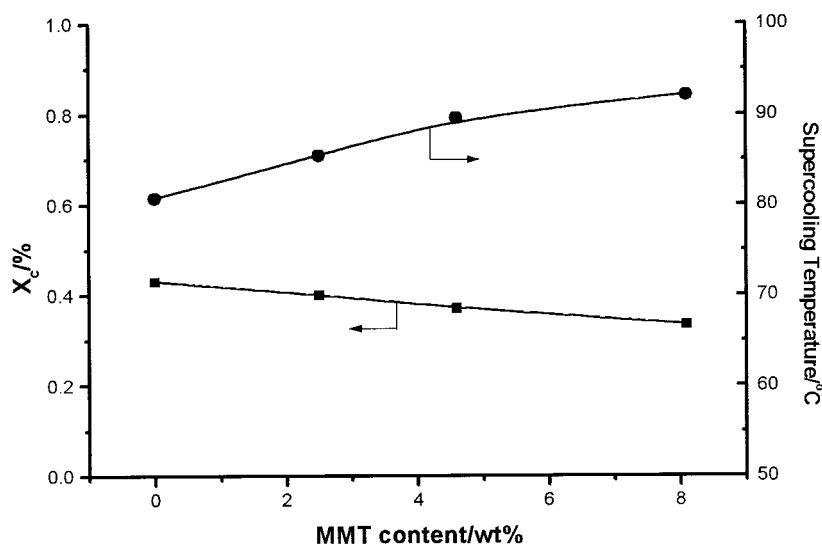


Figure 3 Relationship between crystallization degree, supercooling temperature, and MMT content at $T_c = 128^\circ\text{C}$.

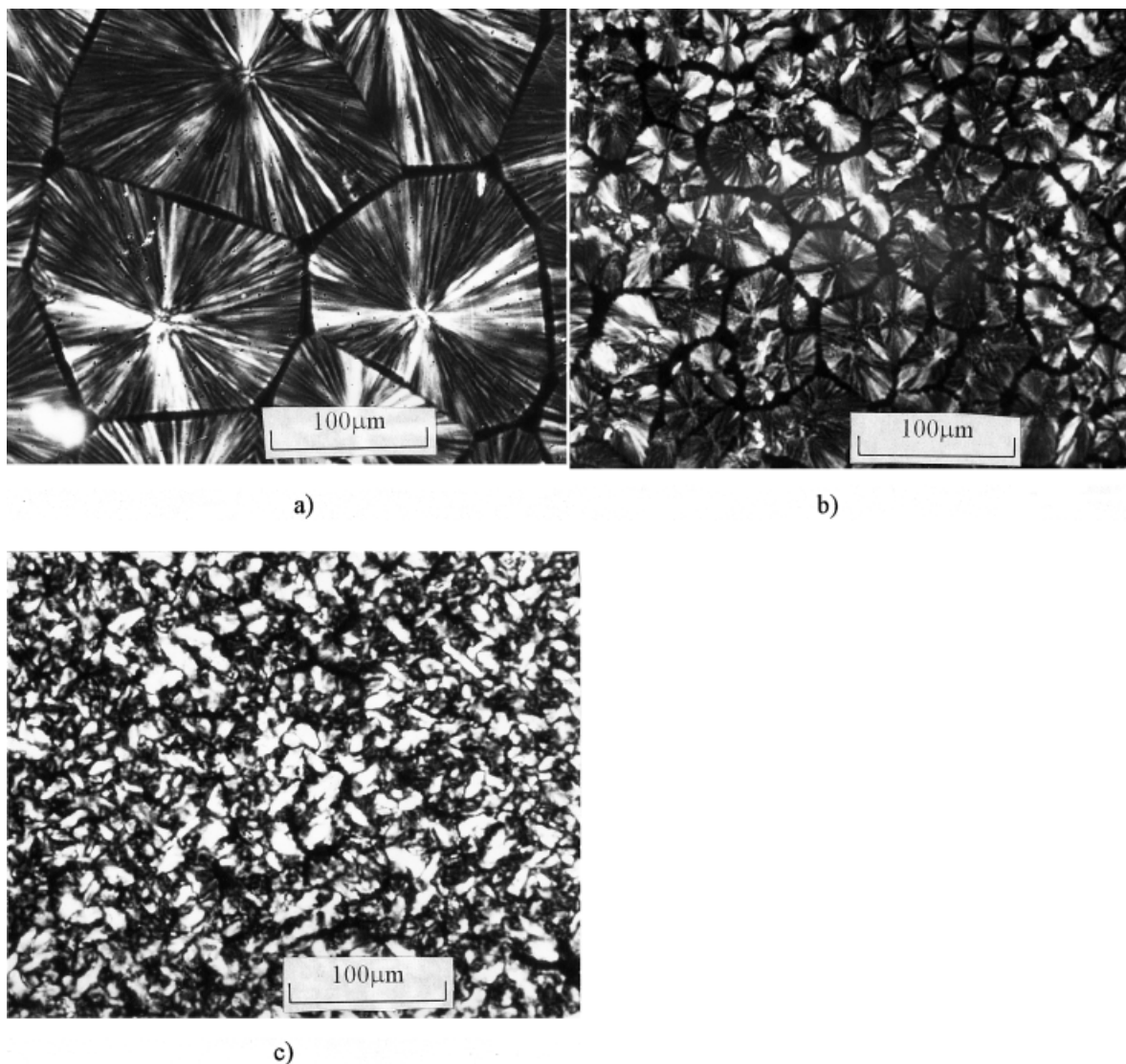


Figure 4 Morphologies of (a) pure PP, (b) PP/MMT2, and (c) PP/MMT3 under a polarizing microscope.

[PP/MMT3, Fig. 4(c)], the shape of the spherulites distorted and the crystalline size decreased much more. It is clear that the introduction of the layered MMT greatly affects the crystallization of PP and the size of the PP spherulites. Because of the colliding and impacting effect of the exfoliated MMT layers, the growth of the PP spherulites is limited. On the other hand, the nucleation of the MMT resulted in a large number of nucleus, causing a large number of spherulites in the limited space. Therefore, the perfect spherulites cannot form when the MMT content is high. In addition, the large number of the nuclei centers will also cause more crystalline defects, leading to a low crystallization degree. This is consistent with the

decrease of the relative crystallinity and the increase of the MMT content.

Isothermal Crystallization Kinetics

The Avrami equation is well known for analyzing the isothermal crystallization of polymers. The relative crystallinity of a polymer at time t , X_t , is given by:

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

where n is the Avrami exponent whose value depends on the mechanism of nucleation and the

form of crystal growth, and k_n is the Avrami rate constant containing the nucleation and the growth parameters.

The Avrami equation describes the overall crystallization behavior of the whole sample, whereas the Hoffman theory¹³ describes the nucleation and growth of single crystals. According to the Hoffman theory, the overall crystallization rate could be expressed by a generalized equation¹⁴

$$\frac{1}{n} \ln k_n + \frac{\Delta F}{RT_c} = A_n - \frac{k_g T_m^0}{T_c \Delta T} \quad (2)$$

where k_n and n are the parameters in the Avrami equation, R is the molar gas constant, T_m^0 is the equilibrium melt point, ΔT is the supercooling temperature ($\Delta T = T_m^0 - T_c$), and ΔF is the activation energy for the transport process at the interface related to the molecule construction and temperature. ΔF can be determined by the Williams-Landel-Ferry Equation for the temperature dependence of polymer:

$$\Delta F_{\text{WLF}} = \frac{C_1 T_c}{C_2 + (T_c - T_g)} \quad (3)$$

where the ordinary parameters are $C_1 = 17.22$ KJ/mol and $C_2 = 51.5$ K. The constant k_g is given by

$$k_g = \frac{4b_0\sigma\sigma_e}{k\Delta H} \quad (4)$$

where b_0 is the thickness of the surface layer, defined by the crystalline lattice parameters. σ and σ_e are interfacial free energies per unit area parallel and perpendicular to the molecular chain direction, respectively. The value of σ can be calculated from an empirical relation given by Hoffman¹³: $\sigma = \beta b_0 \Delta H$, where β is a numerical constant and equal to 0.1 for polymers. k is the Boltzmann constant and ΔH is the heat of fusion per unit volume.

Equation (1) can be reformed as

$$\log[-\ln(1 - X_t)] = n \log t + \log k_n \quad (5)$$

Therefore, the Avrami coefficient n and the crystallization kinetic constant k_n can be determined by plotting $\log[-\ln(1 - X_t)]$ versus $\log t$ and calculating the slope and intersect with the y axis of the straight line. [On the other hand, k_g can be determined graphically from the slope of the plot of $(1/n)\ln k_n + (\Delta F/RT_c)$ versus $(T_m^0/T_c \Delta T)$ based on eq. (2), and therefore, σ_e can be obtained by substituting k_g into eq. (5).]

As an example, the Avrami plots of the nanocomposite PP/MMT2 at various temperatures are graphically illustrated in Figure 5. There is good

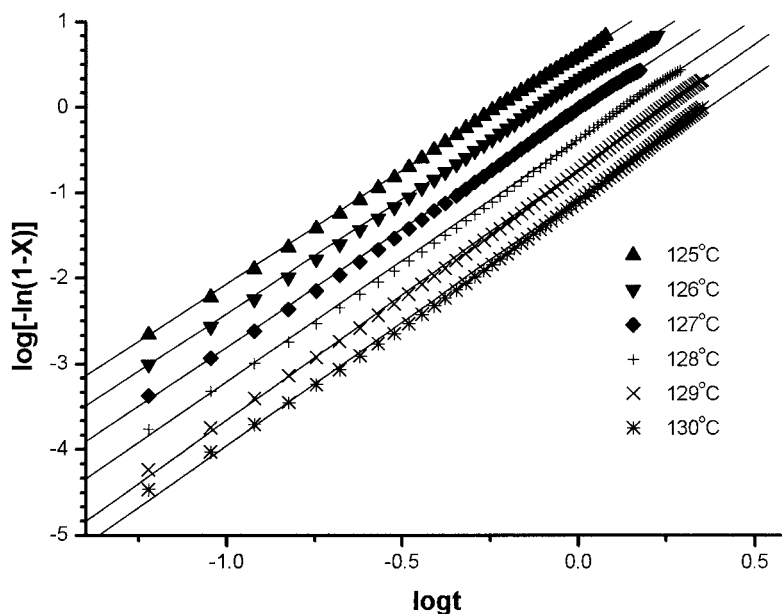


Figure 5 Avrami plots for isothermal crystallization of PP/MMT with the MMT content of 4.6 wt % at various temperatures.

Table II Various Parameters of Pure PP and PP/MMT from Avrami Equation

	T_c (°C)	n	k_n (s ⁻ⁿ)	$t_{1/2}$ (s)	t_{\max} (s)
PP	125	2.37	3.46×10^{-6}	3.42	3.15
	126	2.26	2.21×10^{-6}	4.14	3.75
	127	2.26	8.45×10^{-7}	5.25	4.80
	128	2.30	3.34×10^{-8}	6.42	5.91
	129	2.41	3.30×10^{-8}	8.01	7.26
	130	2.45	7.27×10^{-8}	10.04	9.20
PP/MMT1 (2.5 wt %)	125	2.84	1.82×10^{-5}	1.76	1.74
	126	2.97	5.09×10^{-6}	1.97	1.92
	127	3.09	6.40×10^{-7}	2.25	2.19
	128	3.12	5.47×10^{-7}	2.55	2.49
	129	3.44	4.84×10^{-8}	3.06	3.00
	130	3.23	5.26×10^{-8}	3.75	3.66
PP/MMT2 (4.6 wt %)	125	2.77	2.51×10^{-5}	1.83	1.8
	126	3.14	2.68×10^{-6}	2.04	1.98
	127	3.07	1.56×10^{-6}	2.31	2.25
	128	2.74	3.13×10^{-6}	2.49	2.4
	129	3.05	3.14×10^{-7}	3.00	2.88
	130	2.71	5.07×10^{-7}	3.66	3.51
PP/MMT3 (8.1 wt %)	125	2.67	7.00×10^{-5}	1.54	1.50
	126	2.68	3.14×10^{-5}	1.71	1.68
	127	2.76	1.10×10^{-5}	1.92	1.89
	128	2.83	3.82×10^{-6}	2.22	2.16
	129	2.93	1.13×10^{-6}	2.58	2.52
	130	2.88	6.32×10^{-7}	3.03	2.94

linearity of $\log[-\ln(1 - X_t)]$ versus $\ln t$ in a wide relative crystallinity range (2–90%). Other PP/MMT nanocomposites have similar results. It is clear that the PP/MMT nanocomposites conform well to the Avrami equation. Therefore, we can use the Avrami equation to analyze our experimental data for characterizing crystallization kinetics of PP/MMT nanocomposites.

The Avrami exponent, n , and the rate constant, k_n , are obtained and listed in Table II together with $t_{1/2}$ and t_{\max} . The Avrami exponents of pure PP fall in the range of 2.26–2.45 over the temperature range studied, in coincidence with the literature,^{9–10,15–16} where the authors pointed out that the crystallization of pure PP proceeds with both heterogeneous and homogenous nucleation mechanisms. The Avrami exponents of PP/MMT nanocomposites fall in the range of 2.67–3.44. The result indicates a typical heterogeneous nucleation mechanism in the crystallization kinetics of PP/MMT nanocomposites, confirming the conclusion made above. The crystallization kinetic constant, k_n , of pure PP and PP/MMT decreases with the increasing crystallization temperature, which means a decrease in the nucleation rate constant and in the growth constant in both pure PP and

PP/MMT. The $t_{1/2}$ and t_{\max} of all nanocomposite samples increase with the crystallization temperature at a much slower rate in comparison to the pure PP. The phenomenon is more manifested at high temperature, suggesting that the dependence of the crystallization kinetics on the crystallization temperature is much weaker for PP/MMT nanocomposites. The results maybe also be ascribed to the differences in the crystallization processes for pure PP and PP/MMT nanocomposites. With heterogeneous nucleation mechanism, PP/MMT has more crystallization nuclei than pure PP, so the crystallization kinetic of PP/MMT is less temperature dependent^{10,15} at the nucleus formation stage of crystallization. The pure PP was affected remarkably by the temperature; especially at high temperature, the pure PP requires much more time in $t_{1/2}$ and t_{\max} than PP/MMT.

The effect of MMT content on the crystallization kinetics is also confirmed by the interfacial free (σ_e). Table III shows the values of σ_e of the PP/MMT nanocomposites. It can be seen that σ_e decreases with an increase of MMT content. Note that σ_e is the interfacial free energy of the side surface of the nuclei. The smaller the σ_e , the

Table III The σ_e Values of PP/MMT Nanocomposite from Hoffman Theory

Sample	PP	PP/MMT1	PP/MMT2	PP/MMT3
σ_e (J/m ²)	0.253	0.178	0.170	0.156

smaller is the work required in folding the macromolecule. It might be concluded that the introduction of MMT in the PP matrix dramatically increases the nucleation rate and hence the overall crystallization rate, which is consistent with the trend of crystallization rate characterized by the reciprocal of $t_{1/2}$. As has been discussed above, the exfoliated MMT layers can act as heterogeneous nuclei in the nucleation of crystallization. The increase of the nucleus density has a positive effect on crystallization. Moreover, the energy to form a nucleus of critical size, which is disclosed by σ_e , decreases for various forms of PP/MMT, compared with pure PP.

CONCLUSION

The isothermal crystallization kinetics of PP/MMT nanocomposites has been investigated by using DSC and POM. The nanoscale MMT layers dispersed in the PP matrices confined the PP chains and hindered the crystallization, resulting in the decrease of crystallinity. On the other hand, the MMT layers acted as heterogeneous nuclei in the nucleation of crystallization, causing a dramatic increase of the crystallization rate and decrease of the spherulite size with the increase of MMT content. The perfect spherulites cannot form for colliding and compacting of a large number of small spherulites in a limited space. The

nucleus density increased with the increase of MMT content, leading to a positive effect on the crystallization, which is in good agreement with the result that the interfacial free energy per unit area perpendicular to PP chains in PP/MMT nanocomposites decreased with increasing MMT content.

REFERENCES

- Ginzburg, V. V.; Singh, C.; Balazs, A. C. *Macromolecules* 2000, 33, 1089.
- Kawasumi, M.; Hasegawa, N.; Kato, M.; Usuki, A.; Okada, A. *Macromolecules* 1997, 30, 6333.
- Hasegawa, N.; Kawasumi, M.; Kato, M.; Usuki, A.; Okada, A. *J Appl Polym Sci* 1998, 67, 87.
- Kurokawa, Y.; Yasuda, H.; Kashiwagi, M.; Oya, A. *J Mater Sci Lett* 1997, 16, 1670–1672.
- Oya, A.; Kurokawa, Y.; Yasuda, H. *J Mater Sci* 2000, 35, 1045–1050.
- Ma, J.-S.; Qi, Z.; Hu, Y. *J Appl Polym Sci* to appear.
- Liu, L.; Qi, Z.; Zhu, X. *J Appl Polym Sci* 1999, 71, 1113–1138.
- Ou, Y.; Si, M.; Yu, Z. *J Appl Polym Sci* 1999, 73, 767–775.
- Yu, J.; He, J. *Polymer* 2000, 41, 891–898.
- Seo, Y.; Kim, J.; Kim, K. U.; Kim, Y. C. *Polymer* 2000, 41, 2639–2646.
- Jiang, S.; Ji, X.; An L.; Jiang, B.; *Acta Polym Sinica* 2000, 4, 452–456.
- Cheng, Y.; Xu, M. *Acta Polym Sinica* 1998, 6671–678.
- Di Lorenzo, M. L.; Silvestre, C. *Prog Polym Sci* 1999, 24, 917–950.
- Grenier, D.; Prud'homme, R. E. *J Polym Sci, Polym Phys Ed* 1980, 18, 1655–1657.
- Godovsky, Y. K.; Slonimsky, G. I. *J Polym Sci, Polym Phys Ed* 1974, 12, 1053–1080.
- Menczel, J.; Varga, J. *J Therm Anal* 1983, 28, 161–172.