Nonisothermal Crystallization and Melting Behavior of β-Nucleated Isotactic Polypropylene and Polyamide 66 Blends

Zhugen Yang,^{1,2} Kancheng Mai¹

¹Materials Science Institute, School of Chemistry and Chemical Engineering, Sun Yat-Sen University, Key Laboratory of Polymeric Composites and Functional Materials of the Ministry of Education, Guangzhou 510275, China Institut des Nanotechnologies de Lyon, UMR 5270 CNRS, Ecole Centrale de Lyon, Equipe Chimie et Nanobiotechnologies, 36 Avenue Guy-de-Collongue, 69134 Ecully, France

Received 7 March 2010; accepted 5 July 2010 DOI 10.1002/app.33040 Published online 30 September 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: A highly novel nano-CaCO₃ supported βnucleating agent was employed to prepare β-nucleated isotactic polypropylene (iPP) blend with polyamide (PA) 66, β -nucleated iPP/PA66 blend, as well as its compatibilized version with maleic anhydride grafted PP (PP-g-MA), maleic anhydride grafted polyethylene-octene (POE-g-MA), and polyethylene-vinyl acetate (EVA-g-MA), respectively. Nonisothermal crystallization behavior and melting characteristics of β-nucleated iPP and its blends were investigated by differential scanning calorimeter and wide angle X-ray diffraction. Experimental results indicated that the crystallization temperature (T_c^p) of PP shifts to high temperature in the non-nucleated PP/PA66 blends because of the α-nucleating effect of PA66. T_c^p of PP and the β-crystal

INTRODUCTION

Isotactic polypropylene (iPP) is one of the most versatile commodity thermoplastic polymers for its exceptional properties such as excellent chemical and moisture resistance, good ductility, and low manufacturing cost. iPP is a crystalline polymer with three known possible crystal forms, namely, monoclinic (α-crystal), trigonal (β -crystal), and triclinic (γ -crystal).^{1–3} Compared to traditional α -iPP, β -iPP has some exceptional advantageous properties including higher thermal deformation temperature, improved elongation at break and impact strength, which are very important from the viewpoint of industrial application.^{1–7} On the other hand, it is not easy to prepare β -iPP due to its lower stability and high content of β -crystal can only be obtained under special crystallization conditions such

content (K_{β}) in β -nucleated iPP/PA66 blends not only depended on the PA66 content, but also on the compatibilizer type. Addition of PP-g-MA and POE-g-MA into βnucleated iPP/PA66 blends increased the β -crystal content; however, EVA-g-MA is not benefit for the formation of β crystal in the compatibilized β -nucleated iPP/PA66 blend. It can be relative to the different interfacial interactions between PP and compatibilizers. The nonisothermal crystallization kinetics of PP in the blends was evaluated by Mo's method. © 2010 Wiley Periodicals, Inc. J Appl Polym Sci 119: 3566-3573, 2011

Key words: polypropylene; polyamide 66; β-crystal; compatibilizer; crystallization and melting behavior

as the introduction of a β -nucleating agent,^{8–13} a temperature gradient,^{14,15} and shearing or elongation of the melt.^{16–19} In addition, the yield strength and elastic modulus of β -iPP are lower than those of α -iPP. To improve the properties of β -iPP, it would be a good method to prepare β -iPP blends with other polymers and more attentions have been focused on it.

Varga²⁰ and Shi²¹ have observed that it is not difficult to prepare β-iPP blends if compounded with amorphous, for example, elastomer. However, if compounded β -iPP with crystalline polymer, the β -crystal content depends on crystallization temperature (T_c^p) of the second component and its *a*-nucleation effect on iPP. The latter is also one of important factors for the formation of a blend with β -iPP.^{22–25} If T_c^p of the second component with *a*-nucleating effect is lower than that of iPP, it has little effect on the formation of β -crystal. On the contrary, if T_c^p of the second component with *a*-nucleating effect is higher than that of iPP, it is very difficult to form β -crystal. For example, in the β -nucleated iPP/poly(vinylidene-fluoride) (PVDF) and iPP/polyamide 6 (PA6) blends, the β crystal can not be formed even in the presence of a highly effective β -nucleating agent. In our recent work,^{25–27} we have adopted a good

method to prepare β -nucleated iPP/PA6 blends with

Correspondence to: K. Mai (cesmkc@mail.sysu.edu.cn).

Contract grant sponsors: China Scholarship Council, Doctoral Fund of Ministry of Education of China, Natural Science Foundation of China; contract grant number: 50873115.

Journal of Applied Polymer Science, Vol. 119, 3566-3573 (2011) © 2010 Wiley Periodicals, Inc.

high β -crystal content. For β -nucleated iPP/PA6 blends, the β -crystal content decreases with increasing PA6 content, but addition of maleic anhydride grafted PP (PP-g-MA) as a compatibilizer can improve the distribution of β -nucleating agent in iPP phase to form a matrix rich in β -crystal. In addition, we have proved the hypothesis that the nucleating agents mainly disperse in the PA6 phase and/or the interface between iPP and PA6 in the process of mixing at high temperature by etching the blends with sulfuric acid. It was supported by the fact that the β -crystal content almost keeps constant in β nucleated iPP, but decreases obviously in βnucleated iPP/PA6 blends after etched with sulfuric acid.^{25,26} However, it is not clear how the β -nucleating agent disperses in β-nucleated iPP/PA66 blends or whether PA66 suppresses the formation of β -crystal or not. Further more, it shall be great meaningful to observe the effects of different lengths of group $-CH_2$ in PA on the crystallization and melting behavior of its blends. As a consequence, the main goal of this study was to find out the effect of PA66 on the crystallization and melting behavior of the β nucleated iPP/PA66 blends. The properties of PA66 are similar with those of PA6 and there are also many reports on iPP/PA66 blends, but to our knowledge this is the first time that such iPP/PA66 blends containing high-content β-crystal have been reported. Additionally, we also prepared the β nucleated iPP/PA66 blends modified with different kinds of compatibilizer and tried to find out the influence of interfacial interaction between various phases on dispersion of the nucleating agent in iPP or PA phase, which will mainly decide the crystallization behavior and the β -crystal content of the blends.

EXPERIMENTAL

Materials

Isotactic polypropylene (iPP, HP500N) was homopolymer grade, supplied by CNOOC and Shell Petrochemicals Co. (HuiZhou, China) [melt flow rate $(MFR) = 12 \text{ g}/10 \text{ min } (230^{\circ}\text{C}, 2.16 \text{ kg})].$ Polyamide 66 (PA66, 8231GHS) was supplied by BASF Chemical Company [Germany, MFR = 250 g/10 min (230°C, 2.16 kg)]. PP-g-MA, EVA-g-MA, and POE-g-MA were commercial products, supplied by Guangzhou Lushan Chemical Materials Co. (Guangzhou, China), and the grafted contents of malice anhydride (MA) is 1.0 wt %. A commercial grade of active nano-CaCO₃ (Enping, Guangdong, China) with the particle diameter between 40 and 60 nm was obtained from Guangping Chemical Industry Limited Co. (China); it had been pretreated with fatty acid in its production process. Aliphatic dicarboxylic acid with purity of 98% was purchased

from Shanghai Hongsheng Industry Co. (Shanghai, China).

Specimen preparation

All the materials were adequately dried in a vacuum oven at appropriate temperatures for 12 h before blending. The nano-CaCO₃ supported β -nucleating agent was prepared from aliphatic dicarboxylic acid supported on surface of nano-CaCO₃ (1/50 wt/wt) in our laboratory.¹¹ For preparing β -nucleated iPP, 5 wt % nano-CaCO₃ supported β -nucleating agents were added to PP phase on a Berstoff ZE25A corotating twin-screw extruder (L/D = 40, D = 35.5 mm) (Nangjin, Jiangsu, China) at 200°C with the screw rotation of 480 rpm and residue time of 40 s. Extrudates were cooled in a water bath and cut into pellets by a pelletizer.

The non- and β -nucleated iPP/PA66 blends were prepared using an internal mixer (Karlsruhe, Germany) (Rheocord 300p, Haake, Germany) at 270°C and 50 rpm, mixed for 8 min. In the binary blends, the amount of PA66 was 10, 20, and 30 wt %. With the same conditions, 5phr PP-*g*-MA, POE-*g*-MA, and EVA-*g*-MA were added into β -nucleated iPP/PA66 (80/20 wt/wt) blend, respectively, to prepare the compatibilized β -nucleated iPP/PA66 blends. All the blends composed of various compositions were shown in Table I.

Differential scanning calorimeter

Differential scanning calorimeter (DSC) measurements were made on a TA DSC Q10 DSC, the temperature calibrated with indium in nitrogen atmosphere. A specimen of about 5 mg sample was weighted very accurately. It was heated to 290°C with 40°C/min, held there for 5 min, and then cooled to 100°C with cooling rate of 10°C/min. This controlled cooling temperature prevents β - α transformation so that the polymorphic composition of the sample can be determined accurately for the melting curves.^{23,25,28} At last, the sample was reheated to 290°C (220°C for iPP) at a heating rate of 10°C/min for a study of melting characteristics.

Wide angle X-ray diffraction

The wide angle X-ray diffraction (WAXD) patterns of the samples were recorded at room temperature using a Rigaku D/Max 2200 unit equipped with Nifiltered Cu Ka radiation in the reflection mode with a wavelength of 0.154 nm. For direct comparison, the specimens were prepared on TA DSC Q10 thermal system under the following condition: they are heated to 290°C with 40°C/min, held there for 5 min, and then cooled to 40°C with cooling rate of

DSC Data of IPP and PA66 Component in IPP/PA66 Blends"												
Samples	$T_{\rm c}^{\rm p}$ (°C)		$-\Delta H_{\rm c}({\rm J/g})$		T^p_m (°C)		$\Delta H_{\rm m}({\rm J/g})$					
	iPP	PA66	iPP	PA66	β-iPP	α-iPP	PA66	β-iPP	K_{β} (%)	α-iPP	PA66	
iPP/PA66	100/0	112.6	_	101.7	_	_	160.2	_	_	103.1	_	_
	90/10	116.2	233.3	98.1	17.5	-	156.8	260.6	-	102.9	63.2	_
	80/20	118.7	236.3	99.9	51.5	_	158.5	261.4	-	102.8	64.5	_
	70/30	119.1	236.9	101.6	63.0	_	159.7	261.6	-	106.6	73.7	_
	0/100	_	230.9	-	69.6	_	-	262.0	-	_	74.5	_
β-iPP/PA66	100/0	124.3	_	87.4	_	150.7	163.1	-	82.4	2.7	_	97
	90/10	123.4	234.7	85.9	24.0	148.7	161.3	260.7	81.0	3.1	43.8	95
	80/20	123.1	235.5	96.0	45.0	148.7	161.4	261.4	79.6	6.1	48.7	88
	70/30	121.8	236.7	89.8	42.6	147.6	160.1	261.3	78.9	8.9	53.3	86
5phr compatibilizer	PP-g-MA	124.5	234.8	98.2	28.9	149.1	161.5	260.9	89.9	3.9	58.8	94
	POE-g-MA	118.6	235.0	90.3	27.6	146.0	152.7	259.4	86.9	4.3	44.6	92
	EVA-g-MA	118.7	235.6	92.9	24.6	146.4	159.7	260.8	82.4	11.8	40.4	85

TABLE I DSC Data of iPP and PA66 Component in iPP/PA66 Blends

^a The enthalpy has been corrected by weight fraction, the compatibilized blends: iPP/PA66 80/20.

 T_c^p , temperature of crystallization peak; \tilde{T}_m^p , temperature of melting peak; ΔH_c , enthalpy of crystallization; ΔH_m , enthalpy of fusion; K_β , the percentage of β -phase calculated according to XRD.

 10° C/min. The operation conditions of the X-ray source were a voltage of 40 kV and a current of 30 mA in the 2 θ range of 5–35° with a step scanning rate of 4°/min.

The relative β -crystal content (K_{β}) for all the blends was calculated according to the equation suggested by Turner-Jones et al.²⁹:

$$K_{\beta} = \frac{I_{\beta 1}}{I_{\beta 1} + I_{\alpha 1} + I_{\alpha 2} + I_{\alpha 3}}$$
(1)

where $I_{\beta 1}$ is the diffraction intensity of β (300) plane, $I_{\alpha 1}$ is the diffraction intensity of α (110) plane, $I_{\alpha 2}$ is the diffraction intensity of α (040) plane, and $I_{\alpha 3}$ is the diffraction intensity of α (130) plane.

RESULTS AND DISCUSSION

Effect of PA66 content on non-nucleated iPP/PA66 blends

Figure 1 illustrates the crystallization and melting curves of non-nucleated iPP/PA66 blends with various PA66 contents, and the relative data are listed in Table I. The results present that the crystallization peaks appearing in the vicinity of 120°C and 235°C are attributed to the crystallization of iPP and PA66 [Fig. 1(a)], respectively. With increasing the PA66 content, the intensity of the crystallization peak of iPP became weaker; in addition, the peak of PA66 appeared and its intensity became stronger. It can be observed from Figure 1(b) that a tiny melting peak of β-crystal at round 150°C appears in neat iPP. However, in the non-nucleated iPP/ PA66 blends, the only melting peak of α -crystal at about 160°C was observed instead of that of β-crystal. Double melting peaks at about 260°C are





Figure 1 (a) Crystallization and (b) melting curves of non-nucleated iPP/PA66 blends with various PA66 contents.

attributed to the melting of PA66 in non-nucleated PP/PA66 blends.

As is shown in Table I, the crystallization temperature (T_c^p) of iPP in the blends is 112.6°C. Addition of 10 wt % PA66 increases the T_c^p of iPP from 112.6°C to 116.2°C. What's more, T_c^p of iPP increased with increasing the PA66 content. It suggested that PA66 had α -nucleating effect on iPP crystallization, which promoted formation of a matrix rich in α crystal.^{22,23,25} It can also be observed from Figure 1 that T_c^p of PA66 shifts to high temperature in the presence of iPP, which indicated that the PA66 crystallizes more easily in the presence of molten iPP.

Effect of PA66 content on the β -nucleated PP/PA66 blends

The crystallization and melting curves of β -nucleated iPP/PA66 blends are presented in Figure 2 and the relative data are listed in Table I. The results show that the crystallization behavior of iPP in β nucleated iPP/PA66 blends is quite different from that in non-nucleated iPP/PA66 blends. First, $T_c^{\rm P}$ of β -nucleated iPP (124.3°C) is much higher than that of non-nucleated PP (112.6°C). Addition of PA66 decreases T_c^p of iPP in the β -nucleated iPP, but is benefit for increasing T_c^p of iPP in the non-nucleated iPP. Second, with increasing the PA66 content, $T_c^{\rm P}$ of iPP decreases for β -nucleated iPP/PA66 blends, but it increases for non-nucleated iPP/PA66. It can be suggested that the competition between α - and β nucleating effects on iPP also exists in β-nucleated iPP/PA66 blends, which is induced by PA66 and β nucleating agent, respectively. In the preparation process of blends, the β -nucleating agent in iPP might move to PA66 phase and/or the interface between iPP and PA66 due to the interaction between the polar groups of β -nucleating agent and the polar groups of PA66. This interaction decreased the concentration of β -nucleating agent in iPP matrix and resulted in the decrease in the nucleation effect of β -nucleating agent and T_c^p of iPP. On the other hand, T_c^p of PA66 shifts from 230.9°C of neat PA66 to 236.9°C in the $\beta\text{-nucleated}$ iPP/PA66 blend containing 30 wt % PA66. It is also indicated that the PA66 crystallizes more easily in the presence of molten iPP, which is similar with non-nucleated iPP/ PA66 blends.²⁵

Figure 2(b) presents that the melting characteristics of iPP much depend on the PA66 content. The intensity of melting peak for β -crystal is very strong and higher than that of α -crystal. The single melting peak of β -crystal changes into double melting peaks and the intensity of the higher-temperature melting peak became much stronger with increasing PA66 content. The β -crystal content (K_{β}) in each blend is very high, more than 85% (Table I), which is indi-



Figure 2 (a) Crystallization and (b) melting curves of β -nucleated iPP/PA66 blends with various PA66 contents.

cated that addition of PA66 has no distinct influence on the β -crystal content in the blends. These results are quite different from β -nucleated iPP/PA6 blends. According to our previous reports on β -nucleated iPP/PA6 blends,²⁵ the β -crystal content gradually decreased with increasing PA6 content, which can be relative to that of the α -nucleating effect of PA6 and the polar interactions between the nucleating agent and PA6 increase with increasing PA6 content. However, for β -nucleated iPP/PA66 blends, the polarity of PA66 is much weaker than that of PA6 due to PA66 containing more -CH2- groups. Therefore, both the α -nucleating effect of PA66 and the polar interactions between groups of the nucleating agent and that of PA66 are not that strong, which makes PA66 a little influence on the formation of high-content β -crystal in the blends.

Figure 3 shows the WAXD spectra of nonnucleated iPP, β -nucleated iPP, and β -nucleated iPP/PA66 blends with various contents of PA66. It



Figure 3 X-ray diffraction of non-nucleated iPP, β -nucleated iPP, and β -nucleated iPP/PA66 blends with various PA66 contents.

can be observed that the iPP exhibited α -crystallization form appeared at $2\theta = 14.3^{\circ}$, 16.8° , and 18.6° , corresponding to the plane (110), (040), and (130) of α -crystal. The reflection at $2\theta = 16.1^{\circ}$ was corresponding to the plane (300) of the β -crystal.^{17,18} The only diffraction peak of α -crystal and β -crystal were observed in the non-nucleated iPP and β -nucleated iPP, respectively. However, the intensity of the diffraction peak of β -crystal decreased a little with increasing the PA66 content in the β -nucleated iPP / PA66 blends. Even for the blend containing 30 wt % PA66, the diffraction peak of the plane (300) of β crystal is still much strong than that of α -crystal, which indicates that a matrix of β -crystal was predominantly formed. It can be suggested that PA66 has a little effect on the formation of β -crystal in β nucleated iPP/PA66 blends. Table I also illustrates that the K_{β} slightly decreased with increasing PA66 content.

Effect of compatibilizers

The crystallization and melting curves of compatibilized β -nucleated iPP/PA66 (80/20) blends are presented in Figure 4 and the relative data are listed in Table I. As is shown that addition of compatibilizer has an obvious effect on the crystallization behavior of iPP and PA 66. The PA66 crystallization peak in its blends compatibilized with EVA-g-MA and POEg-MA becomes much weak, and that are even almost absent in the blend compatibilized with PP-g-MA. It is relative to that addition of MA-grafted compatibilizers increased the homogeneity of PA66 phase dispersion in the iPP matrix with a reduction in the size of the domains due to the compatibilization of compatibilizers. And the PP-*g*-PA66 copolymer is formed at the interface, which made the crystallizability of PA66 reduced.³⁰ Besides, addition of compatibilizer also has significant effects on the crystallization behavior of iPP. It can be seen from Table I and Figure 4(a) that T_c^p of iPP in blends compatibilized with EVA-*g*-MA and POE-*g*-MA shifted to the low temperature. However, addition of PP-*g*-MA slightly increased T_c^p of iPP in the compatibilized blend.

As is shown in Figure 4(b) and Table I, the melting characteristics and the β -crystal content (K_{β}) in the compatibilized β -nucleated iPP/PA66 blends are dependent of the kinds of compatibilizer. Both PP-*g*-MA and POE-*g*-MA are benefit for the formation of β crystal and the K_{β} increased for the compatibilized β -nucleated iPP/PA66 blend. However, addition of EVA-*g*-MA decreased the β -crystal content in the compatibilized β -nucleated iPP/PA66 blend, which



Figure 4 (a) Crystallization and (b) melting curves of iPP/PA66 80/20 blends with various kinds of compatibilizers (5phr).

may be relative to the effect of compatibilization. For example, the K_{β} in the blend compatibilized with PP-g-MA increased from 88 to 94%, on the contrary, addition of EVA-g-MA reduced the β -crystal content (K_{β}) to 85%. In addition, the WAXD spectra of the blends (Fig. 5) also show that the peaks at $2\theta =$ 16.1°, with respect to the (300) plane of β -crystal, are all very intensive, indicating that iPP crystallized predominantly in the β form. However, the peak respect to the plane of β -crystal appears a little intensive in β-nucleated iPP/PA66 blend compatibilized with EVA-g-MA, which indicated EVA-g-MA as a compatibilizer is not benefit for increasing the K_{β} value. What's more, double melting peaks of β crystal were observed in β-nucleated iPP/PA66 blends compatibilized with POE-g-MA and EVA-g-MA. This effect is typically associated with melting followed by recrystallization into more stable crystals and remelting of the recrystallized material at higher temperature, which has been discussed in detail in another report.³¹

As our previous reports on the β -nucleated iPP/ PA6 blends,^{25,26} there is also a competition between α - and β -nucleating effect on iPP crystallization in compatibilized β -nucleated iPP/PA66 blends, which is induced by PA66 and β-nucleating agent, respectively. However, for the β -nucleated iPP/PA66 blends modified with MA-grafted compatibilizers (PP-g-MA, POE-g-MA, and EVA-g-MA), the β -nucleating agent plays a more significant role, which can be suggested from the formation of a matrix rich in β-crystal. Addition of MA-grafted compatibilizers decreases the interaction between the β -nucleating agent and PA66 to suppress the distribution of β nucleating agent into PA66 phase, but facilitates the dispersion of the β -nucleating agent into iPP and/or interface between iPP and PA66 phase.22,23,25 In addition, it can also increase the homogeneity of PA66 phase dispersion in the PP matrix with a reduction in the size of the domains and facilitates the formation of PP-g-PA copolymer at the interface, which also made the crystallinity of PA reduced.^{32,33} All of above factors are benefit for obtaining high K_{β} in the blend. In β -nucleated iPP/PA66 blends modified with different compatibilizers, the interfacial interaction between compatibilizer and PA66 are the same due to the same polar groups (maleic anhydride) in compatibilizers. For each compatibilized blend, it is obvious that the interfacial interactions between compatibilizers and iPP are different, which depends on compatibility between iPP and the long hydrocarbon chain in compatibilizer through physical entanglements and van der Waals interactions. Therefore, the compatibility between compatibilizer and iPP would have a great effect on the crystallization and melting behavior of β -nucleated iPP/PA66 blend.



Figure 5 X-ray diffraction of iPP/PA66 80/20 blends with various kinds of compatibilizers (5phr).

For the β-nucleated iPP/PA66 blend compatibilized with PP-g-MA, iPP and PP chain in PP-g-MA are completely miscible due to the same molecular chain. The good miscibility and interfacial interaction between PP-g-MA and PA66 facilitates the dispersion of β -nucleating agent into iPP phase and/or interface between iPP and PA66, which increases the T_c^p of iPP and the K_β for the blend. For the β nucleated iPP/PA66 blends compatibilized with POE-g-MA or EVA-g-MA, both iPP with POE in POE-g-MA and iPP with EVA in EVA-g-MA are partial miscible or even immiscible. The partial miscible or even immiscible interface between iPP and POE or EVA is not benefit for the crystallization of iPP. Therefore, the T_c^p of iPP in the blend compatibilized with both POE-g-MA and EVA-g-MA is lower than that of uncompatibilized blend, respectively. For the partial miscibility in the β -nucleated iPP/PA66 blend compatibilized with POE-g-MA, the β -nucleating agent can also play a great role of formation β -crystal to increase the K_{β} value. However, for the β nucleated iPP/PA66 blend compatibilized with EVA-g-MA, the immiscible interface between iPP and EVA retards the distribution of the β -nucleating agent into iPP phase. What's more, the strong polarity of EVA may also interact with the β -nucleating agent to suppress the formation of β -crystal and reduce the value of K_{β} .

Nonisothermal crystallization kinetics analysis

The most commonly used isothermal crystallization kinetic equation is the well-known Avrami equation.³⁴ The application of this model to nonisothermal conditions was solved by Ozawa and Mo.^{35,36} There are several other approximations that deal with nonisothermal crystallization kinetics. A review



Figure 6 Plots of log *R* versus log *t* for β -nucleated iPP (a) and iPP in β -nucleated iPP/PA66 80/20 blend uncompatibilized (b) and compatibilized with PP-*g*-MA (5phr) (c). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

article of Di Lorenzo and Silvestre³⁷ discussed the most important nonisothermal crystallization kinetic models. The double logarithmic form of Avrami

equation is³⁴:

$$\log[-\ln(1 - X(T))] = \log Z_t + n \log t$$
 (2)

where X(T) is the relative crystallinity at the crystallization time t; Z_t , and n are crystallization kinetic constant and Avrami exponent, respectively, and both are related to the rate and mechanism of crystallization.

Ozawa derived an equation which double logarithmic form is³⁶:

$$\log[-\ln(1 - X(T))] = \log K(T) - m \log R$$
(3)

where *R* is the cooling rate, K(T) is a function related to the overall crystallization rate; *m* is the Ozawa index, which is somewhat similar to the Avrami exponent and depends on the type of nucleation and growth dimensions.

Mo and coworkers³⁵ proposed a different equation by combining the Avrami and Ozawa equations, giving rise to the relationship between cooling rate R and crystallization time t at a given relative crystallinity:

$$\log Z_t + n \log t = \log K(T) - m \log R \tag{4}$$

$$\log R = \log F(T) - \alpha \log t \tag{5}$$

where the kinetic parameter, $F(T) = [K(T)/Z_t]^{1/m}$. F(T) has a definite physical and practical meaning, the smaller the value of F(T) is, the higher the crystallization rate becomes. The Mo exponent α is the ratio of the Avrami exponent *n* to the Ozawa exponent *m*, that is, $\alpha = n/m$.

After fitting our experimental results to Ozawa equation and Mo's method, we found only Mo's method can satisfactorily describe the nonisothermal crystallization behavior of the researched blends. At a given relative crystallinity, plots of log *R* against log *t* of β -nucleated iPP, iPP in β -nucleated iPP/PA66 blend, and β -nucleated iPP/PA66 blend compatibilized with PP-*g*-MA are given in Figure 6. Obviously, the plots are straight lines, implying agreement of the experimental results with Mo's theoretical prediction. The values of *F*(*T*) and α can be obtained from the slopes and intercepts of the

TABLE II On-Isothermal Crystallization Kinetic Parameters of β-Nucleated iPP/PA66 Blends

X (t) (%)		10	30	50	70	90
β-Nucleated PP	F(t)	2.79	3.95	4.78	5.72	7.81
-	α	1.24	1.26	1.29	1.34	1.44
β-Nucleated PP/	F(t)	3.02	4.14	4.94	5.84	7.84
PA66 80/20	α	1.17	1.20	1.24	1.28	1.36
β-Nucleated PP/PA66/	F(t)	2.65	3.89	4.76	5.69	7.70
PP-g-MA 80/20/5	α	1.34	1.35	1.37	1.40	1.46

straight lines, respectively, tabulated in Table II. For each specimen, F(T) increased systematically with increasing the relative degree of crystallinity and the values of α increased slightly. However, at the same X(T), the values of F(T) for these specimen ranked as: β -nucleated iPP/PA66 > β -nucleated iPP > β nucleated iPP/PA66/PP-g-MA, which means that to reach the same X(T), the crystallization time needed of β -nucleated iPP/PA66 is the longest, indicating that PA66 was not benefit for the formation of β -crystal. It is interesting that the crystallization time of iPP in β -nucleated iPP/PA66 blend compatibilized with PP-g-MA is shorter than that of neat β -nucleated iPP. It is attributed that PP-g-MA facilitates the dispersion of the β -nucleating agent into iPP phase to accelerate iPP crystallization. These results were in agreement with the crystallization behavior and polymorphic composition discussed above.

CONCLUSIONS

On the basis of our results, addition of PA66 into non-nucleated iPP shifts the crystallization temperature (T_c^p) of iPP to high temperature due to the α nucleating effect of PA66, on the contrary, it decreases the T_c^p of iPP in the β -nucleated iPP/PA66 blends. The β -crystal content (K_{β}) in β -nucleated iPP/PA66 blends depends on both PA66 content and the type of compatibilizers. The K_{β} decreased with increasing PA66 content, but the effect is slight due to the weak polarity of PA66. PP-g-MA and POE-g-MA increase the K_{β} for the blend, which can be attributed to that both of them not only improve the dispersion of PA66 into the iPP phase, resulting in decrease in the crystalline ability and α -nucleating ability of PA66, but also facilitate the dispersion of the β -nucleating agent into the iPP phase and/or the interface between iPP and PA66 to play a significant role of β-nucleation on iPP. However, EVA-g-MA decreases K_{β} for the blend due to its strong polarity and EVA immiscible with iPP. The nonisothermal crystallization process of β -nucleated iPP, iPP in β nucleated iPP/PA66 blend, and PP-g-MA compatibilized β-nucleated iPP/PA66 blend can be successfully described by Mo's method.

References

- 1. Zhang, R. H.; Shi, D.; Tjong, S. C.; Li, R. K. Y. J Polym Sci Part B: Polym Phys 2007, 45, 2674.
- 2. Grein, C. Adv Polym Sci 2005, 188, 43.
- 3. Raab, M.; Scudla, J.; Kolarik, J. Eur Polym Mater 2004, 40, 1317.

- Kotek, J.; Raab, M.; Baldrian, J.; Grellmann, W. J Appl Polym Sci 2002, 85, 1174.
- 5. Grein, C.; Plummer, C. J. G.; Kausch, H. H.; Germain, Y.; Beguelin, P. Polymer 2002, 43, 3279.
- Chen, H. B.; Karger-Kocsis, J.; Wu, J. S.; Varga, J. Polymer 2002, 43, 6505.
- Raab, M.; Kotek, J.; Baldrian, J.; Grellmann, W. J Appl Polym Sci 1998, 69, 2255.
- Chvatalova, L.; Navratilova, J.; Cermak, R.; Raab, M.; Obadal, M. Macromolecules 2009, 42, 7413.
- Bai, H. W.; Wang, Y.; Zhang, Z. J.; Han, L.; Li, Y. L.; Liu, L.; Zhou, Z. W.; Men, Y. F. Macromolecules 2009, 42, 6647.
- Zhang, Z. S.; Wang, C. G.; Yang, Z. G.; Chen, C. Y.; Mai, K. C. Polymer 2008, 49, 5137.
- 11. Zhang, Z. S.; Tao, Y. J.; Yang, Z. G.; Mai, K. C. Eur Polym Mater 2008, 44, 1955.
- Yi, Q. F.; Wen, X. F.; Dong, J. Y.; Han, C. C. Polymer 2008, 49, 5053.
- Mohmeyer, N.; Schmidt, H.-W.; Kristiansen, P. M.; Altstaedt, V. Macromolecules 2006, 39, 5760.
- Meille, S. V.; Ferro, D. R.; Bruckner, S.; Lovinger, A. J.; Padden, F. J. Macromolecules 1994, 27, 2615.
- 15. Lovinger, A. J. J Polym Sci Part B: Polym Phys 1983, 21, 97.
- 16. Moitzi, J.; Skalicky, P. Polymer 1993, 34, 3168.
- Somani, R. H.; Hsiao, B. S.; Nogales, A.; Srinivas, S.; Tsou, A. H.; Sics, I.; Balta-Calleja, F. J.; Ezquerra, T. A. Macromolecules 2000, 33, 9385.
- Somani, R. H.; Hsiao, B. S.; Nogales, A.; Fruitwala, H.; Srinivas, S.; Tsou, A. H. Macromolecules 2001, 34, 5902.
- Huo, H.; Jiang, S. C.; An, L. J.; Feng, J. C. Macromolecules 2004, 37, 2478.
- 20. Varga, J. J Therm Anal 1989, 35, 1891.
- Shi, G. Y. Recent Studies on β-Crystalline Form of Isotactic Polypropylene; Springer Verlag: Berlin, 1994.
- 22. Menyhárd, A.; Varga, J.; Liber, A.; Belina, G. Eur Polym Mater 2005, 41, 669.
- 23. Menyhárd, A.; Varga, J. Eur Polym Mater 2006, 42, 3257.
- Tao, Y. J.; Pan, Y. X.; Zhang, Z. S.; Mai, K. C. Eur Polym Mater 2008, 44, 1165.
- 25. Yang, Z. G.; Zhang, Z. S.; Tao, Y. J.; Mai, K. C. Eur Polym Mater 2008, 44, 3754.
- Yang, Z. G.; Chen, C. Y.; Liang, D. W.; Zhang, Z. S.; Mai, K. C. Polym Int 2009, 58, 1366.
- Yang, Z. G.; Zhang, Z. S.; Tao, Y. J.; Mai, K. C. J Appl Polym Sci 2009, 112, 1.
- 28. Varga, J. J Macromol Sci Phys 2002, 41, 1121.
- 29. Turner-Jones, A.; Aizlewood, J. M.; Beckett, D. R. Makromol Chem 1964, 75, 134.
- Sacchi, L.; Bighardi, E.; Corona, S.; Beninati, T.; Lo, N.; Franceschi, A. Tissue Cell 2004, 36, 43.
- Yang, Z. G.; Mai, K. C. Thermochim. Acta (2010), doi:10.1016/ j.tca.2010.08.007.
- 32. Ohlsson, B.; Hassander, H.; Tornell, B. Polymer 1998, 39, 6705.
- Roeder, J.; Oliveira, R. V. B.; Goncalves, M. C.; Soldi, V.; Pires, A. T. N. Polym Test 2002, 21, 815.
- 34. Avrami, M. J Chem Phys 1940, 8, 212.
- Liu, T. X.; Mo, Z. S.; Wang, S. G.; Zhang, H. F. Polym Eng Sci 1997, 37, 568.
- 36. Ozawa, T. Polymer 1971, 12, 150.
- 37. Di Lorenzo, M. L.; Silvestre, C. Prog Polym Sci 1999, 24, 917.