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Nonisothermal crystallization kinetics of isotactic polypropylene nucleated with a novel supported β-nucleating agent

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Abstract The introduction of β-nucleating agent into isotactic polypropylene (iPP) is the most effective method to prepare β-iPP. In this paper, iPP nucleated with a novel highly efficient supported β-nucleating agent (NA100), calcium pimelate (CaHA) supported on the surface of nano-$CaCO_3$, was prepared and its nonisothermal crystallization kinetic, melting characteristic, and crystallization activation energy are investigated and compared with those of pure iPP, nano-$CaCO_3$ filled iPP, and β-nucleating agent CaHA nucleated iPP. The results indicate that addition of nano-$CaCO_3$ increases the crystallization temperature of iPP and has no influence on the crystal form of iPP. iPP and nano-$CaCO_3$ filled iPP mainly crystallize in the form of α-crystal. Although NA100 and CaHA induce iPP to mainly form β-crystal, NA100 nucleated iPP shows higher crystallization temperature, melting temperature, and β-phase content than that nucleated with CaHA without supports. Nonisothermal crystallization kinetic is well described by the equations of Avrami and Mo, and the crystallization activation energy was calculated from Kissinger's method. It was found that the decreased crystallization activation energy is favorable to increase the crystallization rate and the content of β-crystal. Although the content of CaHA in 5 wt% NA100 nucleated iPP was less than that in 0.1 wt% CaHA nucleated iPP, the former formed more β-iPP than the latter, indicating that the β-nucleating agent CaHA supported on the surface of nano-$CaCO_3$ exhibits higher efficiency for preparation of β-iPP than pure CaHA powder.

Keywords Polypropylene · β-Nucleating agent · Nonisothermal crystallization kinetic · Melting characteristic · Crystallization activation energy

Introduction

In order to improve the physical and mechanical properties of isotactic polypropylene (iPP), α- and β-nucleating agents are generally used for iPP crystallization. It is found that the addition of α-nucleating agent increases the crystallization rate, shortens the half-crystallization time, reduces the spherulite size and improves the toughness, strength and transparency of iPP and so on [1–7].

Recently, β-nucleated polypropylene (β-iPP) has attracted a great number of interests [8–33] due to its excellent thermal and mechanical performance, especially super toughness [34, 35] and high heat distortion temperature, which are very important from the viewpoint of industrial application. Until now, the introduction of β-nucleating agents into iPP is most effective to obtain a high level of the β-crystal of iPP. Four classes of compounds have been used as β-nucleating agents for preparation of β-iPP. The first class is a minority of aromatic ring compounds, for example γ-quinacridone (Dye Permanent Red E3B) [10]. The second class is a certain group IIA metal salts or their mixtures with some specific dicarboxylic acids [11–13], for example, calcium pimelate (CaHA) or suberate. The third class is a minority of aromatic amide compounds, for example N,N'-dicyclohexyl terephthalamide [14, 15]. And the last one is rare earth

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β-nucleating agents [16]. However, the novel highly efficient supported β-nucleating agent has little been reported.

Because the physical and mechanical properties of β-nucleated iPP depend on the crystallization behavior, the crystallization behavior and melting characteristics of β-nucleated iPP have been widely investigated. Varga et al. [17, 18] compared the nucleating efficiency and selectivity of different β-nucleating agents and found that a calcium suberate and pimelic acid (HA) possess higher β-nucleating selectivity and efficiency than commercial nucleator NJ Star (NJS). They indicated that calcium suberate or CaHA is a thermally stable β-nucleating agent with high efficiency and selectivity. Dou [19] studied the influence of the composition ratio of pimelic acid/calcium stearate bicomponent nucleator on the β-crystal content of iPP. It was found that the β-crystal content increased continuously with increasing amount of calcium stearate at a constant amount of pimelic acid. It was shown that pimelic acid and calcium stearate could react to produce a high effective β-nucleator (CaHA) "in situ" during the melt-mixing of iPP and the bicomponent nucleator.

Xiao et al. [24] investigated the influence of a novel rare earth-containing (WBG) β-nucleating agent on the structure, morphology, and nonisothermal crystallization behavior of iPP. An analysis of the nonisothermal crystallization kinetics revealed that the introduction of WBG significantly shortened both the apparent incubation period for crystallization and the overall crystallization time. Zhao et al. [25] found a highly active novel β-nucleating agent cadmium bicycle [1, 2] hept-5-ene-2,3-dicarboxylate (BCHE30) and investigated its effects on the mechanical properties, the content of β-crystal, and crystallization behavior of iPP. The results show that the impact strength and crystallization peak temperature of nucleated iPP are greatly increased, while the spherulite size of nucleated iPP are dramatically decreased compared to that of pure iPP. The crystallization active energy (ΔE) was achieved by Kissinger method. The ΔE of pure iPP and nucleated iPP during nonisothermal crystallization were determined to be 283 and 300 kJ mol^{-1}, respectively. Yi et al. [26] introduced a kind of β-nucleating agent, namely a stearic acid and stearate lanthanum complex (NAb) into iPP via an in situ polymerization method for the first time. The crystallization peak temperature of β-nucleated iPP was greatly increased while the spherulite size dramatically decreased compared to those of iPPs. The nonisothermal crystallization kinetics of β-nucleated iPP was studied with Mo equation and crystallization activation energy estimated by Kissinger method. The ΔE of iPPs with the contents of β-iPP of 0, 8.5 77.8, and 91.2% during nonisothermal crystallization are determined to be 260, 256, 172, and 164 kJ mol^{-1}, respectively. Xiao et al. [24, 27] investigated the effect of two kinds of β-nucleating agents, named a rare earth complex (WBG) and a N,N'-dicyclohexyl terephthalamide (TMB5) on crystallization and melting behavior of iPP and indicated that WBG had more pronounced effect than TMB5 in increasing the overall crystallization rate. WBG was more effective not only in increasing the nucleus number but also in accelerating the growth rate of crystallization. Bai et al. [28, 29] compared the nonisothermal crystallization and subsequent melting behaviors of iPP nucleated with α- and β-nucleating agents, and their compounds, which indicated that the nonisothermal crystallization behaviors and crystalline structures of iPP are dependent on the composition of nucleating agents. It is found that the nucleating ability of α-nucleating agent was higher than that of β-nucleating agent for iPP crystallization.

Although β-iPP possesses excellent thermal and mechanical performances, the yield stress and stiffness of β-iPP are lower than those of non-nucleated or α-iPP. In order to increase the nucleation efficiency β-nucleating agent and improve the mechanical properties of β-nucleated iPP, the preparation of a novel highly efficient β-nucleating agent is an interesting subject.

It is well known that the CaHA is a highly efficient β-nucleating agent for preparation of β-iPP. In order to increase the β-nucleating ability and decrease the cost of CaHA, we prepared a novel highly efficient β-nucleating agent, CaHA supported on the surface of nano-$CaCO_3$ in our laboratory based on the preparation principles of high efficiency supported catalyst of ethylene and propylene polymerization. The nano-$CaCO_3$ with large surface area used as support may not only increase the efficiency of β-nucleating agent but also expect to increase the yield stress and stiffness of β-nucleated iPP due to the reinforcing and toughening effect of nano-$CaCO_3$. Our research showed that the CaHA supported on the surface of nano-$CaCO_3$ exhibited higher β-nucleating ability than that of CaHA [30, 31]. It should be noted that there are no literature data about supported β-nucleating agent—apart from ours. In order to explore the β-nucleating ability of CaHA supported on nano-$CaCO_3$, the nonisothermal crystallization kinetic, melting characteristic, and crystallization activation energy of iPPs were compared with those of iPP nucleated with CaHA β-nucleating agent and with CaHA β-nucleating agent supported on nano-$CaCO_3$ in this paper.

Experimental

Materials

The N-T30S grade iPP homopolymer (MFR = 2.5 g 10 min^{-1} at 200 °C) used in the study was supplied by Sinopec Group, Maoming petroleum Chemical Industry

Limited Company, China. Nano-$CaCO_3$ (CC) used as support with the particle diameter between 40 and 60 nm was obtained from Guangping Chemical Industry Limited Company, China. Calcium pimelate (CaHA) supported on CC (NA100 means that the weight ratio of pimelic acid to CC was 1/100) and CaHA β-nucleating agents were prepared in our laboratory [32, 33].

Specimen preparation

All materials were dried in an oven at 60 °C for 12 h. The pure iPP, iPP with β-nucleating agent, or CC were homogenized at 180–190 °C for 8 min, and 50 rpm using an internal mixer SLJ-40 made by Jinlin University science instrument factory, China.

Characterization of PP/$CaCO_3$ samples

The crystallization behaviors and melting characteristics of pure iPP, CC filled iPP, and β-nucleated iPP were evaluated on a Perkin–Elmer differential scanning calorimetry DSC-7 under a nitrogen atmosphere. About 5 mg of sample was weighted accurately. The samples were heated from ambient temperature to 220 °C at a heating rate of 100 °C min^{-1} and the temperature was held at 220 °C for 5 min to eliminate the thermal and mechanical history before it was cooled down to ambient temperature for nonisothermal crystallization at a different cooling rate. Finally, the samples were heated to 220 °C at heating rate of 10 °C min^{-1}. The second endothermic and exothermic flows were recorded as a function of temperature. The temperature and the enthalpy have been calibrated with indium at different rate in our experiments.

Results and discussion

Crystallization behaviors

DSC analysis was performed to investigate and compare the nonisothermal crystallization behavior of iPP, iPP filled with CC, and iPPs nucleated with CaHA and NA100 β-nucleating agent with variable cooling rate. Figure 1a shows the crystallization curves of iPP in all samples crystallized nonisothermally at cooling rate of 10 °C min^{-1}. The crystallization peak temperatures (T_{cp}) of iPP are plotted in Fig. 1b as a function of cooling rate (Φ). It can be observed that the T_{cp} increases with decreasing the cooling rate. The addition of CC slightly increases the T_{cp} of iPP. It is attributed to the heterogeneous nucleation of CC in iPP crystallization process. The T_{cp} of iPP nucleated with NA100 and CaHA is higher than that of iPP filled with CC. The T_{cp} of iPP nucleated with NA100 is higher than that of iPP nucleated with CaHA. The result indicates that the heterogeneous nucleation of NA100 is more advanced than that of CaHA for iPP crystallization. Although the T_{cp} of iPP depends on the cooling rate, the effect of cooling rate on the T_{cp} of iPP nucleated with NA100 is less than that of iPP nucleated with CaHA, especially for samples crystallized at high cooling rate. It means that the dependence of the T_{cp} of iPP on cooling rate for iPP nucleated with NA100 is less than that for iPP nucleated with CaHA.

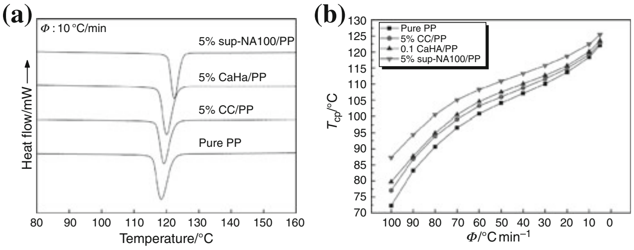

Fig. 1 The DSC **a** crystallization curves and **b** the plots of T_{cp} as a function of Φ of samples

Melting characteristics

The melting behavior of β-iPP is unique, which manifested in the melting memory effect detailed discussed in the literature [36–38]. According to the phenomenon of melting memory effect of β-iPP, the melting behavior depends strongly on the post-crystallization thermal history of samples. There is a critical temperature (TR = 100–105 °C) which controls the $\beta \rightarrow \alpha$ transition recrystallization of β-iPP taking place or not. While the crystallization temperature cooled below the critical temperature, the $\beta \rightarrow \alpha$ transition recrystallization of β-iPP would take place, and it is difficult to understand the endothermic melting process of β-iPP.

However, in order to study the crystallization structure of β-nucleated PP prepared at the industrial production conditions, the samples were cooled to room temperature in the present study. And DSC is used to characterize the different crystals of iPP due to different melting behavior of α-and β-crystals. Figure 2 shows the melting curves of iPP, iPP filled with CC, and iPPs nucleated with NA100 and CaHA after crystallized under different cooling rate. It can be seen that the shapes of melting peaks of iPP filled with CC are similar to those of pure iPP. The melting peak around 165 °C can be attributed to the melting of α-crystal. iPP and iPP filled with CC mainly crystallize in the form of α-crystal. Although the addition of CC increases the crystallization temperature of iPP due to the heterogeneous nucleation of CC, CC does not have the β-crystal nucleating ability.

However, the melting characteristics of iPP nucleated with NA100 and CaHA are different from those of pure iPP and iPP filled with CC. The melting behavior of iPP nucleated with NA100 is also different from that of iPP nucleated with CaHA. It is well known that the CaHA is a highly efficient β-nucleating agent for iPP crystallization. It can be seen from Fig. 2c that there are four melting peaks for iPP nucleated with CaHA. It is generally suggested that the two low-temperature melting peaks belong to the β-crystals. The lower-temperature melting peak is caused by the melting of β_1-crystal and the higher-temperature melting peak is attributed to melting of β_1–β_2 recrystallization. It can be seen that the melting temperature and intensity of β_1-crystal increase but the intensity of β_2-crystal decreases with decreasing the cooling rate. One melting peak of β-crystal is obtained at the cooling rates below 10 °C min^{-1}. The melting peak of β_1-crystal is always present and considered to reflect the melting of the more or less disordered β-iPP. The second one has been attributed to the melting either of the melt-recrystallized β_1-crystal into a more stable β_2-crystal during scanning [39, 40] or of a perfected and thickened existing lamellae without any changes in geometry and order of the crystals [41]. The latter two high-temperature melting peaks belong to the α-phases. The first lower-temperature melting peak belongs to the melting of the less stable α-crystal with disorder-limiting structure (α_1-crystal). The higher-temperature melting peak is attributed to melting of β-α recrystallization with order-limiting structure (α_2-crystal) [26, 42]. The melting peaks of α_1- and α_2-crystal also shift to high temperature with decreasing the cooling rate. The intensity of melting peak of α_1-crystal increases and the intensity of melting peak of α_2-crystal decreases with decreasing the cooling rate. When the cooling rate is below 5 °C min^{-1}, three distinct melting peaks are observed, the lower-temperature melting peak belonging to the β-crystal and the two high-temperature melting peaks to the α-crystal.

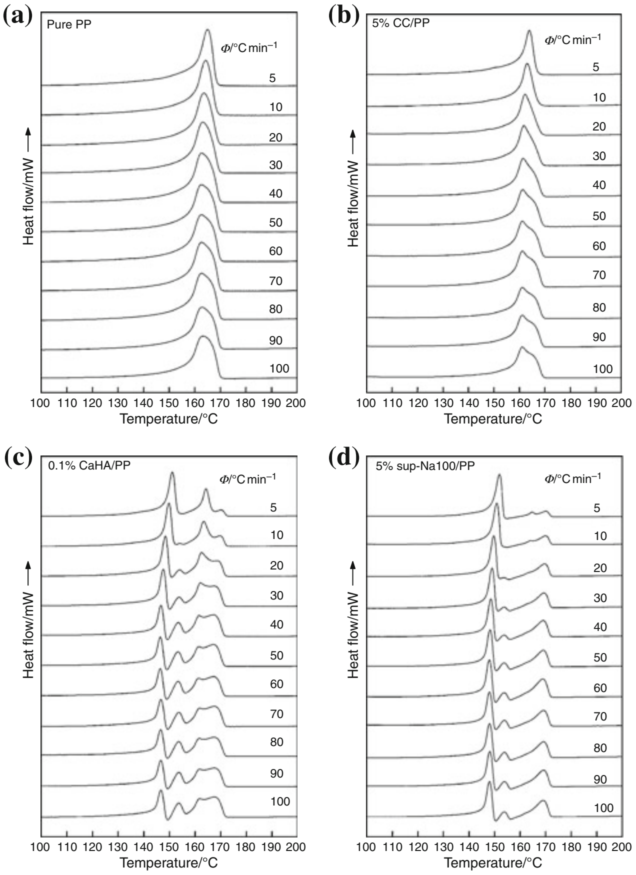

Fig. 2 The DSC melting curves of the samples crystallized with different cooling rates

It is obviously seen from Fig. 2c, d that the melting behavior of iPP nucleated with NA100 is different from that of iPP nucleated with CaHA. There are three melting peaks for iPP nucleated with NA100 at high cooling rates. The two low-temperature melting peaks are attributed to melting of β_1- and β_2-crystal and one high-temperature melting peak is attributed to melting of α_2-crystal. No melting peak of α_1-crystal is observed, indicating that iPP nucleated with NA100 mainly formed β-crystal. The result also indicated that the CaHA β-nucleating agent supported on CC possesses higher β-nucleating ability than CaHA.

Nonisothermal crystallization kinetic

The relative crystallinity, X_t, is defined as

$$X_t = \int_{T_0}^{T} (\mathrm{d}H_\mathrm{c}/\mathrm{d}T)\mathrm{d}T \Bigg/ \int_{T_0}^{T_\infty} (\mathrm{d}H_\mathrm{c}/\mathrm{d}T)\mathrm{d}T \tag{1}$$

where T_0 and T_∞ are the onset and end temperatures of crystallization, respectively, and H_c is the enthalpy of crystallization. Using the following equation, $t = (T_0 - T)/\Phi$ (where T is the temperature at crystallization time t, and Φ is the cooling rate), the abscissa of temperature could be transformed into a timescale. Figure 3 shows the relative crystallinity, X_t, as a function of crystallization temperature T, or crystallization time t for iPP and nucleated iPP at various cooling rates. The higher the cooling rate, the shorter the crystallization time span. The half time of nonisothermal crystallization, $t_{1/2}$, was estimated from Fig. 3 for iPP and β-nucleated iPP, the results are listed in Table 1.

The Avrami equation [43–45] is widely used to describe the polymer isothermal crystallization.

$$1 - X_t = \exp[-Z_t/t^n] \tag{2}$$

where the X_t is the relative crystallinity at the crystallization time t. The n is Avrami exponent. The Z_t is the rate constant for crystallization. The double logarithm of the Eq. 2 gives the following relationships:

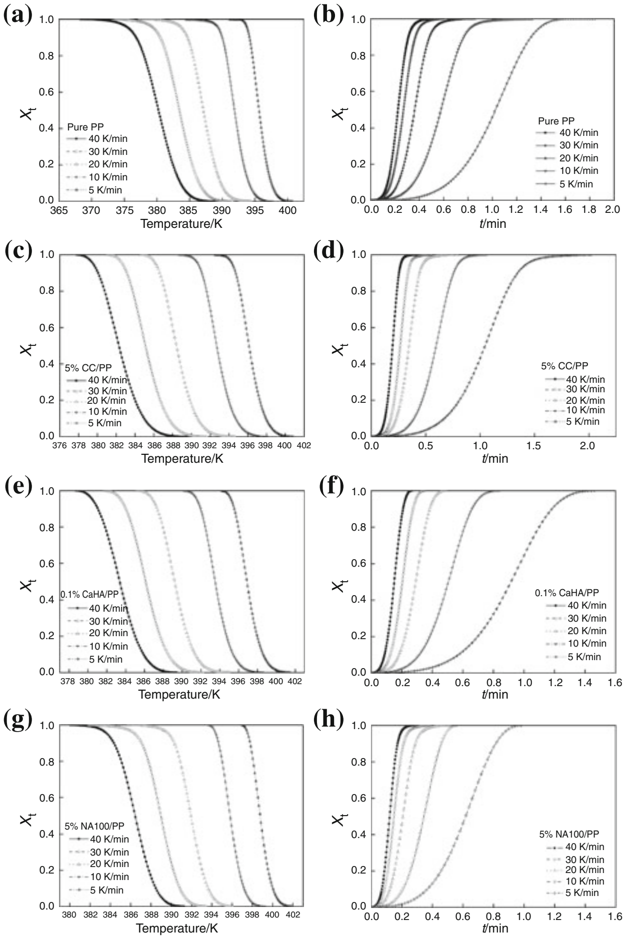

Fig. 3 Plots of X_t versus T or t for crystallization of samples at different cooling rates in DSC

$$\ln[-\ln(1-X_t)] = \ln Z_t + n \ln t. \tag{3}$$

For the nonisothermal crystallization process, $t = (T_0 - T)/\Phi$, where the t, T_0, T, and Φ are crystallization time, onset crystallization temperature, crystallization temperature, and cooling rate, respectively. Figure 4 presented the plot of ln [$-$ln(1 $-$ X_t)] versus ln t of iPP and nucleated iPPs with preferable linear relationships. The values of n and Z_t can be obtained by the fitting of the linear slopes and the intercepts of the lines, respectively. The rate constant of crystallization, Z_c, can be obtained based on Eq. 4 [46]. The values of n and Z_c are listed in Table 1.

$$\lg Z_c = \frac{\lg Z_t}{\Phi} \tag{4}$$

As expected, it can be seen from Table 1 that the crystallization peak temperature, T_p, and the value of $t_{1/2}$ decreases and the Z_c increases with increasing the cooling rate for all the samples. The lower $t_{1/2}$ and higher Z_c for iPP filled with CC are attributed to the presence of the heterogeneous nucleation of CC. The $t_{1/2}$ is lower and the T_p and Z_c are higher for nucleated iPPs compared to that of pure iPP under the same cooling rate, especially for iPP nucleated with NA100 β-nucleating agent. The value of $t_{1/2}$ of iPP nucleated with NA100 is lower than that of iPP nucleated with CaHA. It means that the crystallization rate of iPP nucleated with NA100 β-nucleating agent is higher than that of iPP nucleated with traditional CaHA nucleating agents. The result indicates that the nucleating effect of NA100 is more significant than that of CaHA for iPP crystallization.

Table 1 Nonisothermal crystallization kinetic data of iPP and nucleated iPPs

Samples	Φ/ °C min^{-1}	n	Z_c	$t_{1/2}$/min	T_{cp}/ °C
PP	5	3.4	0.85	1.03	122.1
	10	3.0	1.08	0.58	118.4
	20	3.1	1.11	0.36	113.7
	30	3.2	1.12	0.27	110.1
	40	3.4	1.12	0.23	107.1
5% CC/iPP	5	3.0	0.87	1.05	122.7
	10	2.7	1.06	0.60	119.2
	20	2.9	1.12	0.35	114.9
	30	3.0	1.12	0.27	111.6
	40	3.0	1.11	0.20	108.8
0.1% CaHA/iPP	5	2.7	0.84	0.91	123.5
	10	2.8	1.09	0.50	120.1
	20	3.0	1.15	0.29	115.7
	30	2.9	1.13	0.20	112.7
	40	2.7	1.11	0.15	110.1
5% NA100/iPP	5	2.5	1.01	0.62	125.4
	10	3.0	1.26	0.34	122.4
	20	2.6	1.16	0.21	118.7
	30	2.8	1.16	0.15	115.8
	40	2.7	1.13	0.12	113.3

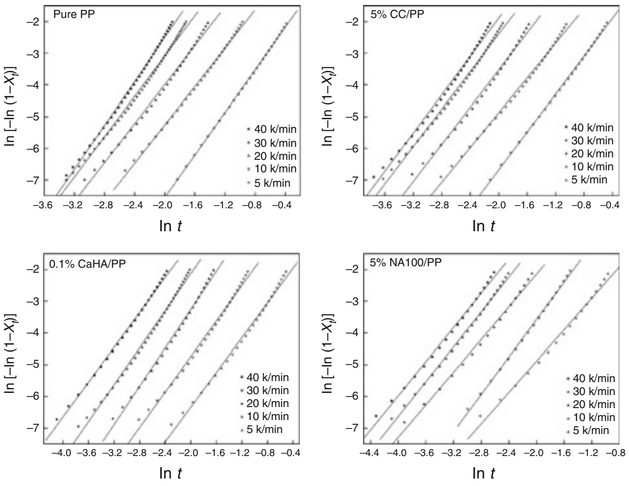

Fig. 4 Plots of ln [$-$ln(1 $-$ X_t)] versus ln t for samples

Based on Mo's equation [47, 48]

$$\ln\Phi = \ln F(T) - a\ln t \tag{5}$$

The plot of ln Φ versus ln t would be a serial straight line. The $F(T)$ value is the rate constant of crystallization. And the parameter a is the ratios of the Avrami exponent n to the Ozawa exponent m. The smaller the value of $F(T)$ is, the higher the crystallization rate becomes. Figure 5 shows the plots of ln Φ versus ln t. The values of $F(T)$ and a can be obtained by the fitting of the linear slopes and the intercepts of the lines, respectively, and are listed in Table 2. It can be observed that the values of $F(T)$ and a increase with increasing the relative crystallinity. It indicated that a higher cooling rate should be required to obtain a higher relative crystallinity in the same crystallization time. At a given relative crystallinity, the value of $F(T)$ of iPP and iPP filled with CC is higher than that of nucleated iPPs. The value of $F(T)$ of iPP nucleated with NA100 is lower than that of iPP nucleated with CaHA. The trend is similar to those of Z_c and $t_{1/2}$. These results indicate that the crystallization rate of iPP nucleated with NA100 β-nucleating agent is higher than that of iPP nucleated with traditional CaHA nucleating agents.

Crystallization activation energy

For the nonisothermal crystallization, the crystallization activation energy can be evaluated from Kissinger method [49]:

$$\mathrm{d}\left[\ln\left(\frac{\Phi}{T_{\mathrm{P}}^2}\right)\right]\Big/\mathrm{d}\left(\frac{1}{T_{\mathrm{P}}}\right) = -\frac{\Delta E}{R} \tag{6}$$

where ΔE is the crystallization activation energy, Φ is the cooling rate, T_{p} is the crystallization peak temperature, and R is the gas constant. The plot of $\ln(\Phi/T_{\mathrm{p}}^2)$ versus $1/T_{\mathrm{p}}$ of iPP and nucleated iPPs are shown in Fig. 6. It can be seen that good linear relations are obtained. From the slopes of the curves, the ΔE can be calculated and are listed in Table 2. The values of ΔE's of iPP, iPP filled with CC, and iPPs nucleated with CaHA and NA100 β-nucleating agent are 208, 187, 178, and 164 kJ mol^{-1}, respectively. The content of β-crystal in iPP, iPP filled with CC, iPP nucleated with CaHA and NA100 β-nucleating agent is also listed in Table 2. It is found the values of ΔE of β-iPP is lower than that of β-PP and decreases with increasing the content of β-crystal in iPP. Han and co-workers [26] had found that the iPP with high content of β-crystal exhibited

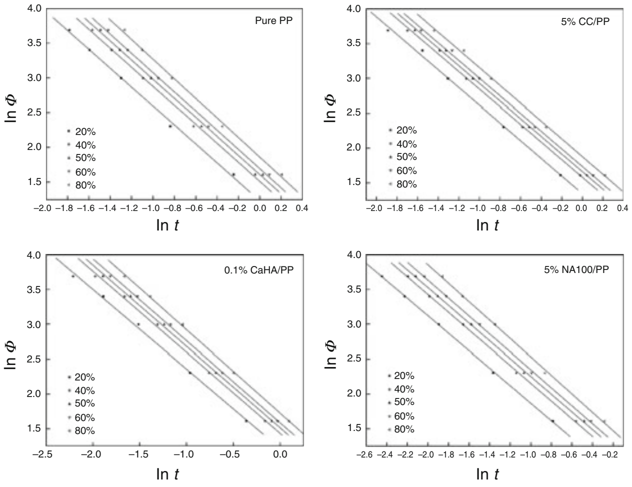

Fig. 5 Plots of lg Φ versus lg t for samples crystallized dynamically

Table 2 Nonisothermal crystallization kinetic parameters of iPP and nucleated iPPs

$X(T)$/%	Sample	$F(T)$/K min^{a-1}	a	ΔE/kJ mol^{-1}
20	Pure iPP	3.4	1.4	207
40		4.5	1.4	$K_\beta = 0$
50		5.0	1.4	
60		5.4	1.4	
80		6.4	1.4	
20	5% CC/iPP	3.8	1.3	187
40		4.9	1.3	$K_\beta = 0$
50		5.3	1.3	
60		5.7	1.3	
80		6.5	1.3	
20	0.1% CaHA/iPP	3.4	1.1	178
40		4.2	1.1	$K_\beta = 0.86$
50		4.5	1.1	
60		4.9	1.2	
80		5.6	1.2	
20	5% NA100/iPP	1.8	1.3	164
40		2.4	1.3	$K_\beta = 0.95$
50		2.7	1.3	
60		2.9	1.3	
80		3.3	1.3	

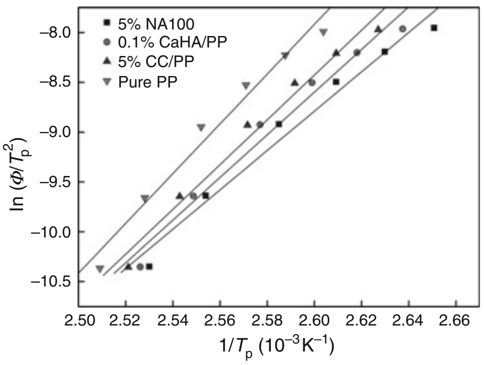

Fig. 6 Plots of ln (Φ/T_{p}^2) versus $1/T_{\mathrm{p}}$ for samples crystallized nonisothermally

lower ΔE. They found that the ΔE's of iPPs with β-crystal contents of 77.8 and 91.2% were 172 and 164 kJ mol^{-1}, respectively. From the kinetic viewpoint, the ΔE could be correlated with the crystallization rate. Our data of crystallization rate and the ΔE for nonisothermally crystallized iPP and β-nucleated iPPs indicated that the samples with lower ΔE would have high crystallization rate. Therefore, it is suggested that low ΔE would accelerate the crystallization and result in the increase of crystallization rate. The low ΔE is favorable to the formation of high content of β-crystal in β-nucleated iPPs.

However, our results and Han and co-workers [26] results are in contrast to those reported for other nucleating agents [25, 50, 51], where the addition of nucleating agents increased ΔE and the crystallization rate of iPP. They considered that the weak interaction between nucleating agents and segments of iPP may baffle the transfer of macromolecular segments from iPP melts to the crystal growth surface. The baffling effect may lead to the increase of ΔE. However, addition of nucleating agent is favorable to the nucleation during crystallization and increases the nucleation rate, resulting in the increase of the overall crystallization rate and crystallization temperature due to the heterogeneous nucleation of nucleating agent.

Therefore, the weak interaction between the nucleating agents and the segments of iPP may be one main reason for the increased ΔE. The improved interaction between the nucleating agents and the segments of iPP would decrease the ΔE. Han and co-workers [26] suggested that the polymerization–dispersion method promoted the interaction between the nucleating agents and segments of iPP that facilitated the crystal growth process. For the iPP nucleated with CaHA β-nucleating agent supported on CC, the presence of CC would promote the interaction between the CaHA β-nucleating agent and segments of iPP that decreased the ΔE, facilitated the crystal growth process and increased the overall crystallization rate.

Conclusions

In this paper, nonisothermal crystallization kinetics, melting characteristics, and crystallization activation energies of iPP nucleated with a novel highly efficient supported β-nucleating agent, calcium pimelate (CaHA) supported on nano-$CaCO_3$ (NA100), are compared with those of iPP nucleated with traditional CaHA β-nucleating agent. Addition of nano-$CaCO_3$ increases the crystallization temperature of iPP and has no influence on the crystal form of iPP. iPP and nano-$CaCO_3$ filled iPP mainly crystallize in the form of α-crystal. The supported β-nucleating agent NA100 and CaHA nucleated iPPs mainly crystallize in the form of β-crystal. However, the crystallization rate, crystallization and melting temperatures, and the content of β-crystal of iPP nucleated with NA100 is higher than that of iPP nucleated with CaHA and the melting behavior of iPP nucleated with NA100 is different from that of iPP nucleated with CaHA. There are three melting peaks for iPP nucleated with NA100 and four melting peaks for iPP nucleated with CaHA at high cooling rates. Avrami and Mo's equation can be used to describe the nonisothermal crystallization kinetic of β-nucleated iPPs. The crystallization activation energy of iPP nucleated with NA100 is lower than that nucleated with CaHA. The decreased crystallization activation energy is favorable to increasing the crystallization rate and the content of β-crystal of iPP. The CaHA β-nucleating agent supported on nano-$CaCO_3$ exhibits higher efficiency for preparation of β-iPP than CaHA.

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