

Effect of the Composition Ratio of Pimelic Acid/Calcium Stearate Bicomponent Nucleator and Crystallization Temperature on the Production of β Crystal Form in Isotactic Polypropylene

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ABSTRACT: The influence of the composition ratio of pimelic acid/calcium stearate bicomponent nucleator on the β crystal form content of isotactic polypropylene (iPP) had been studied at the crystallization temperature of 120°C and duration of 30 min. It was found that the β crystal form content increased continuously with increasing amount of calcium stearate at the constant amount of 0.15% pimelic acid. High β crystal form content polypropylene could be produced when the amount of calcium stearate was greater than 0.30% (the mass composition ratio of pimelic acid/calcium stearate was less than 1/2, the mole ratio was less than 1.89/1). It was shown that pimelic acid and calcium stearate could react to produce a high effective β nucleator (calcium pimelate) "in situ" during the melt-mixing of iPP and the bicomponent nucleator.

The influence of crystallization temperatures (100–140°C) on the β crystal form content of iPP had also been studied at the constant composition ratio of 0.15% pimelic acid/0.5% calcium stearate (the calcium pimelate produced *in situ* was 0.16%, which was calculated from stoichiometry). It was found that the β crystal form content increased continuously with increasing crystallization temperature and it maximized at 130°C. β Crystal form content decreased sharply at the crystallization temperature of 140°C. It was shown that $\beta \rightarrow \alpha$ modification transformed between 130 and 140°C. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 958–965, 2008

Key words: poly(propylene); nucleation; polymorphism; β crystal form; pimelic acid; calcium stearate

INTRODUCTION

Isotactic polypropylene (iPP) has several polymorphs such as α , β , γ , and smetic form. Among them, α crystal form is the most stable one and other forms will transform to it under some conditions, such as heat treatment, extension, etc. β Crystal form iPP have attracted many researchers' interest because of its unique properties such as improved toughness, microvoid from $\beta \rightarrow \alpha$ transformation and may be used in toughened plastics products, microporous membrane, fiber, etc. High content β crystal form iPP (β -iPP) may be produced by β nucleating agents, such as quinacridone pigment, pimelic acid/calcium stearate mixture, *N,N*-dicyclohexyl-2,6-naphthalenedicarboxamide, etc.^{1–3} Among them, the pimelic acid/calcium stearate mixture is an important one and had been studied by many researchers. Shi and Zhang et al.^{4–9} were creative inventors of the β -nucleator (consisting of equal amount of pimelic acid and calcium stearate); they studied the effect of

the β -nucleator on the crystallization, melting behavior, and mechanical properties of iPP and ethylene/propylene random and block copolymers. The maximum values of $T_{m\beta}$ and $\Delta H_{m\beta}$ were obtained at nucleator content around 0.005 wt % for iPP samples crystallized under both isothermal and nonisothermal conditions. The less ordered β -phase was formed for iPP samples containing a much higher amount of nucleator and crystallized at a much higher rate.^{4,5} The nucleation constant for β -phase PP was determined and the fold surface free energy of β -phase PP was estimated for different samples to lie between 48.2 and 55.2 erg/cm².⁶ The crystal perfection of β -nucleated PP was shown to vary with crystallization temperature. The observed multiple peaks in differential scanning calorimetry (DSC) spectra could be related to a β_1 -phase with defective inclination of the chains, a recrystallized or original β_2 -phase of more perfect inclination, and the α -phase.⁷ β -Nucleator was more effective in the E/P block copolymer than in the E/P random copolymer. The dependence of K value on crystallization temperature for the block copolymer was similar to that for iPP, i.e., the K value starts to decrease significantly only above 135°C. However, for random copolymer, it started to

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decrease at a much lower crystallization temperature.⁸ β -Phase copolymer had higher impact strength, slightly lower yield strength, and a higher degree of stress whitening than the α -phase copolymer. A stretching-induced or impact-induced β - α transformation in parallel with microcrazing was noticed.⁹ Tjong et al.¹⁰⁻¹² studied the morphological behavior and impact properties of β -crystalline-phase polypropylene produced by a bicomponent β -nucleator (equal amounts of pimelic acid and calcium stearate). The addition of 0.1 wt % β -nucleator led to high purity β -form PP and the β -spherulites exhibited a sheaf-like structure with no clear boundaries between them. The improvement in impact toughness was due to the larger energy dissipation, which was associated with the formation of microfibrils. Trongtorsak et al.¹³ studied the effect of calcium stearate and pimelic acid addition (1 : 1 w/w ratio) on the mechanical properties of heterophasic iPP/ethylene-propylene rubber blend. It was revealed that iPP/EPR blend loaded with 0.001% Ca-Pim showed the highest improvement in the notched Izod impact strength (an increase of ~ 3.5 -fold over that of the unfilled sample) at the expense of both the tensile strength at yield and flexural modulus and the presence of β -crystals (with the K_{β} value being 0.75) was responsible for the great improvement. Sterzynski and Oysaed¹⁴ studied the influence of a bicomponent nucleating system [a powder mixture of pimelic acid and calcium stearate with a constant ratio of both components (1 : 1)] on the selective α and β crystalline phase development. It was found that the form of the DSC melting curve and consequently the structural-physical effects in iPP during melting were properties that were strongly dependent upon nucleation and thermal history. Li and Cheung et al.^{15,16} used a unique method to prepare a β -nucleating agent by mixing 1% ethanol solution of pimelic acid and 2% suspension of calcium stearate in ethanol. The doped PP powder contained 1% of the β -nucleating agent (pimelic acid/calcium stearate = 1/1). They found that pimelic acid alone could not stimulate the formation of β -phase PP. Over 90% of β -phase could be obtained in resin doped with pimelic acid/calcium stearate, and this was attributed to finer particle size and better dispersion of the nucleating agent. They^{17,18} studied the effect of mold temperature on the formation of α/β PP blends in injection molding and the deformation mechanisms of β -PP prepared by doping with 1%¹⁷ or 0.6 wt %¹⁸ of the β -nucleating agent (pimelic acid/calcium stearate = 1/2). The percent of β -phase crystals increased with mold temperature (60–140°C), while the crystallinity of α phase crystals dropped correspondingly. The β -phase was mechanically stable at room temperature up to yielding point during tensile test. The β -phase transformed to α -phase over

the necking region. Li and Cheung¹⁹⁻²¹ also studied the heat of fusion, conversion of growth and recrystallization, and the lamellar structure of β -phase in PP doped with 1%¹⁹ or 1.5%²⁰ or 0.6%²¹ of the β -nucleating agent (pimelic acid/calcium stearate = 1/1.5). The heat of fusion of the β - and α -crystal was 168.5 and 177.0 J g⁻¹, respectively. It was indicated a major conversion of the β -growth to α -growth occurred near 85°C by a two-step crystallization process in a DSC. The β -PP spherulites crystallized isothermally at 130°C had a Category 2 morphology and the lamellae had a long period of 20 nm. It is summarized from the above researches that the pimelic acid/calcium stearate bicomponent nucleator used was under the constant composition ratio and was premixed before blending with PP. The amount of calcium stearate was less than that of pimelic acid from the view of mole ratio (1 : 1). The study on the influence of the composition ratio of pimelic acid/calcium stearate on the β crystal form content and the nucleation mechanism of the bicomponent nucleator is rare. Furthermore, the formation and contents of β crystal form in iPP were influenced by the crystallization temperature considerably.^{7,8,20,22-24} It was found that the formation of pure β -iPP has an upper [$T(\beta\alpha) = 140$ – 141 °C] and lower limit temperature [$T(\alpha\beta) = 105$ °C].³ Therefore, the effect of the composition ratio of pimelic acid/calcium stearate and crystallization temperatures (100–140°C) on the production of β crystal form in iPP had been studied respectively, in this article.

EXPERIMENTAL

Materials

iPP powder (MFR = 1 g/10 min at 230°C and 21.2 N load) was produced by Jinling Plastics and Rubber Chemical Co., Ltd. (Nanjing, China). Pimelic acid [$C_7H_{12}O_4$, chemical pure reagent, melting point: 106°C, pass through 100 mesh sieve (particle size ≤ 150 μ m)], calcium stearate [$Ca(C_{17}H_{35}COO)_2$, chemical pure reagent, melting point: 149–155°C, pass through 200 mesh sieve (particle size ≤ 75 μ m)], and B215 (industrial antioxidant) were commercially available. Calcium pimelate [Capt, $C_7H_{10}O_4Ca$, pass through 200 mesh sieve (particle size ≤ 75 μ m)] was synthesized by neutralization of pimelic acid and calcium hydroxide in my laboratory.

Preparation of nucleated iPP samples

Five hundred grams of iPP was intensely mixed with 0.5 g B215, 0.75 g pimelic acid (PA), and variable amount of calcium stearate (Cast) in a 2-L box for 2 min. The mixtures were compounded in a corotating twin-screw extruder (TE-20, $D = 20$ mm,

$L/D = 32/1$, Jiangsu Keya Chemical Equipment). The rate of feeding screw and main screw was 30 and 230 rpm, respectively, the temperature of the extruder was set at 200, 210, 210, and 200°C from the hopper to the die. The melt was cooled and pelletized. iPP doped with 0.15% calcium pimelate was prepared in a similar way. A granule of nucleated iPP was placed between two glass slides on a hot stage kept at $(220 \pm 2)^\circ\text{C}$ for 10 min to allow the sample to melt completely and remove thermal memory, squeezed on the top slide to form a film, then immersed it in a glycerin bath set at a certain temperature $(100\text{--}140^\circ\text{C} \pm 1^\circ\text{C})$ and isothermally crystallized for 30 min, then quenched it in the icy water. The thickness of samples was between 20 and 40 μm .

Differential scanning calorimetry measurement

Melting behavior of the nucleated iPP sample was performed in a DSC instrument (CDR-34P, made by Shanghai Precision Scientific Instrument) under a dry nitrogen atmosphere. The instrument was calibrated with pure indium for temperature and heat flow. For sample measurement, about 5–10 mg of each sample was sealed into an aluminum pan, heated from room temperature to 220°C at a heating rate of 10°C/min. The heat flow versus temperature was recorded and peak melting temperatures of α crystal form ($T_{m,\alpha}$) and β crystal form ($T_{m,\beta}$) were got from melting curves. Enthalpy of α crystal form ($H_{m,\alpha}$) and β crystal form ($H_{m,\beta}$) were got from the separation of the area of the α and β melting peaks according to the method recommended by Li and Cheung.¹⁸ Crystallinity of α crystal form (X_α) and β crystal form (X_β) and β crystal form content (K_{DSC}) were calculated as follows:

$$X_\alpha = H_{m,\alpha}/H_{m,\alpha}^0 \quad (1)$$

$$X_\beta = H_{m,\beta}/H_{m,\beta}^0 \quad (2)$$

$$K_{\text{DSC}} = H_{m,\beta}/(H_{m,\alpha} + H_{m,\beta}) \quad (3)$$

where $H_{m,\alpha}^0$ is the enthalpy of fusion of α -iPP with 100% crystallinity and it is 177 J/g; $H_{m,\beta}^0$ is the enthalpy of fusion of β -iPP with 100% crystallinity and it is 168.5 J/g.¹⁹

Wide angle X-ray diffraction measurement

Wide angle X-ray diffraction (WAXD) diffraction patterns of the nucleated iPP samples were recorded in a X-ray diffractometer (XRD-6000, Shimadzu) equipped with Ni-filtered Cu K α radiation ($\lambda = 1.54 \text{ \AA}$). It was operated at a voltage of 40 kV and a filament current of 30 mA. Radial scans of intensity

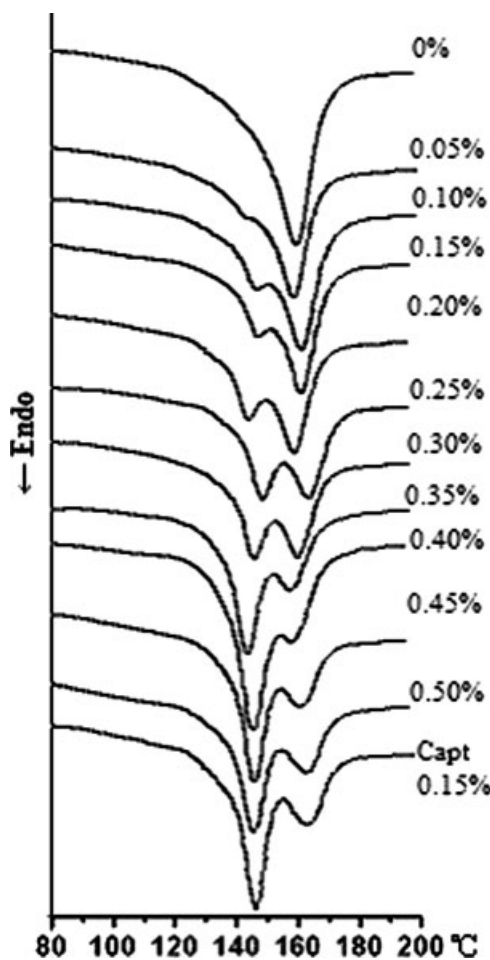


Figure 1 DSC melting curves of iPP doped with 0.15% PA and different content of Cast after crystallized at 120°C for 30 min (except the last one of iPP doped with 0.15% Capt).

versus diffraction angle (2θ) were recorded in the range of $5^\circ\text{--}50^\circ$. The scanning rate was $4^\circ/\text{min}$.

The relative content of β crystal form was measured in terms of the K_{WAXD} proposed by Turner-Jones et al.²³

$$K_{\text{WAXD}} = H_{\beta 1}/(H_{\beta 1} + H_{\alpha 1} + H_{\alpha 2} + H_{\alpha 3}) \quad (4)$$

where $H_{\alpha 1}$, $H_{\alpha 2}$, and $H_{\alpha 3}$ were the heights (from the top of the peak to the background curve) of three strong α crystal form peaks (110), (040), and (130) at $2\theta = 14.1^\circ$, 16.9° , and 18.8° , respectively. $H_{\beta 1}$ was the height of β crystal form peak (300) at $2\theta = 16^\circ$.

Polarized light microscopy observation

Crystal morphology of the nucleated iPP sample was observed on a polarized light microscope (LW-200-4JS, Shanghai LW Scientific) equipped with cross polars and a CCD camera. Pictures were captured and stored in a computer.

TABLE I
Melting Points, Enthalpy, Crystallinity, and K Values of iPP Doped with 0.15% PA and Different Content of Cast After Crystallized at 120°C for 30 min

Cast (%)	$T_{m,\alpha}$ (°C)	$T_{m,\beta}$ (°C)	$H_{m,\alpha}$ (J/g)	$H_{m,\beta}$ (J/g)	X_α (%)	X_β (%)	K_{DSC} (%)	K_{WAXD} (%)
0	162.0		106.29		60.05		0	8.99
0.05	161.2	145.4	106.72	1.04	60.29	0.61	0.97	13.32
0.10	163.6	149.3	103.56	9.22	58.51	5.47	8.18	37.33
0.15	161.5	146.3	92.67	11.07	52.36	6.57	10.67	39.32
0.20	161.3	146.6	89.52	21.89	50.58	12.99	19.65	42.22
0.25	165.9	151.4	66.03	30.61	37.31	18.17	31.67	54.54
0.30	160.8	148.5	72.38	34.81	40.89	20.66	32.48	55.26
0.35	160.2	146.4	59.19	55.81	33.44	33.12	48.53	72.43
0.40	160.8	148.5	54.36	52.47	30.71	31.14	49.12	76.72
0.45	162.9	148.8	57.02	70.31	32.21	41.73	55.22	78.47
0.50	165.4	148.5	39.20	59.40	22.15	35.25	60.24	92.71
Capt 0.15 (%)	163.2	147.4	42.72	66.31	24.14	39.35	60.82	91.08

RESULTS AND DISCUSSION

Effect of the composition ratio of pimelic acid/calcium stearate on the production of β crystal form in iPP

DSC melting curves of iPP doped with 0.15% PA and different content of Cast after crystallized at 120°C for 30 min were shown in Figure 1, their relative parameters were shown in Table I. K values of iPP doped with 0.15% PA and different content of Cast after crystallized at 120°C for 30 min were shown in Figure 2. As can be seen, the melting peak area of β crystal form increased with increasing Cast content, but the melting peak area of α crystal form decreased continuously. The melting peak area of β crystal form was bigger than that of α crystal form obviously when the Cast content was more than 0.30% ($\geq 0.35\%$), i.e., the mass composition ratio of pimelic acid/Cast was less than 1/2 (the mole ratio was less than 1.89/1), K_{DSC} increased abruptly, and high β crystal form content was got. The mass composition ratio of pimelic acid/Cast (1/1) (the mole ratio was 3.79/1) was applied in the literatures,⁴⁻¹⁴

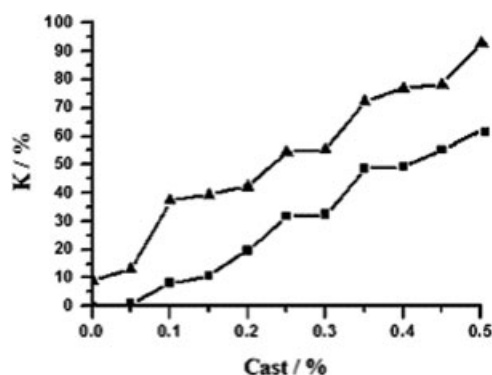


Figure 2 K values of iPP doped with 0.15% PA and different content of Cast after crystallized at 120°C for 30 min (\blacktriangle : K_{WAXD} ; \blacksquare : K_{DSC}).

which was bigger than that of 1/2 in the present study. This may be attributed to the premixing of pimelic acid and Cast before adding to iPP in the literatures,⁴⁻¹⁴ but pimelic acid and Cast were added to iPP without premixing in the present study. High purity β crystal form was got when the Cast content was more than 0.45% (= 0.50%), i.e., the mass composition ratio of pimelic acid/Cast was less than 1/3 (the mole ratio was less than 1.49/1), K_{DSC} was 60.24%.

WAXD spectra of iPP doped with 0.15% PA and different content of Cast after crystallized at 120°C for 30 min were shown in Figure 3. K_{WAXD} was shown in Table I and Figure 2, respectively. It was shown K_{WAXD} increased continuously with increasing Cast content. There were three jumps in the curve of K_{WAXD} versus Cast content, i.e., the Cast content was more than 0.05% (the mass composition ratio of pimelic acid/Cast was less than 3/1, the mole ratio was less than 11.36/1), the Cast content was more than 0.30% (the mass composition ratio of pimelic acid/Cast was less than 1/2, the mole ratio was less than 1.89/1), and the Cast content was more than 0.45% (the mass composition ratio of pimelic acid/Cast was less than 1/3, the mole ratio was less than 1.49/1). The curves of K_{WAXD} versus Cast content and K_{DSC} versus Cast content had the similar trend, so the characterization of β crystal form by DSC was as good as that of WAXD. High purity β crystal form were got when the Cast content was more than 0.45% (= 0.50%), i.e., the mass composition ratio of pimelic acid/Cast was less than 1/3 (the mole ratio was less than 1.49/1), K_{WAXD} was 92.71%.

Polarized light microscopy (PLM) photographs of iPP doped with 0.15% PA and different content of Cast after crystallized at 120°C for 30 min were shown in Figure 4. As can be seen, a little of bright β crystallites could be seen accidentally in the iPP doped with 0.15% pimelic acid. A great deal of bright colored β crystals appeared when Cast was

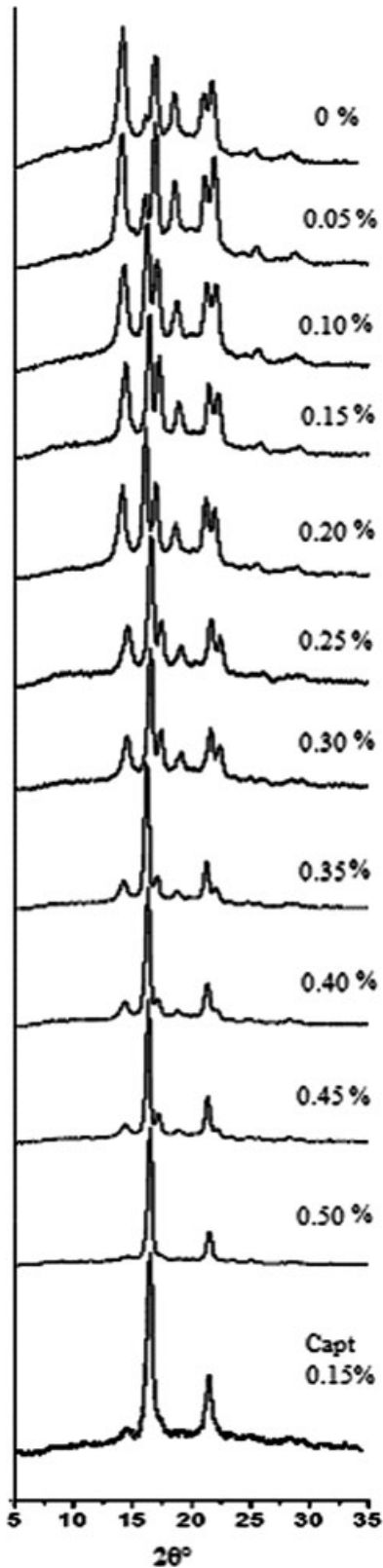


Figure 3 WAXD spectra of iPP doped with 0.15% PA and different content of Cast after crystallized at 120°C for 30 min (except the last one of iPP doped with 0.15% Capt).

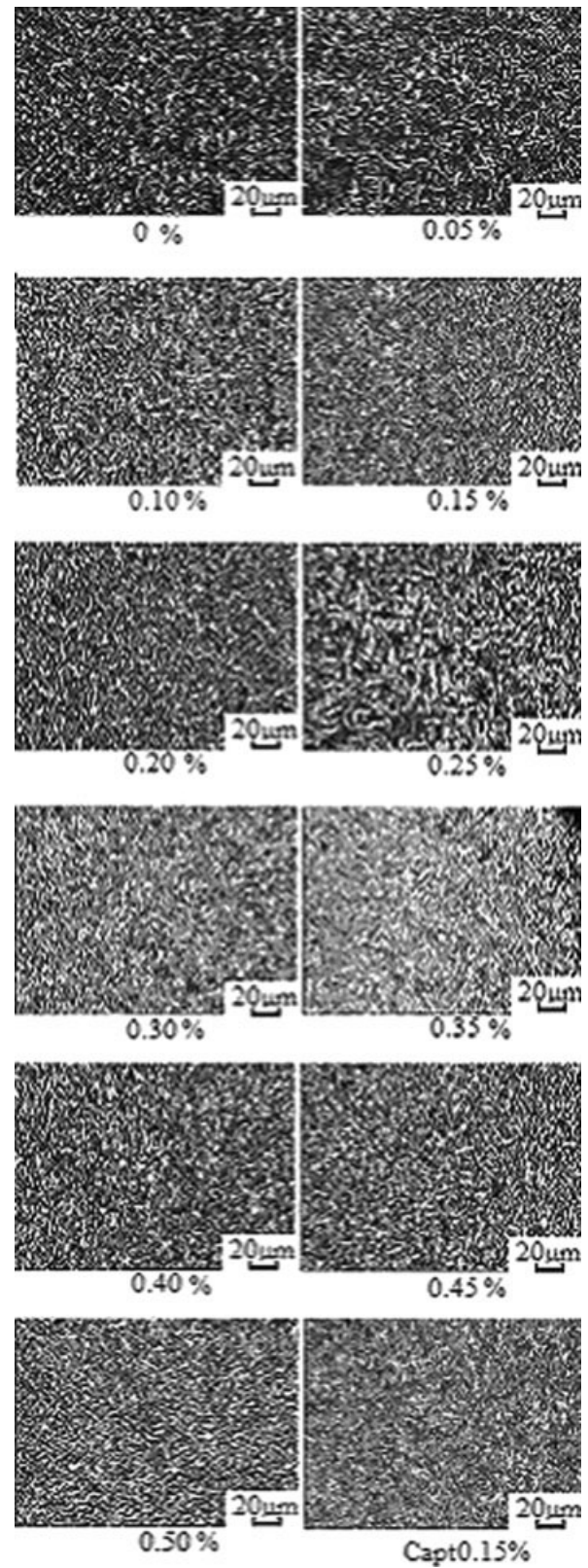


Figure 4 PLM photographs of iPP doped with 0.15% PA and different content of Cast after crystallized at 120°C for 30 min (except the last one of iPP doped with 0.15% Capt).

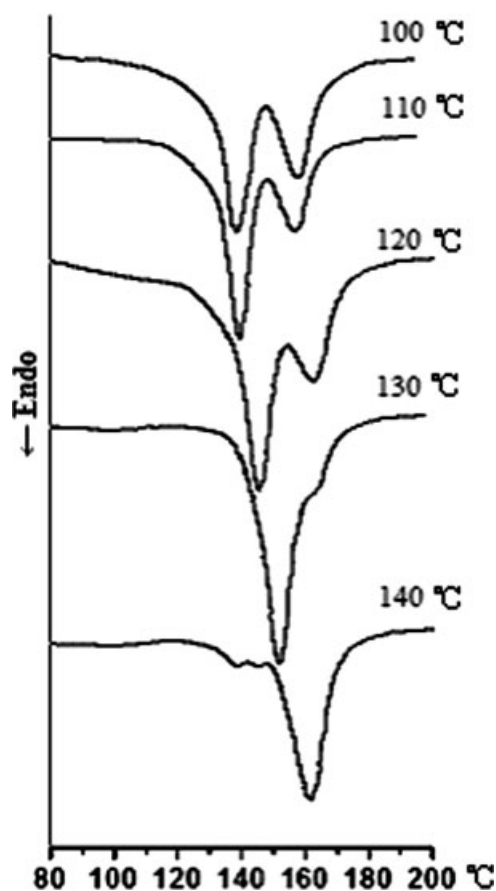


Figure 5 Influence of crystallization temperatures on the DSC melting curves of iPP doped with 0.15% PA and 0.5% Cast.

added, especially the Cast content was more than 0.10%.

Analysis of the nucleation mechanism of pimelic acid/calcium stearate bicomponent β nucleator

What is the mechanism of the nucleation of the β crystal form by pimelic acid/calcium stearate bicomponent nucleator? Zhang and Shi⁸ thought it is most probable that the primary nuclei for the β -form is the liquid pimelic acid absorbed in or complexed with the active surface of calcium stearate, but it is not convincing. From the above results, it was found

that few amount of β crystal form was produced in the iPP doped with 0.15% pimelic acid only. β Crystal form content increased continuously with increasing Cast content in the bicomponent nucleator, and K_{DSC} and K_{WAXD} increased continuously too. K_{DSC} was greater than 48.53% and K_{WAXD} was greater than 72.43% when the Cast content was more than 0.30% (the mass composition ratio of pimelic acid/Cast was less than 1/2, the mole ratio was less than 1.89/1). It was shown that high β crystal form content was produced when the Cast content was more than 0.30% ($\geq 0.35\%$, the Capt produced *in situ* was $\geq 0.11\%$, which was calculated from stoichiometry) in the bicomponent nucleator. Li and Cheung^{15,16} found that pimelic acid, calcium stearate, or stearic acid alone could not stimulate any β -growth, while calcium pimelate were very effective for β -phase PP crystals. The pimelic acid/calcium stearate system that Li and Cheung adopted was calcium pimelate virtually because a replacement reaction between pimelic acid and calcium stearate occurred in their ethanol solution to produce calcium pimelate. Varga et al.,^{25–33} Li et al.,³⁴ and Huy et al.³⁵ also found calcium pimelate was an effective β -nucleator. The DSC melting curve of iPP doped with 0.15% Capt after crystallized at 120°C for 30 min was shown in Figure 1; its relative parameters were shown in Table I. Its WAXD spectrum and PLM photograph were shown in Figures 3 and 4, respectively. As can be seen, calcium pimelate was a high effective β nucleator, K_{DSC} was 60.82%, and K_{WAXD} was 91.08% for iPP doped with 0.15% Capt, which were similar to K_{DSC} (60.24%) and K_{WAXD} (92.71%) for iPP doped with 0.15% PA and 0.50% Cast (the Capt produced *in situ* was 0.16%, which was calculated from stoichiometry). Therefore, a reaction should occur “*in situ*” between pimelic acid (melting point: 106°C) and Cast (melting point: 149–155°C) during the melt-blending of iPP with the bicomponent nucleator in a corotating twin-screw extruder, and a high effective β nucleator (Capt) was produced. The reaction probability between pimelic acid and Cast increased with increasing Cast content and the production amount of Capt increased too, so the β crystal form content increased continuously.

TABLE II
Influence of Crystallization Temperatures on the Melting Points, Enthalpy, Crystallinity, and K_{DSC} of iPP Doped with 0.15% PA and 0.5% Cast

Crystallization temperature (°C)	$T_{m,\alpha}$ (°C)	$T_{m,\beta}$ (°C)	$H_{m,\alpha}$ (J/g)	$H_{m,\beta}$ (J/g)	X_α (%)	X_β (%)	K_{DSC} (%)
100	160.42	141.48	50.62	50.74	28.60	30.11	50.06
110	159.79	142.43	39.25	55.85	22.18	33.15	58.73
120	165.43	148.53	39.20	59.40	22.15	35.25	60.24
130	167.8	154.72	30.84	68.43	17.42	40.61	68.93
140	164.63	141.33, 147.57	82.34	3.91	46.52	2.32	4.54

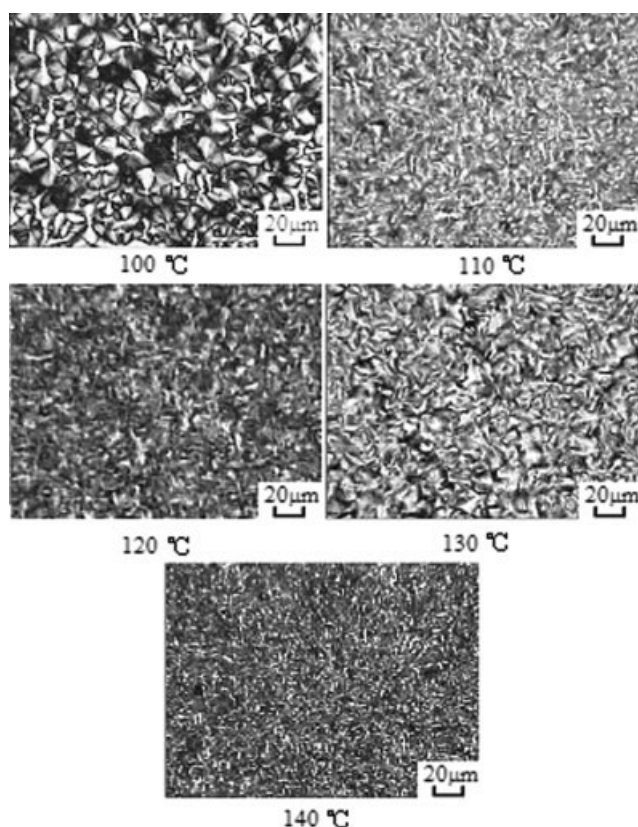


Figure 6 Influence of crystallization temperatures on the PLM photographs of iPP doped with 0.15% PA and 0.5% Cast.

Effect of crystallization temperatures on the production of β crystal form in iPP nucleated by 0.15% pimelic acid/0.5% Cast

From the above results, β crystal form content maximized when iPP doped with 0.15% PA/0.5% Cast after crystallized at 120°C for 30 min. It was shown that β crystal form content was dependent on the crystallization temperatures in the literatures.^{3,7,8,20,22–24} Therefore, the influence of crystallization temperatures on the DSC melting curves of iPP doped with 0.15% PA and 0.5% Cast was shown in Figure 5, their relative parameters were shown in Table II. The influence of crystallization temperatures on the PLM photographs of iPP doped with 0.15% PA and 0.5% Cast was shown in Figure 6. As can be seen in Figure 5 and Table II, $T_{m,\alpha}$, $T_{m,\beta}$, X_{β} , and K_{DSC} increased with increasing crystallization temperature and maximized at 130°C, but X_{α} decreased continuously and minimized at 130°C. Subsequently, $T_{m,\alpha}$, $T_{m,\beta}$, X_{β} , and K_{DSC} decreased sharply, X_{α} increased at the crystallization temperature of 140°C. It was shown that $\beta \rightarrow \alpha$ modification transformation occurred between 130 and 140°C. Two small β melting peaks appeared in the DSC curve at the crystallization temperature of 140°C,

which might relate to short crystallization time and incomplete $\beta \rightarrow \alpha$ modification transformation at higher temperature. As can be seen in Figure 6, the amount of bright colored β crystals increased with increasing crystallization temperature (100–130°C), especially the most distinctive PLM photograph of colored curved β crystals was got at the crystallization temperature of 130°C. Only imperfect crystallites were produced at the crystallization temperature of 140°C. This might relate to the lower crystallization rate and short crystallization time at the higher crystallization temperature.

CONCLUSIONS

K_{DSC} and K_{WAXD} increased continuously along with increasing Cast content under the condition of a constant amount of 0.15% pimelic acid. K_{DSC} was greater than 48.53% and K_{WAXD} was greater than 72.43% when the Cast content was more than 0.30% (the mass composition ratio of pimelic acid/Cast was less than 1/2, the mole ratio was less than 1.89/1). It was shown that high β crystal form content was produced when the Cast content was more than 0.30% ($\geq 0.35\%$, the Capt produced *in situ* was $\geq 0.11\%$) in the bicomponent nucleator. A chemical reaction should occur “*in situ*” between pimelic acid and Cast during their melting blending with iPP, and a high effective β nucleator (calcium pimelate) was produced. The production amount of calcium pimelate increased continuously with increasing Cast content, so β crystal form content increased continuously. β crystal form content increased continuously with increasing crystallization temperature (100–130°C) and K_{DSC} maximized to 68.93% at the crystallization temperature of 130°C for iPP doped with 0.15% PA/0.5% Cast (the Capt produced *in situ* was 0.16%), but K_{DSC} was only 4.54% at the crystallization temperature of 140°C. It was shown that $\beta \rightarrow \alpha$ transformation occurred between 130 and 140°C.

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