

Effects of Rosin-Type Nucleating Agent and Low Density Polyethylene on the Crystallization Process of Polypropylene

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ABSTRACT: In this article, the influence of rosin-type nucleating agent (Nu–Na) and low density polyethylene (LDPE) on the crystallization process of polypropylene (PP) from the melt state was studied by differential scanning calorimeter and polarization microscope. It was found that LDPE obstructed the crystallization of PP, decreased the crystallization rate of PP. The rosin-type nucleating agent Nu–Na substantially improved the rate of crystallization, and decreased the size of spherulites also. The cooperative effect of LDPE and Nu–Na made the crystallization rate of PP increase greatly, the spherulites of PP became much

smaller and dispersed more uniformly, and the transparency of PP was further improved evidently. The crystallization temperature (T_c) and melting temperature (T_m) of PP and LDPE in PP/LDPE/Nu–Na (97:3:0.5) were not affected by the number of mixed passes—the nuclei migration from PP to PE had not happened in the mixed passes. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 2804–2809, 2003

Key words: poly(propylene); polyethylene; nucleation; crystallization

INTRODUCTION

In the last few years, a new kind of rosin-type nucleating agent for polypropylene (PP), which can greatly improve the transparency of PP, was reported in several patents.^{1–3} Other than the conventional nucleating agents widely used before, this compound has a framework of phenanthrene as shown in Figure 1. In our earlier works,^{4,5} the effects of the rosin-type nucleating agent on PP crystallization had been studied; it was found that the rosin-type nucleating agent accelerated the overall crystallization rate of PP and diminished the size of spherulites, and the transparency of PP was improved to a certain extent.

Crystallization of PP is controlled by nucleation, spherulite growth rate, the degree of supercooling, and the rate of cooling. The effect of low density polyethylene (LDPE) on the crystallization of PP has been studied widely.^{6–10} It was reported that two-phase structure were observed in the blends with less than 50% of LDPE; the overall crystallization rate of PP was strongly reduced by the addition of LDPE. The reduction in the overall rate was attributed to a de-

crease in the nucleating density as the effect of the spherulite growth rate was found to be negligible.^{6–9,11} However, Avalos and coworkers¹² reported that a small addition of LDPE (10%) caused the depression of spherulite growth rate of PP and increased the chain folding energy in PP crystallization. This was interpreted as partial miscibility of PP and LDPE in the melt.

Up to now, only a few studies have been reported on the effects of nucleating agent and polyethylene (LDPE) on the crystallization process of PP. Gateski et al.^{8,13} studied the spherulite nucleation in PP blends with LDPE, where a nucleating agent (sodium benzoate) was added into one component and then the blends were melt mixed several times. The nuclei density was found decreased in PP phase after blending.

In this article, the effect of rosin-type nucleating agent and LDPE on the crystallization process of PP was studied under nonisothermal and isothermal conditions. The crystal structure of PP was also investigated.

EXPERIMENTAL

Materials

Isotactic PP (grade PP K1008, melting index 7.0 g/10 min) and LDPE (grade LDPE 1C7A, melting index 7.0 g/10 min) was obtained from Yanshan Petrochemical Industrial Co., Beijing, China. Dehydroabietic acid

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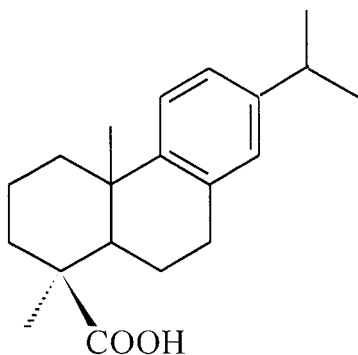


Figure 1 Structure of dehydroabietic acid.

(MW 300, mp173°C, UV268 nm, 276 nm) was separated from disproportionated rosin (Wuzhou Rosin Plant, Guanxi, China) according to the usual procedure.¹⁴

Preparation

Rosin-type nucleating agents was prepared by reaction of 1 mol dehydroabietic acid with 0.5 mol NaOH in ethanol to neutralize the acid to 50%, then cocrystallized at 60°C. The cocrystal of sodium dehydroabiectate and dehydroabiectic acid was separated, dried in vacuum, and then ground into powder with a nominal particle size of 65 μm , and marked as Nu-Na.

PP powder was mixed with LDPE and Nu-Na in a $\Phi 30$ twin screw extruder, respectively. The nucleated PP samples were dried and then injection molded into 1 mm thick sheet in an injection-molding machine (SZ-160/68 NB) at 230°C.

Measurements

Differential scanning calorimeter (DSC)

A Perkin-Elmer differential scanning calorimeter, DSC-7, interfaced with a BBC-Master computer via analogue to digital converter, was used to detect the thermal transition and to monitor the rate of heat flow from samples during crystallization. The amount of 5 ± 2 mg of each sample was placed in a DSC pan and rapidly heated at a rate of 80°C/min to 230°C for 10 min to remove all the memory of previous thermal and mechanical history.

To detect the crystallization temperatures of PP samples, this treatment was followed by cooling at a rate of 10°C/min to room temperature to complete crystallization.

In the experiments performed to study kinetics of isothermal crystallization, the samples were submitted to the same thermal treatment in melt state and then cooled at a rate of 200°C/min to the appropriate crystallizing temperature. The rate of heat flow during the development of crystalline phase against time was

recorded up to vanishing thermal effect and analyzed according to the usual procedure to give the relative degree of crystallinity as a function of time.

Polarization microscope (PLM)

The amount of 0.1 g of each PP sample was placed on a hot stage and melted at 230°C. Each PP sample was pressed between glass slides and coverslips, and kept there for 10 min to remove all the memory of previous thermal and mechanical history, then quickly transferred to another hot stage and kept at a constant temperature of 130°C for 1 h. After that, they were quenched in liquid nitrogen. The thickness of PP samples was about 20 μm . The morphology of spherulites was observed by a polarization microscope, Leica MPS30.

Haze measurement

The haze was measured by a WGT-S hazemeter according to National Standard Testing Methods GB2410-80, the lower the haze, the higher the transparency.

RESULT AND DISCUSSION

Nonisothermal crystallization

From a technical point of view, nonisothermal crystallization conditions approach more closely the industrial conditions of polymer processing, so that the study of crystallization of polymers under nonisothermal conditions is of great practical importance. Figure 2 shows DSC cooling curves of PP, LDPE, PP/LDPE, PP/Nu-Na, and PP/LDPE/Nu-Na at a rate of 10°C/min.

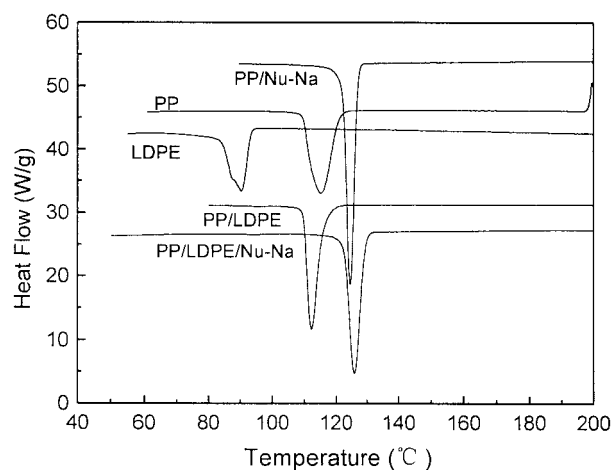


Figure 2 DSC cooling curves of PP, LDPE, PP/LDPE (97:3), PP/Nu-Na (100:0.5), and PP/LDPE/Nu-Na (97:3:0.5).

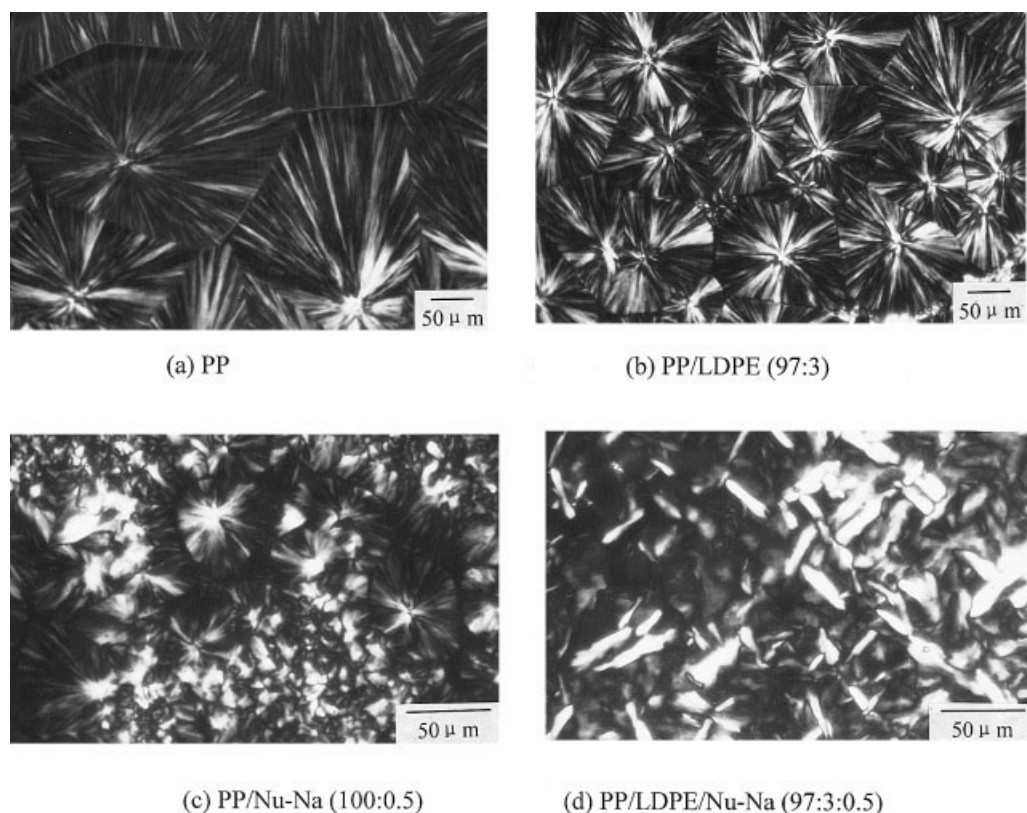


Figure 3 PLM micrographs of (a) PP, (b) PP/LDPE (97:3), (c) PP/Nu-Na (100:0.5), and (d) PP/LDPE/Nu-Na (97:3:0.5).

Only an exothermic peak can be found in Figure 2 for all samples. The crystallizing peak temperature (T_{CP}) of pure PP and pure LDPE are 115.2 and 90.3°C, respectively. The exothermic peaks of PP/LDPE, PP/Nu-Na, and PP/LDPE/Nu-Na in Figure 2 belong to the PP crystallizing peak, which are 112.2, 124.5, and 126.2°C, respectively. The T_{CP} of PP/LDPE was decreased 3.0°C compared with pure PP. The decrease in T_{CP} indicates that LDPE obstructs the crystallization of PP and decreases the crystallization rate of PP. This was because a small addition of LDPE ($\leq 10\%$) and PP in melt was partially miscible, and a small addition of LDPE ($\leq 10\%$) caused the depressed of spherulite growth rate of PP.¹²

Oppositely, compared with pure PP, the increase in T_C was 9.3°C for PP/Nu-Na, and 11.0°C for PP/LDPE/Nu-Na. The larger T_{CP} values and much sharper peak of PP/Nu-Na indicate that the crystallization rate of PP was increased with addition of Nu-Na, and the T_{CP} of PP was further increased with addition of a few LDPE, it may be that LDPE had higher melt flow index than PP at PP processing temperature, lower melt viscosity of PP/LDPE¹⁵ made Nu-Na dispersed in PP more uniformly, so that the nucleating efficiency was improved greatly, it compensated the delaying effect of LDPE on the PP crystallization. The above assumption was proved by PLM photographs of spherulites. Figure 3 shows the pho-

tographs of spherulites in four PP samples, Pure PP, PP/LDPE, PP/Nu-Na, and PP/LDPE/Nu-Na.

All these spherulites developed in the same condition (130°C, 1 h). For pure PP and PP/LDPE, the PP all show entire spherulites, and the spherulites' boundary appears clear. The average diameter of spherulites in Figure 3(a) and (b) is 250 and 100 μm , respectively. Since LDPE can depress the spherulite growth rate of PP, the diameter of spherulites in PP/LDPE is smaller than that in pure PP. Nu-Na provided a larger number of heterogenous nuclei, so the size of spherulites are much smaller than that in pure PP and PP/LDPE, and the spherulites' boundary appears rough. In comparison with Figure 3(c), the spherulites in Figure 3(d) became smaller and dispersed more uniformly with the addition of 3% LDPE, the entire spherulites could not be seen. Generally, the smaller the PP spherulites, the higher the transparency of PP. The transparency of PP/LDPE/Nu-Na (Table I) was the best among four PP samples and proved the results of Figure 3 also.

TABLE I
The Haze of PP Samples

Samples	Pure PP	PP/LDPE (97:3)	PP/Nu-Na (100:0.5)	PP/LDPE/Nu-Na (97:3:0.5)
Haze (%)	67.2	46.9	30.9	17.5

Due to a small addition of LDPE (3%) in PP/LDPE and PP/LDPE/Nu-Na, the crystallization peak of LDPE cannot be seen in Figure 2 directly. When the DSC cooling curves of PP/LDPE and PP/LDPE/Nu-Na were magnified (Fig. 4), the LDPE exothermic peak appeared in 95.3 and 93.5°C, respectively. This indicates that LDPE crystallized after PP. Li et al.¹⁶ found a new exothermic peak that appeared in the PP/LDPE (20:80) blend at around 80°C in addition to the normal crystallization peaks of PP and LDPE; the additional lower temperature peaks in the PP/LDPE were identified as the crystallization of PP. This explanation for this was that PP was able to dissolve in the LDPE partly in melt state.¹¹ No new peak was found at around 80°C in addition to the normal crystallization peaks of PP and LDPE in Figure 4; this indicated that a small addition of LDPE (3%) in PP could not form PE-rich phase, it dissolved entirely in the PP.

Galeski et al.^{8,13} found that the overall crystallization rate of PP was strongly reduced by the addition of LDPE. The reduction in the overall rate was attributed to a decrease in the nucleation density, which was caused by the nuclei migration from PP to PE. The nuclei density was found decreased in PP phase after each blending, which was in turn caused by interfacial energy difference. Figure 5 shows DSC cooling curves of PP/LDPE/Nu-Na with different numbers of mixed passes at a rate of 10°C/min. From Figure 5, it can be found that the crystallization temperature of PP and LDPE did not change at all after each blending; this demonstrated that the overall crystallization rate of PP was not affected by the numbers of mixed passes and the nuclei migration from PP to PE had not happened in the mixed passes. The result was different from that of Galeski et al. The reason may be that the amount of LDPE in the PP/LDPE blends was above 10% in the study of Galeski et al., PP and LDPE were immiscible,

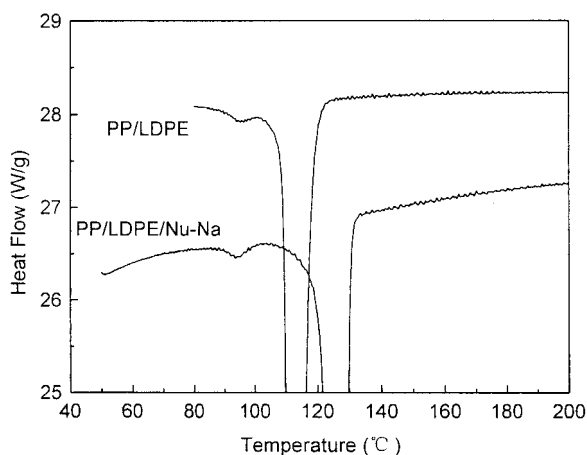
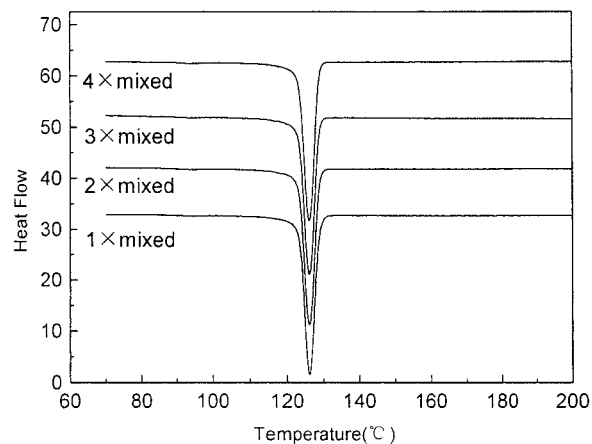
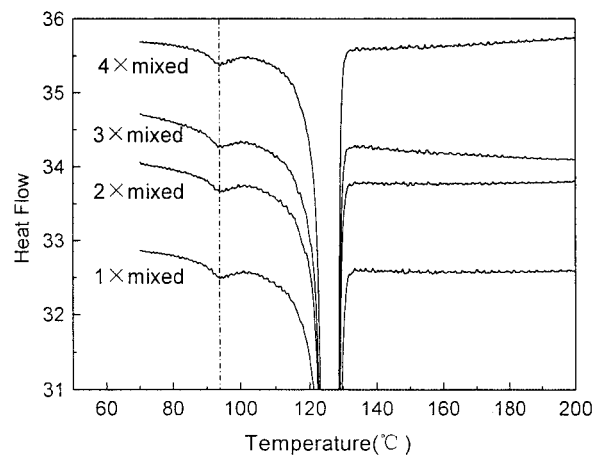


Figure 4 Magnified DSC cooling curves of PP/LDPE (97:3) and PP/LDPE/Nu-Na (97:3:0.5).



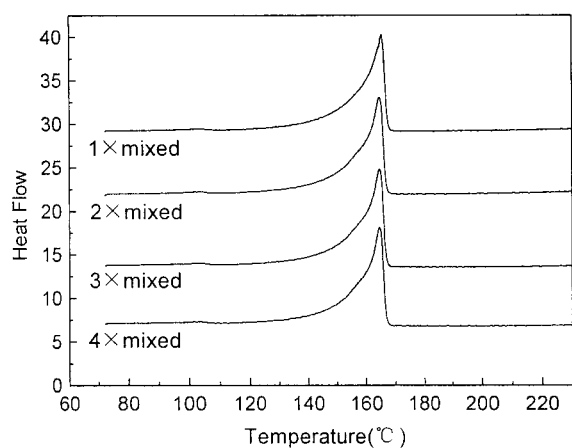
(a)



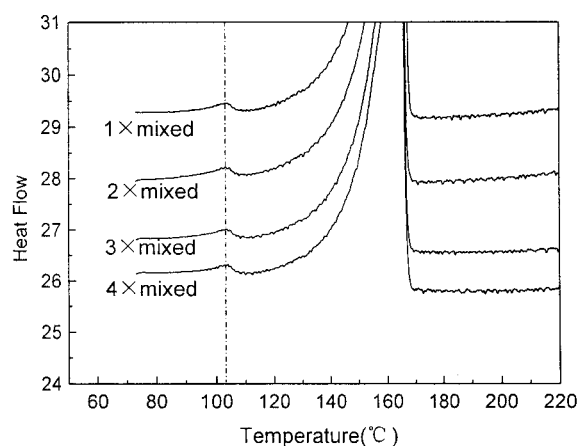
(b)

Figure 5 DSC cooling curves of PP/LDPE/Nu-Na (97:3:0.5) with different numbers of mixed passes.

there was liquid-liquid phase separation in PP and LDPE, and the nuclei migration from PP to PE could happen in the PP/LDPE mixed passes. In this work, the amount of LDPE in the PP/LDPE blends was only 3%, the LDPE was miscible with PP, and they formed only one phase, so the nuclei migration from PP to PE in PP/LDPE could not happen in the mixed passes. On the contrary, LDPE could improve the dispersion of Nu-Na in PP; thus the nucleating efficiency of Nu-Na was further increased. Figure 6 shows the DSC heating curves of PP/LDPE/Nu-Na (97:3:0.5) with different numbers of mixed passes. It can be found that the melting temperature (T_m) of PP and LDPE do not change also after each blending.



(a)



(b)

Figure 6 DSC heating curves of PP/LDPE/Nu-Na (97:3:0.5) with different numbers of mixed passes.

Isothermal crystallization

Isothermal crystallization of polymers can be described by the Avrami equation. The relative degree of crystallinity θ at time t is given by¹⁷

$$\theta = \frac{X_c(t)}{X_c(\infty)} = \frac{\int_0^t \frac{dH(t)}{dt} dt}{\int_0^{\infty} \frac{dH(t)}{dt} dt} \quad (1)$$

where $X_c(t)$ and $X_c(\infty)$ are the absolute degrees of crystallinity at time t and the completing crystallization time respectively, and $dH(t)/dt$ is the rate of heat flow in the process of isothermal crystallization at time t . Time t was measured from the moment when the

sample was cooled to the appropriate crystallization temperature. The θ can also be obtained from the expression^{17,18}

$$1 - \theta = \exp(-Kt^n) \quad (2)$$

$$\ln(-\ln(1 - \theta)) = n \ln t + \ln K \quad (3)$$

The n is the Avrami exponent, which is determined by the mode of crystal nucleation and the crystal growth geometry in actual circumstance; K is the rate constant, which is also a function of nucleation and growth of crystals. The plot of $\ln[-\ln(1 - \theta)]$ against $\ln t$ is a straight line, whose slope is n and its intercept on ordinate is $\ln K$.

When $\theta = 0.5$ in formula (3), it gives out the data of crystallization half time $t_{1/2}$, which is the time taken for 50% of the total crystallization to occur:

$$t_{1/2} = \left(\frac{\ln 2}{K} \right)^{\frac{1}{n}} \quad (4)$$

The lowest temperature for isothermal crystallization was chosen to be above the highest temperature at which the LDPE was able to crystallize. Results of $t_{1/2}$, n , and K of PP samples are listed in Table II.

In the ideal state of heterogeneous nucleation of PP crystallization,¹⁷ n should be exactly 3. In the actual process of crystal growth, the real circumstance cannot satisfy the ideal state that the Avrami equation supposes to have. In addition, the practical measurement is determined by both the temperature and thermal history of crystal growth.¹⁸ It was found that the values of n increased slightly as the crystallization tem-

TABLE II
Avrami Values of n , K , and $t_{1/2}$

Sample	T_c (°C)	n	K (s ⁻ⁿ)	$t_{1/2}$ (s)
Pure PP	119	1.7	1.71×10^{-3}	37
	121	1.7	0.73×10^{-3}	53
	123	1.8	0.26×10^{-3}	87
	124	1.8	0.13×10^{-3}	118
	125	1.8	0.09×10^{-3}	157
PP/LDPE	121	2.1	6.01×10^{-5}	83
	123	2.4	4.31×10^{-6}	148
	125	2.2	4.68×10^{-6}	226
	126	2.3	9.13×10^{-7}	338
	127	2.2	1.31×10^{-6}	387
PP/Nu-Na	129	1.8	1.17×10^{-3}	33
	131	2.2	5.35×10^{-5}	68
	133	2.4	4.98×10^{-6}	150
	135	2.3	8.19×10^{-7}	423
PP/LDPE/Nu-Na	129	1.2	2.24×10^{-2}	16
	131	1.5	3.60×10^{-3}	32
	133	2.2	4.71×10^{-5}	77
	135	2.0	2.59×10^{-5}	159
	137	2.1	3.06×10^{-6}	386

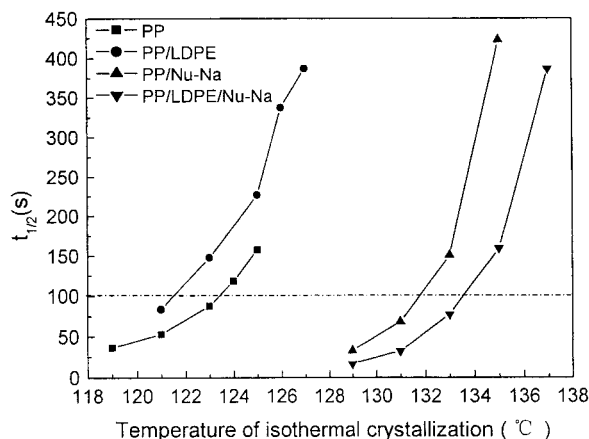


Figure 7 Curves of half time of isothermal crystallization vs temperature.

perature increased, but they all were close to 2, indicating that the crystallization process was heterogeneous and took place within two dimensions.¹⁹

In Table II, the rate constant K decreases as temperature increases. Temperatures at which isothermal crystallization was conducted are higher than that of the maximum rate of crystallization. Consequently, the higher the temperature of isothermal crystallization, the larger the distance from the temperature of the maximum rate of crystallization, and the lower the rate of crystallization.

Figure 7 shows the crystallization half time $t_{1/2}$ vs temperature. The rate of crystallization of polymers can be estimated by the crystallization half time, when the crystallization temperature is the same, or by the excessive cooling degree (ΔT) that the crystallization needs, when the rate of crystallization is the same (same crystallization half time). The excessive cooling degree is defined as difference between the equilibrium melting temperature (T_m^0) and crystallization temperature (T_c).

$$\Delta T = T_m^0 - T_c \quad (5)$$

The excessive cooling degree that the different samples need at the same rate of crystallization is different. The samples that need a smaller excessive cooling degree have a faster rate of crystallization, if they crystallize at the same crystallization temperature. When $t_{1/2}$ of PP samples is 100 s, for pure PP, PP/LDPE, PP/Nu-Na, and PP/LDPE/Nu-Na, T_c is 123.4, 121.5, 131.8, and 133.6°C, respectively, namely, ΔT is 74.6, 76.5, 66.2, and 64.4°C ($T_m^0 = 471\text{K}$),¹² respectively. Obviously, PP/Nu-Na and PP/LDPE/Nu-Na need smaller excessive cooling degree than pure PP; this indicates that Nu-Na can accelerate the rate of crystallization for PP, and act as an effective nucleating agent of PP. At the same time, LDPE can improve

the dispersion of Nu-Na in PP, and the nucleating efficiency can be further increased. On the contrary, PP/LDPE needs a bigger excessive cooling degree than pure PP; the presence of LDPE reduced the rate of crystallization. These results are consistent with that of nonisothermal crystallization.

CONCLUSIONS

The rosin-type nucleating agent Nu-Na substantially improved the crystallization temperatures of PP, namely the rate of crystallization, and decreased the size of spherulites also. When a small amount of LDPE (3%) was added in PP, they were partially miscible in melt state, and formed one phase, so the nuclei migration from PP to PE could not happen in the mixed passes. As PP/LDPE had lower melt viscosity at the PP processing temperature than PP, it allowed Nu-Na to be dispersed in PP more uniformly; thus the nucleating efficiency of Nu-Na was improved greatly, and the delaying effect of LDPE on the PP crystallization was compensated. Thus, the cooperative effect of LDPE and Nu-Na made the crystallization rate of PP increase greatly, the spherulites of PP became much smaller and dispersed more uniformly, and the transparency of PP was improved evidently.

Kinetics analysis of PP isothermal crystallization proved that the values of the Avrami exponent n increased slightly as the crystallization temperature increased, but they all were close to 2, indicating that the crystallization process was heterogeneous and took place within two dimensions.

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