Isothermal Crystallization Behavior and Melting Characteristics of Injection Sample of Nucleated Polypropylene

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ABSTRACT: The isothermal crystallization behavior and melting characteristics of pure polypropylene (PP) and PPs nucleated with a phosphate nucleating agent (A) and a sorbitol derivative (D) have been studied by differential scanning calorimetry (DSC). Compared with pure PP, nucleated PPs show a shorter half-times of crystallization. Dependence of crystallization rate of nucleated PP on the crystallization temperature is stronger than that of pure PP at the higher crystallization temperature, whereas the opposite results are obtained at the lower crystallization temperature. Addition of nucleating agent shifts the temperature at the deviation from the baseline of DSC melting curve, T_m^o, and the temperature at the completion of melting, T_m^f, to higher temperatures, indicating that nucleated PPs exhibit a higher perfection of PP crystals. A shoulder peak in the high temperature range of melting peak of nucleated PP and a wider low temperature region in the melting peak of pure PP are observed. Obviously, PP and nucleated PPs form different distribution of crystal perfection in the isothermal crystallization process. According to the half-time of crystallization, nucleating agent A is more effective than D. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 78: 2547–2553, 2000

Key words: polypropylene; nucleating agent; isothermal crystallization; melting characteristics

INTRODUCTION

Addition of nucleating agent to polypropylene (PP) has become an important method to optimize the physical and mechanical properties of PP. There are many articles reporting on nucleated PP.[1–15] Nucleating agents not only increase the mechanical properties of PP, but also shorten the cycle time of production. Although many of nucleating agents are used in practice, most of nucleating agents are discovered empirically. There are many details concerning the relationship be-

tween certain types of polymers and physical and chemical characteristics of nucleating agent that are not yet completely understood.[8] Binsbergen[1] believed that good nucleating agents of PP were crystal and included carbon hydrogen group (compatible with PP) and polar group or aromatic ring structure (incompatible with PP). Smith et al.[9] demonstrated that the nucleating agents of sorbitol derivatives, in the shape of a cleft, binded and stabilized the helical PP chains as PP was cooled below its melting point. This binding stabilized the helix, thereby increased the number of helix or decreased the number that returned to a random conformation. Sterzynski et al.[8] found that the nucleating effect of dibenzylidene (DBS) and di-p-methylbenzylidene sorbitol (MDBS) was

much better than that of sodium benzoate (NaBz). They stated that DBS and MDBS could form a three-dimensional network of twisted filaments constructed from their axialite crystals, and this continuous network of fine filaments might perform a better degree of dispersion and increase an interface area between polymer and nucleating agent. On the other hand, NaBz was dispersed in PP as solid particles. Shepard et al.[12] also thought that MDBS in PP formed a three-dimensional network of nanofibrils. At low concentrations of MDBS, the nanofibrils served as nucleating sites to induce heterogeneous nucleation of PP spherulites. The activity of nucleating agent depended on its size, shape, the morphology of the seed surface, the precise chemical nature of the seed after incoperation into the polymer,[16] and even on its thermal history.[8]

According to the chemical structure of nucleating agents, they can be divided into the inorganic nucleating agent and the organic nucleating agent. The inorganic nucleating agents include talc, silica, kaolin, carbon black, and so on. Binsbergen[2] thought that the nucleating effect of the inorganic nucleating agents was poor. Compared with the inorganic nucleating agents, the organic nucleating agents show good nucleating effect. The organic nucleating agents include NaBz,[12] the sorbitol derivatives,[4–9,17,18] and the organic phosphate. The most effective nucleating agents are the sorbitol derivatives and the organic phosphate. The different nucleating agents not only show different nucleating effect, but also influence differently the physical and mechanical properties of nucleated PP. Some of nucleating agents cause PP to crystallize in β modification, such as calcium pimelate,[19] quinacridone, and cadmium,[20] some mainly improve the optical clarity of nucleated PP, such as the sorbitol derivatives, and some mainly improve the mechanical properties of nucleated PP, such as the organic phosphate.

The research on PP nucleated with the organic nucleating agents is very extensive.[4–9] Kim and Kim[17] studied the crystallization behaviors of PP nucleated with the sorbitols. The addition of the nucleating agent up to their saturation concentration in PP increased the number of effective nuclei by three orders of magnitude, and the crystallization peak temperature by 17°C. If the concentration of nucleating agent was too high, the number of nuclei decreased due to agglomeration. Mai et al.[21] compared the effect of different nucleating agents on mechanical properties and crystallization temperature of PP. Kim et al.[7] observed that isothermal crystallization behavior of nucleated PP strongly depended on the crystallization temperature. The nucleating agent increased the number of crystallization sites, reduced the spherulite size of PP,[6,17,22] and improved clarity of PP. Chen and Xu[23] stated that the nucleating agent only influenced the rate of crystallization but exerted no effect on the equilibrium melting point of PP. They also studied the thermal stability of PP nucleated with calcium carbonate, NaBz, and terephthalic acid.[24]

Although there are many papers on PP nucleated with the inorganic nucleating agents and the sorbitol derivatives, few papers on PP nucleated with the organic phosphate are seen. In the present work, isothermal crystallization behavior and melting characteristics of injection samples of PP and PPs nucleated with an organic phosphate (A) and a sorbitol derivative (D) are studied by DSC in detail. At the same time, the nucleating effect of the nucleating agents is studied and compared.

EXPERIMENTAL

Materials

A commercial grade of PP (J 900 GP) was supplied by Idemitsu Petrochemical Co. Ltd (Japan). The nucleating agent A is sodium 2,2′-methylene-bis(4,6-di-tert-butylphenyl) phosphate (tradename: NA-11) supplied by Asahi Denko Co. Ltd (Japan), and the nucleating agent D is bis(p-ethylbenzylidene) sorbitol (tradename: NC-4) supplied by Mitsul Tontsu Chemicals (Japan).

Sample Preparation

Preparation of Masterbatches of Nucleated PP

The nucleating agent was dissolved easily in volatile solvent and a solution was obtained. PP and the solution were mixed in a high-speed blending machine. After the solvent evaporated completely, the mixtures were extruded with a twin-screw SHJN-200 extruder produced by Xinli Plastic Mechanical Factory of Nanjing Aerospace University. The extruding temperatures were 205–220°C, and the screw rotation rate was 80 r/min. The masterbatches of nucleated PP containing 2.1% nucleating agent were prepared. PP alone was also treated similarly as blank sample.

Table I DSC Isothermal Crystallization Results of PP and Nucleated PP Crystallized at Different Temperatures for 30 min

Sample	T_c (°C)	t_o (Min)	t_p (Min)	t_f (Min)	$t_{1/2}$ (Min)	t_{on} (Min)	ΔH_c (J/g)
PP	125	0.8	3.6	7.5	3.7	1.0	100.2
	126	1.1	5.0	10.4	5.1	1.4	96.0
	127	1.5	6.3	14.2	6.7	2.2	98.5
	128	1.7	8.5	16.9	8.8	2.3	100.0
PPA	135	0.8	2.4	7.5	2.5	1.0	101.4
	137	1.3	4.3	8.8	4.5	1.7	95.1
	138	1.8	5.1	11.7	6.0	2.5	98.1
	139	2.2	7.8	15.8	8.0	2.6	96.3
	140	2.4	10.2	17.9	10.1	6.4	97.9
PPD	133	1.9	3.6	7.1	3.8	2.2	102.9
	134	2.6	4.5	15.3	4.8	2.8	94.8
	135	2.4	5.3	10.6	5.6	3.1	98.6
	136	2.9	6.0	11.8	6.5	3.5	94.1
	137	3.8	9.5	18.0	10.3	5.4	98.2

T_c, isothermal crystallization temperature; t_o, time at the deviation from the baseline of DSC crystallizing curve; t_p, time required to reach the exothermic maximum; t_f, time at the completion of crystallization; T_{on}, time at the onset of crystallization; $t_{1/2}$, half time of crystallization; ΔH_c, heat of crystallization.

Preparation of Injection Sample of Nucleated PP

The nucleated masterbatches and PP (w/w : 1/20) were mixed. The tensile bars were injection-molded by 150ME-NC injection molder (Zhengde Plastic Mechanical Limited Co.) with set temperatures of 225–230°C. PP mixed with blank sample, and PPs nucleated with nucleating agent A and D were named PP, PPA, and PPD, respectively.

Isothermal Crystallization Process

Isothermal crystallization analysis was carried out in Perkin-Elmer DSC-7 in nitrogen atmosphere. The DSC specimens cut out from tensile bars were heated to 210°C at a rate of 100°C/min, held at 210°C for 3 min to eliminate thermal history, then cooled to designated crystallization temperatures at a rate of 100°C/min and isothermally crystallized for 30 min, and finally cooled to 50°C at a rate of 100°C/min. In order to study their melting characteristics, the crystallized specimens were heated from 50°C to 210°C at a rate of 20°C/min.

RESULTS AND DISCUSSION

Effect of Nucleating Agent on Isothermal Crystallization Behavior of PP

The DSC isothermal crystallization results of pure PP and nucleated PPs crystallized at differ-

ent temperatures after melted in 210°C for 3 min are presented in Table I. In the isothermal crystallization, the half-time of crystallization is used to evaluate the crystallization rate.[25] If the half-time of crystallization is short, this indicates that the crystallization is fast. Because nucleated PP crystallizes at high temperature at which pure PP hardly crystallizes, it is difficult to compare isothermal crystallization rates of pure PP and nucleated PPs in the same crystallization temperature. However, it can be seen from Table I that the half-times of crystallization of nucleated PPs at the higher crystallization temperature are still shorter than that of pure PP at the low crystallization temperature. For example, the half-time of crystallization of PP crystallized at 128°C is 8.8 min, whereas the half-time of crystallization of PPA crystallized at 135–139°C is 2.5–8.0 min and the half-time of PPD crystallized at 133–136°C is 3.8–6.5 min. It is suggested that the nucleating agents A and D significantly shorten the crystallization time and increase the crystallization rate of PP. It is very advantageous to shorten the cycle time of production. When the crystallization temperature (T_c) is 135°C, the half-time of crystallization of PPA is 2.5 min and that of PPD is 5.6 min; When the crystallization temperature (T_c) is 137°C, the half-time of crystallization of PPA is 4.5 min and that of PPD is 10.3 min. Therefore, the crystallization rate of PPA is faster than that of PPD and the nucleating effect of A is better than that of D. This result corroborates the con-
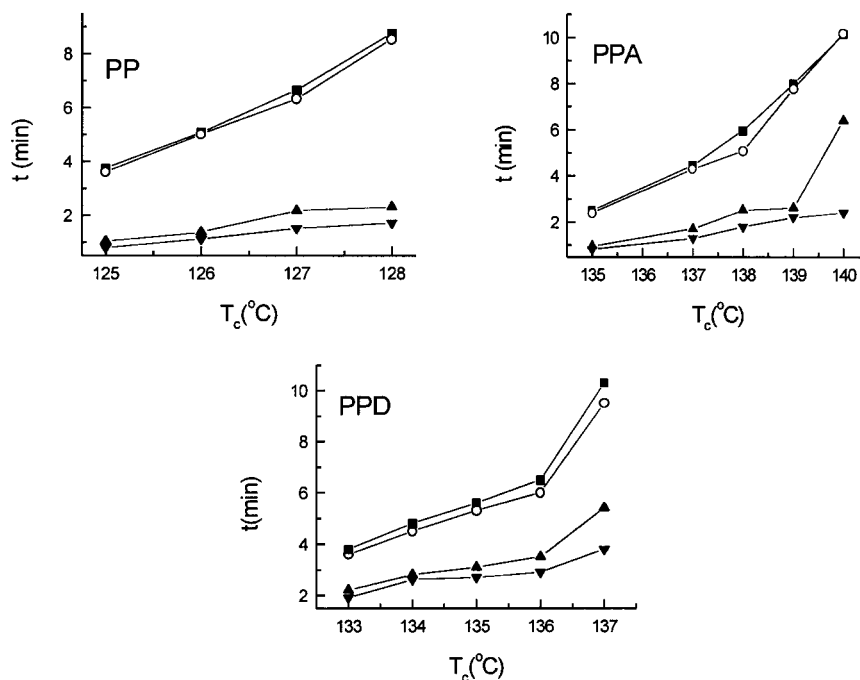
Figure 1 Effect of T_c on $t_{1/2}$ (■). t_p (○). t_{on} (▲). t_o (▼) of PP and nucleated PP.

clusion of nonisothermal crystallization, in which the crystallization peak temperature (T_c^p) is used to evaluate the nucleating effect of different nucleating agents.[26]

Dependence of Crystallization Rates of PP and Nucleated PPs on the Crystallization Temperature

The crystallization temperature (T_c) is one of main factors that influence crystallization behavior of polymer. The effect of the crystallization temperature on $t_{1/2}$, t_p, t_{on}, and t_o of PP and nucleated PPs is shown in Figure 1. The $t_{1/2}$, t_p, t_{on}, and t_o of PP and nucleated PPs increase as the crystallization temperature increases. It can be seen from Figure 2 that the $t_{1/2}$ and t_p of pure PP increase linearly with the increase of the T_c.
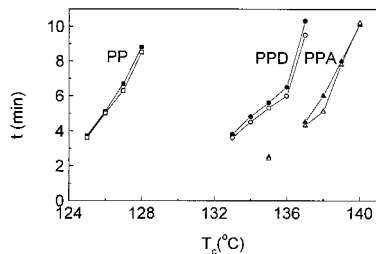

Figure 2 Effect of T_c on $t(1/2)$ (solid). t_p (open) of PP and nucleated PPs.

For nucleated PPs, the curves have two linear parts and exhibit transition points at a certain temperature (PPA at 137°C and PPD at 136°C). The slopes of linear parts of nucleated PPs at low crystallization temperature are smaller than that of pure PP, but the adverse results are observed when the T_c is at high crystallization temperature. It means the dependence of crystallization rate of nucleated PPs on the crystallization temperature when the T_c is below 136–137°C is smaller than that of pure PP, but the opposite results are obtained when the T_c is above 136–137°C. When the crystallization temperatures are below 136–137°C, the nucleation effect of nucleating agents is still effective and the dependence of crystallization rate of nucleated PPs on the crystallization temperature is smaller than that of pure PP. Because the T_c above 136–137°C is high enough to significantly reduce the nucleation effect of nucleating agent, the dependence of crystallization rate of nucleated PPs on the crystallization temperature is larger than that of pure PP. Kim et al.[7] studied the temperature dependence of nucleating effect of PPD (PP nucleated with NC-4) in the T_c of 135.8–144.1°C. They only observed that dependence of the effective nucleous number of nucleated PP on the crystallization temperature was stronger than that of pure PP. They stated that the logarithmic number of effec-

Table II   DSC Melting Results of PP and Nucleated PP after Crystallized in Different Temperatures for 30 min

Sample	T_c (°C)	T_m^o (°C)	T_m^p (°C)	T_c^f (°C)	ΔT_m (°C)	T_m^{on} (°C)	$\Delta T_m^{1/2}$ (°C)	ΔH_m (J/g)
PP	125	129.4	166.5	172.3	42.9	159.7	7.5	98.3
	126	130.0	165.4	171.0	41.0	161.0	5.3	99.3
	127	131.9	166.3	171.7	39.8	161.9	5.6	96.5
	128	132.1	166.4	171.9	39.8	161.3	6.6	101.3
PPA	135	138.8	166.3	175.6	36.8	150.6	13.6	99.7
	137	141.5	166.2	176.2	34.7	151.0	14.4	98.5
	138	141.9	166.2	175.6	33.7	151.3	14.9	100.5
	139	143.3	167.6	179.2	35.9	152.3	15.0	99.9
	140	144.6	167.8	178.5	33.9	152.5	15.5	102.0
PPD	133	137.5	164.0	172.5	35.0	149.3	14.4	100.1
	134	138.3	165.8	174.6	36.3	149.1	14.7	98.1
	135	139.4	165.6	174.6	35.2	149.2	14.4	101.5
	136	140.8	166.1	175.4	34.6	150.3	14.3	97.7
	137	141.3	165.7	175.0	33.7	151.8	14.3	97.9

T_c, isothermal crystallization temperature; T_m^o, temperature at the deviation from the baseline of DSC melting curve; T_m^p, peak temperature of melting curve; T_m^f, temperature at the completion of melting; T_m^{on}, temperature at the onset of melting; $\Delta T_m = T_m^f - T_m^o$, melting peak width; $\Delta T_m^{1/2}$, half-height width of melting peak; ΔH_m, heat of fusion.

tive nuclei decreased linearly with decreasing the degree of supercooling. The temperature dependence of the effect of the nucleating agent on PP crystallization was presented in terms of the deactivation factor, which was defined as the fraction of the active particles at one temperature but inert at the temperature one degree higher. The pure PP gave the smallest deactivation factor. The temperature dependence of nucleating effect of other nucleating agents had been observed, such as NaBz,[25] and talc.[3] It can be seen from Figure 1 and Table I that although t_p of PP and nucleated PPs is a little lower than $t_{1/2}$, t_p is very close to $t_{1/2}$. Therefore t_p is generally used to compare the crystallization rate of polymer crystallization.

Effect of Nucleating Agents on Melting Characteristics of PP

Table II shows the differential scanning calorimetry (DSC) melting results of PP and nucleated PPs after crystallized at different temperatures for 30 min. As the crystallization temperature increases, the T_m^o, T_m^{on}, T_m^p, and T_m^f of PP and nucleated PPs all shift to the higher temperature. This indicates that the crystal perfection of PP is improved as crystallization occurs at the higher temperature. Although the nucleating agents have no effect on T_m^p of nucleated PP, their T_m^o

and T_m^f shift to high temperature, suggesting that the addition of nucleating agents improves the crystal perfection of PP. However, the changing tendency of T_m^{on} is the opposite of the changing tendencies of T_m^o and T_m^f: T_m^{on} of nucleated PPs is lower than that of pure PP. The reason is that the shape of melting peak of PP is changed by addition of nucleating agents.

Effect of Nucleating Agent on the Shape of Melting Peak of PP

It can be seen from Figure 3 that the shapes of the melting curves of nucleated PPs are obviously different from those of pure PP. The fact that ΔT_m of PP is larger than that of nucleated PP demonstrates that the width of the melting peak of PP is wider than that of nucleated PP. Although the high temperature region of the melting peak of PP is narrow, there is a long "tail" in the low-temperature region. The long "tail" belongs to the poor perfect crystals that formed at the isothermal crystallization or during the cooling process after the completion of isothermal crystallization. Although the widths of the melting peaks of nucleated PPs are narrower than those of PP, the half-height widths of melting curves of nucleated PPs are wider than those of PP. It is possible that the addition of the nucleating agent would change the poor perfect crystals ("tail") to the good perfect crystals, so the half-height width
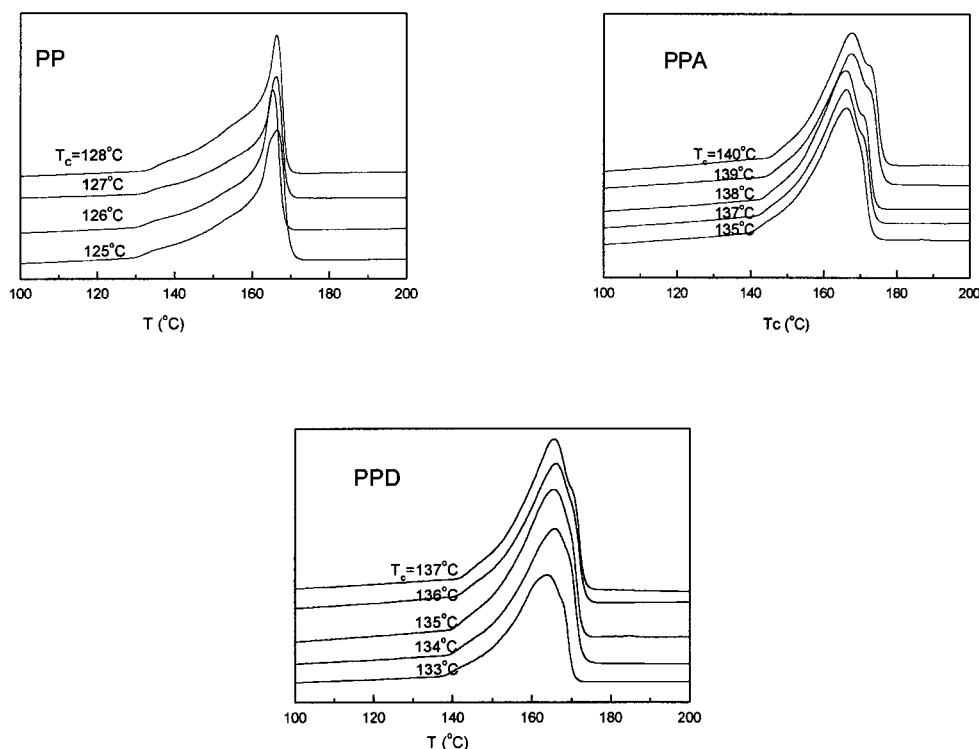
Figure 3 DSC melting curves of PP and nucleated PP crystallized in different temperatures for 30 min.

increases. The most interested fact is that the melting curves of PP have single melting peaks, but those of PPA and PPD have shoulder peaks in the high-temperature region and the shoulder peak becomes more significant as the crystallization temperature increases. This phenomenon has not been reported. It is suggested that the addition of nucleating agents change the distribution of PP crystal size, and PP and nucleated PPs form different crystal perfection. Nucleated PP not only form a part of crystals with similar melting peak temperature to that of PP, but also form crystals with better perfection. The perfection of nucleated PP increases with the increment of crystallization temperature.

CONCLUSION

1. The addition of nucleating agent NA-11 and NC-4 increases the crystallization rate and shortens the crystallization time of PP, and this effect of NA-11 is more obvious than that of NC-4.
2. The dependence of crystallization rate of nucleated PPs on the crystallization temperature at the crystallization temperature below 136–137°C is smaller than that of pure PP, but the opposite results are obtained at the crystallization temperature above 136–137°C.
3. The shape of the melting peak of nucleated PP is different from that of PP. The width of the melting peak of nucleated PP is narrower and the half-height width is wider than that of PP. A shoulder peak at the high-temperature region of the melting peak is present for nucleated PPs, whereas a single melting peak is observed for PP.

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