

Crystallization Behaviors of Polypropylene and Functional Polypropylene

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Received 27 November 2001; accepted 14 March 2002

ABSTRACT: The crystallization behaviors of polypropylene (PP) homopolymer and its blends with 0–15% functional polypropylene (FPP), the backbones of which were grafted with guanidine and diamide polymer chains, were investigated with differential scanning calorimetry and wide-angle X-ray scattering. The crystallization kinetics were studied with spectral depolarization. The results revealed that the presence of FPP reduced the crystallinity and crystallite size of PP. Meanwhile, FPP increased the crystallization rate. Compared with that of the PP homopolymer, the crystallization temperature of PP/FPP blends was increased by more than 10°C. During isothermal crystalliza-

tion, the relative crystallinity, developed as a function of time, was described by the Avrami equation. The half-time of crystallization for PP/FPP blends was much shorter than that for the PP homopolymer. The half-time of crystallization of PP/FPP blends depended much less on the crystallization temperature than that of the PP homopolymer. Therefore, FPP accelerated the crystallization rate of PP in a manner similar to that of a nucleator. © 2003 Wiley Periodicals, Inc. *J Appl Polym Sci* 88: 872–877, 2003

Key words: poly(propylene) (PP); crystallization; nucleation; differential scanning calorimetry (DSC); WAXS

INTRODUCTION

Polypropylene (PP) is a widely used material because of its outstanding mechanical properties and low cost. However, it has disadvantages. PP fiber is hydrophobic and difficult to dye because of the lack of dye sites to which dye molecules can be attached. The high crystallinity of PP also makes it difficult for dye molecules to penetrate into the interior of fibers. Grafting a highly hydrophilic monomer onto PP fibers is a well-known approach that overcomes these drawbacks.

A great amount of effort has been spent in researching polypropylene-graft-maleic anhydride,^{1–3} polypropylene-graft-acrylic acid (or methacrylic acid),^{4,5} and so forth. Such grafted PPs are usually used as compatibilizers in blends of PP and nylon, PP and polyester, and so on.^{6–9} However, these blends have a common shortcoming: it is difficult to find a compromise between excellent compatibility and dyeability.

The crystallization behavior of PP has a great effect on its mechanical properties and dyeability. Numerous investigations have been undertaken concerning the crystallization behavior of PP in its blends with other polymers. It has been reported that the crystallization of PP blends is influenced by the presence of the second component.^{10–15}

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The functional polypropylene (FPP) used in this study was manufactured by the grafting of guanidine and diamide polymers onto the backbones of PP. Therefore, it had excellent compatibility with PP; at the same time, FPP could offer enough dye sites without the addition of other polymers [e.g., nylon and poly(ethylene terephthalate)]. In previous work, we reported the effect of FPP on the dyeability of PP/FPP blends.¹⁶

In this work, the crystallization behaviors of PP and its blends with FPP were studied by differential scanning calorimetry (DSC) and wide-angle X-ray scattering (WAXS). The crystallization kinetics was studied by spectral depolarization.

EXPERIMENTAL

Materials and blend preparation

The PP homopolymer used in this work was Polypropylene Y1600 (Shanghai Petrochemical Co., Ltd., Shanghai, China), and FPP was purchased from Shanghai Sujie Science-Technology Co., Ltd. (Shanghai, China), without further purification. There was about 10 wt % of a modifying agent (guanidine and diamide polymers) grafted onto the backbone of PP in FPP. Figure 1 shows the IR spectra of PP and FPP. The IR spectra of FPP show the characteristic bands of

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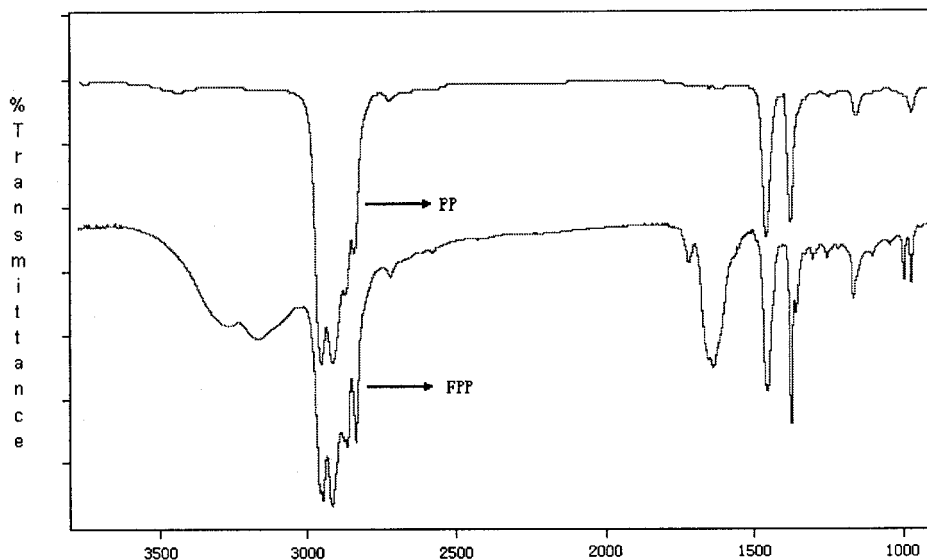


Figure 1 IR spectra of PP and FPP.

amidocyanogen and guanido groups at 3180, 3280, and 1640 cm^{-1} , respectively.

PP/FPP blends were prepared with a twin-screw extruder (SHL-35, Shanghai 4th Chemical Machine Factory, Shanghai, China). Before being extruded, PP and FPP were dried at 80°C for over 4 h. Mixtures of PP and FPP in appropriate ratios were extruded at 180°C under a screw speed of 110 rpm. The extruded strands were cooled via quenching in a water bath at room temperature and then were granulated.

Methods

DSC measurements were conducted with a PerkinElmer (DSC7) thermal analyzer (Foster City, CA). The samples

were heated up to 190°C at a rate of $20^\circ\text{C}/\text{min}$ under a nitrogen atmosphere and held there at 190°C for 5 min to destroy anisotropy. Afterward, the samples were cooled to room temperature at a rate of $400^\circ\text{C}/\text{min}$. The samples were measured from room temperature to 190°C at a rate of $10^\circ\text{C}/\text{min}$, held for 2 min, and then cooled to room temperature at the same rate. Both melting and crystallization parameters were obtained from the heating and cooling scans.

WAXS was performed with a Rigaku WAXS diffractometer (Japan) set at 40 kV and 30 mA with Cu $K\alpha$ radiation ($\lambda = 1.541\text{Å}$).

The crystallization kinetics were studied by spectral depolarization with a crystallization speedometer (JJY-1A, Testing Instruments Co., Yinkou, China). A

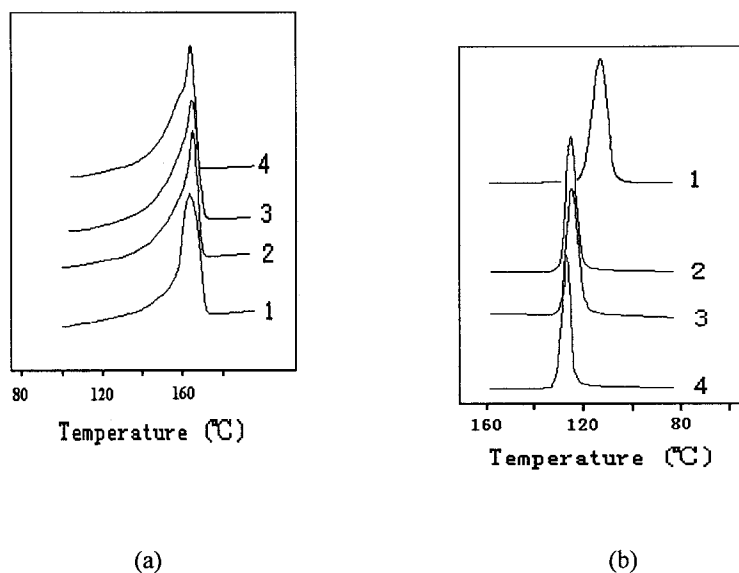


Figure 2 DSC thermograms of PP and PP/FPP blends: (a) heating scans and (b) cooling scans [(1) PP, (2) 95/5 PP/FPP, (3) 90/10 PP/FPP, and (4) 85/15 PP/FPP].

TABLE I
DSC Data for PP and PP/FPP Blends

Composition (PP/FPP w/w)	Melting (from heating scans)				Crystallization (from cooling scans)			
	Onset (°C)	T_m (°C)	ΔT_m (°C)	ΔH_f (J/g)	Onset (°C)	T_c (°C)	ΔT_c (°C)	ΔH_c (J/g)
100/0	157.1	164.8	16.3	95.8	126.6	113.1	18.9	99.9
95/5	145.9	165.5	25.4	104.7	135.2	125.5	13.9	105.1
90/10	148.1	166.7	25.7	105.0	134.1	124.9	14.2	102.6
85/15	146.8	164.3	25.8	99.6	137.6	126.9	14.1	99.7

crystalline polymer has the property of birefractance. In the process of the crystallization of a polymer sample put between orthogonal polarizers, the intensity of depolarized light will increase proportionally to the crystallinity of the sample.

RESULTS AND DISCUSSION

Effect of FPP on the crystallization behavior

The results of DSC heating and cooling scans for PP and PP/FPP blends are shown in Figure 2. The differences in the DSC curves of PP/FPP and PP are obvious.

The crystallization parameters of the samples obtained from the heating and cooling scans are given in Table I. The ΔH_f and ΔH_c are the melting and crystallization enthalpy per gram of the samples, respectively. The melting temperature (T_m) of the blends almost remains the same as that of PP (164.8°C). The onset T_m and the melting peak width (ΔT_m) are related to the least stability and distribution of crystallites, respectively. A clear decrease in the onset T_m in PP/FPP blends is found with respect to that of the PP homopolymer. The values of the onset T_m for PP/FPP blends are about 10°C lower than that of the PP homopolymer (157°C). Therefore, the values of ΔT_m for PP/FPP blends are wider by about 10°C than that of the PP homopolymer (16°C). These results indicate that the crystallites in the PP/FPP blends are less perfect than those in the PP homopolymer. A shift in the onset crystallization temperature represents the modification of the nucleation process. The onset crystallization temperatures of PP/FPP blends are about 8–11°C higher than that of the PP homopolymer (113°C). The crystallization peak temperature (T_c) represents the temperature at the maximum crystallization rate. Also, these temperatures of the PP/FPP blends are about 12–13°C higher than that of the PP homopolymer. Changes in the crystallization peak width (ΔT_c) represent the variation in the homogeneity of the crystallization. The ΔT_c values for the blends are about 5°C narrower than that of the PP homopolymer (19°C).

The observed crystallization behavior of the PP/FPP blends can be explained in terms of heterogeneous nu-

cleation. During the cooling process of the polymer melt, the polar macromolecules of FPP were excluded by the nonpolar matrix of PP and assembled to develop nuclei. Unlike other heterogeneous nucleation, such as blending with polyamide 6, poly(ethylene terephthalate), or another nucleator, the modifying agent used in this work was grafted onto the backbones of PP, so FPP had excellent compatibility with PP. The narrowed ΔT_c indicates that the crystallization rate of the PP/FPP blends is quicker than that of the PP homopolymer. The slope of the initial portion of the exotherm [i.e., from the onset temperature to the exotherm peak; see Fig. 2(b)] is indicative of the rapidity of nucleation. A higher value of this initial slope means a faster rate of nucleation. The higher or lower value of the onset temperature may be taken as indicative of the rate of the overall crystallization process (which includes both nucleation and growth).^{10–13} This is because of the increase in the nuclei. However, the increase in the nuclei may make it difficult to form a perfect crystalline structure. It is consistent with the lower values of the onset T_m and the widened ΔT_m for PP/FPP blends.

Effect of FPP on the crystallinity and crystal parameters

PP is a semicrystalline polymer. The WAXS diffractograms for PP and a PP/FPP blend, shown in Figures 3 and 4, have similar features. Both curves exhibit scattering angles at $2\theta = 13.920$, 16.660 , and 18.400 , indicating an α -phase monoclinic structure.¹⁷ The broadened background scattering area of the curves sug-

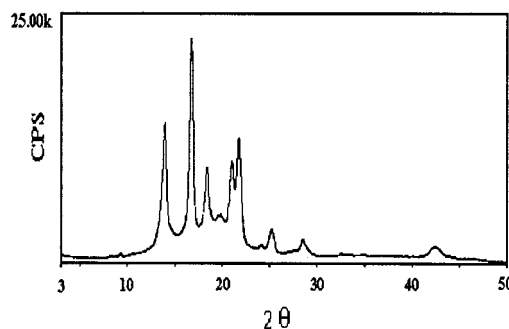


Figure 3 WAXS diffractogram of the PP homopolymer.

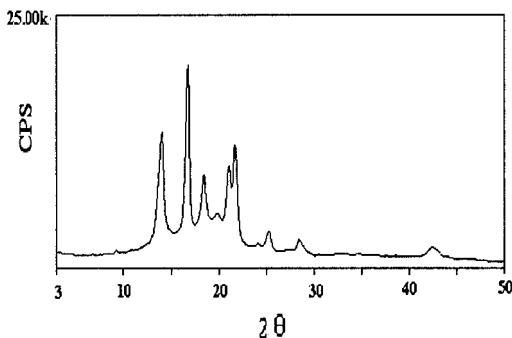


Figure 4 WAXS diffractogram of the 90/10 PP/FPP blend.

gests the presence of an amorphous structure. The degree of crystallinity can be estimated with the following formula:

$$\text{Crystallinity (\%)} = \frac{S_c}{S_c + S_a} \times 100$$

where S_c is the area of crystallization and S_a is the amorphous area.

As can be seen in Figure 5, the crystallinity decreases with an increase in the FPP content in the PP/FPP blends.

The crystallite size (D) vertical to the lattice plane (hkl) can be obtained by Scherrer's equation:

$$D = \frac{k\lambda}{\beta \cos\theta}$$

where k is the factor of the crystal figure, λ is the wavelength of the X-ray ($\lambda = 1.541\text{\AA}$), and θ is the diffraction angle. β is equal to $(B^2 - b_0^2)^{1/2}$, where B is the width at half-tallness of the diffraction peak and b_0 is the broadening factor of the instrument. If we take no account of the lattice distortion, the equation can be simplified as follows:

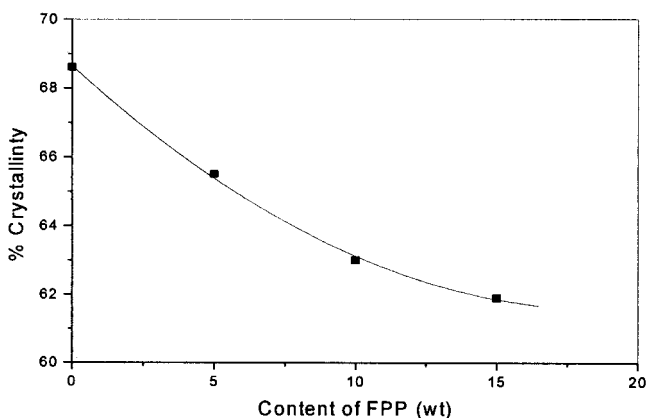


Figure 5 Crystallinity of the PP/FPP blends.

TABLE II
Crystal Parameters of PP and PP/FPP Blends

Composition (PP/FPP)	hkl	2θ	d_{hkl} (Å)	I	B (°)	D (Å)
100/0	110	13.82	6.40	65	0.42	188.56
	040	16.60	5.34	100	0.43	184.77
	130	18.26	4.85	42	0.51	156.14
95/5	110	13.92	6.36	62	0.48	165.01
	040	16.66	5.32	100	0.45	176.57
	130	18.40	4.82	43	0.51	156.17
90/10	110	14.02	6.31	62	0.48	165.03
	040	16.66	5.29	100	0.48	165.53
	130	18.48	4.80	43	0.51	156.17
85/85	110	13.94	6.35	65	0.63	126.04
	040	16.74	5.32	100	0.54	147.17
	130	18.40	4.82	45	0.54	147.50

$$D = \frac{0.89\lambda}{B \cos\theta}$$

The results of WAXS for PP and PP/FPP blends are shown in Table II and Figure 6. In Table II d_{hkl} is the space between lattice planes (hkl) and I is the relative intensity of the crystalline peaks.

As shown in Table II and Figure 6, D also decreases with an increasing amount of FPP, of which D for the lattice planes 110 and 040 decreases more evidently than that of lattice plane 130. These results indicate that the crystallization of PP/FPP blends is less perfect than that of PP homopolymers. As mentioned previously, many modifiers grafted onto the backbones of PP act as nucleators and lead to a decrease in crystallinity and the perfectibility of spherulites.

Isothermal crystallization kinetics

The isothermal crystallization kinetics of a material represent its crystalline conversion as a function of time at a constant temperature, which can be described by the Avrami equation:¹⁸⁻²⁰

$$1 - C = \exp(-Kt^n)$$

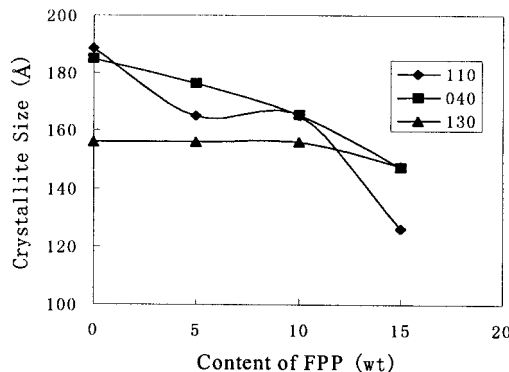


Figure 6 Crystallite size of the PP/FPP blends.

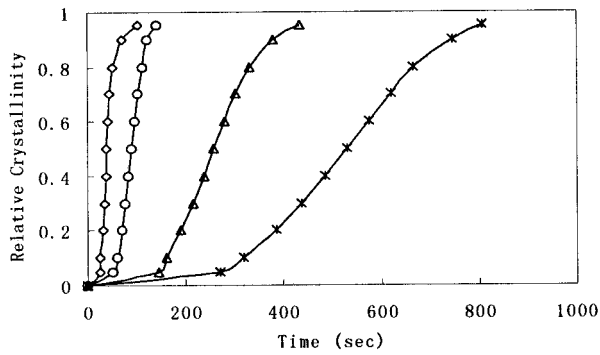


Figure 7 Development of the relative crystallinity with time for the isothermal crystallization of 90/10 PP/FPP at (\diamond) 115, (\circ) 120, (\triangle) 125, and (\times) 128°C.

where C is the crystallinity at time t , K is the crystallization rate constant, and n is the Avrami exponent that depends on the mechanism of nucleation and the form of crystal growth.

If the variety of the intensity of depolarized light at time t is $I_t - I_0$, the variety of the intensity of depolarized light when crystallization is completed is $I_\infty - I_0$, and C at time t can be represented as follows:

$$C = \frac{I_t - I_0}{I_\infty - I_0}$$

The Avrami equation can be rearranged as follows:

$$\frac{I_\infty - I_t}{I_\infty - I_0} = \exp(-Kt^n)$$

This equation can further be expressed in a logarithmic form:

$$\log[-\ln\left(\frac{I_\infty - I_t}{I_\infty - I_0}\right)] = n \log t + \log K$$

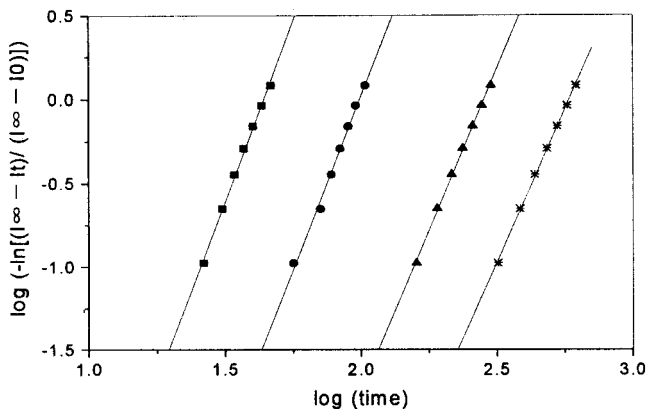


Figure 8 Plot of $\log\{-\ln[(I_\infty - I_t)/(I_\infty - I_0)]\}$ versus $\log t$ for the isothermal crystallization of 90/10 PP/FPP at (\blacksquare) 115, (\bullet) 120, (\blacktriangle) 125, and (\times) 128°C.

TABLE III
Kinetic Parameters from the Analysis of Isothermal Crystallization

Composition (PP/FPP)	Temperature (°C)	n	Log k	$t_{1/2}$ (s)
100/0	110	4.88	-8.3	45
	115	3.45	-7.4	126
	120	2.67	-7.6	611
	122	2.81	-8.6	1010
90/10	115	4.29	-7.1	40
	120	4.13	-8.2	90
	125	3.83	-9.4	258
	128	3.64	-10.1	529
85/15	115	5.38	-8.3	32
	120	4.56	-8.8	77
	125	4.58	-10.6	192
	128	3.90	-10.8	525

By plotting the left side in the equation against $\log t$, we can get a straight line. The n (slope of the straight line) and K (intersection with the y axis) values can be calculated.

Figures 7 and 8 present the results of the isothermal crystallization kinetics for 90/10 PP/FPP blends. Similar trends were observed for the blends at other mixing ratios. The overall kinetic parameters are summarized in Table III.

As can be seen in Figures 7 and 8, the lower the crystallization temperature is, the faster the crystallization rate is. It can also be found in Table III and Figure 9 that the half-time of crystallization ($t_{1/2}$) increases with the crystallization temperature. Compared with that of PP, $t_{1/2}$ of PP/FPP blends is much shorter, and $t_{1/2}$ decreases slightly with an increase in the content of FPP in the blends. This suggests that the crystallization rate of PP/FPP blends is faster than that of PP at the same crystallization temperature. From the results of the influence of the crystallization temperature on $t_{1/2}$, it is clear that the crystallization rate of PP/FPP blends depends much less on the temperature than that of PP. The $\log k$ values decrease as the crystallization temperature increases, and this implies a decrease in the nucleating rate.

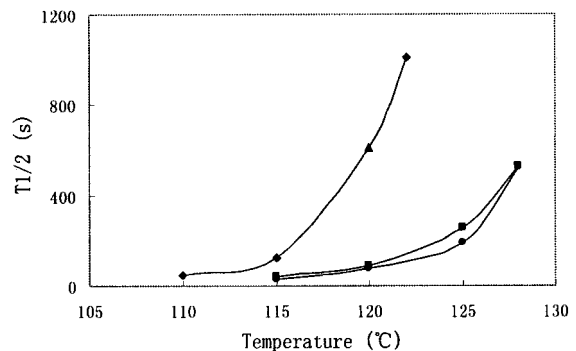


Figure 9 $t_{1/2}$ -temperature curves of PP and PP/FPP blends: (\blacktriangle) PP, (\blacksquare) 90/10 PP/FPP, and (\bullet) 85/15 PP/FPP.

The differences in the n values for the samples mean different crystallization mechanisms. In an ideal state, n should be 3 for heterogeneous nucleation and 4 for homogeneous nucleation. The number 3 represents the dimensions of the spherulitic development, and 4 represents the dimensions of the spherulitic development with a time dimension of nucleation added. However, the n values usually are not integers because of the complexity of the nucleating mechanism and the nonconstant growth rate of the spherulite. The nonintegral value indicates overlapping of different types of crystals. The n values for PP/FPP blends are larger than those for PP at corresponding crystallization temperatures. Therefore, the crystallization of PP proceeds mainly by a homogeneous nucleation mechanism, whereas that of PP/FPP blends proceeds by both homogeneous and heterogeneous nucleation mechanisms. The homogeneous nucleation starts spontaneously by chain aggregation below T_m , which takes a longer time. In contrast, the heterogeneous nuclei form simultaneously as soon as the sample reaches the crystallization temperature. Consequently, homogeneous nucleation requires longer times and lower crystallization temperatures.

FPP acts as a nucleator and accelerates the nucleation. The overall crystallization rate of PP/FPP blends is affected by both heterogeneous and homogeneous nucleation. There are two kinds of nuclei: one accelerated by FPP and the other not accelerated by FPP. The process of nucleation of PP/FPP blends is a kind of typical periodical heterogeneous nucleation. The homogeneous nucleation is weaker than heterogeneous nucleation at high crystallization temperatures because the free energy of formation of a growth embryo is high. However, the homogeneous nucleation should not be ignored at low crystallization temperatures. The nucleation mechanism is more complex at low temperatures than that at high temperatures. At lower temperatures, the n values for the samples are even over 4, such as 4.88 for PP at 110°C, 4.29 for 90/10 PP/FPP at 115°C, and 5.38 for 85/15 PP/FPP at 115°C. However, with the increase in the crystallization temperature, the crystallization rate decreases, and the nucleation mechanism changes to instantaneous homogeneous nucleation, leading to the decrease in the nuclei density and n .^{14–16}

Because the presence of FPP accelerates the nucleation and increases the number of nuclei significantly, the spherulite size is reduced in the blends. This is

consistent with the findings obtained from DSC and WAXS measurements.

CONCLUSIONS

FPP addition has a remarkable effect on the crystallization behaviors of PP blends. FPP acts as a nucleation agent and accelerates the crystallization. The crystallization temperature of PP/FPP blends is 10°C higher than that of PP. Compared with that of the PP homopolymer, $t_{1/2}$ of PP/FPP blends is much shorter and depends less on the crystallization temperature.

However, blending with FPP does not alter the crystal conformation α -phase monoclinic structure. The crystallinity decreases as the FPP content increases, and so does D . These results indicate that the crystallization of PP/FPP blends is less perfect than that of the PP homopolymer.

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