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Nonisothermal Crystallization Kinetics of Polypropylene/Polyethersulfone Blend

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Summary

The nonisothermal crystallization kinetics of PP and PP/PES (80/20 wt%) blend was investigated by using differential scanning calorimetry (DSC). It was observed that the crystallization peak temperature (T_p) and the half time ($t_{1/2}$) of crystallization of PP/PES blend are slightly but consistently lower than those of PP at various cooling rates. The nonisothermal crystallization data were analyzed by using Avrami equation, Ozawa and Mo method. The validity of the different kinetics models to the nonisothermal crystallization process of two samples is discussed. The Mo method can successfully explain the overall nonisothermal crystallization process of PP and PP/PES blend. The activation energy (ΔE) for nonisothermal crystallization of PP and PP/PES blend is determined by using the Kissinger method. The result shows that the ΔE value of PP is slightly higher than that of PP/PES blend.

Introduction

Polypropylene (PP) is semi-crystalline polymer. PP resins have been extensively used in various products such as automobile, furniture, packaging and so on. However, PP has a poor impact strength at lower temperatures that limits PP to be used as an engineering plastic. So PP has been improved by blending various materials [1-3], such as PP/EP [4], PP/LDPE [5], ethylene-propylene-diene terpolymer (EPDM) [6,7], talc-filled PP [8], metallocene PP [9] and so on. Nowadays, much attention has been paid to polymer blends. The blending of two or more polymers has become an important technique in order to improve the cost performance ratio of commercial plastics. The former examples are PP composites blending the other common plastics. In recent years, PP nanocomposites has been studied extensively, including PP-carbon nanotubes [10], PP-surface-treated SiO_2 [11], isotactic PP-$CaCO_3$ [12], PP-montmorillonite [13], etc. However, to our knowledge, PP blends with special engineering plastics were seldom studied. So we chose Polypropylene/Polyether-sulfone (PES) blend as the object of study to investigate its performance. PES is a versatile thermoplastic and possesses high mechanical intensity, thermal stability and chemical resistance. In addition, it has low creep property, flame retardancy, excellent insulation property and high dielectric strength. Therefore, PES is widely used in aeronautic materials, microelectronics, automobile, membrane separation etc [14].

The crystallization behavior of PP and its blends is very important for the manufacture of plastics because the physical properties of the blends depend on the crystallinity, morphology, and glass-transition temperature etc. A good understanding of crystallization mechanisms is necessary for being able to design materials with better mechanical properties. In this paper, the nonisothermal crystallization behavior of PP and PP/PES (80/20 wt%) blend were studied and compared. Our aim is mainly that we attempted to use PES as a modifier material of PP. Considering the price of PES is relatively high, when PES was blended with PP resin; its content in PP matrix should remain relative low. In the PP/PES (80/20) blend, the ratio of 80/20 is randomly selected to research in order to obtain the first-hand information on PP/PES blends. The next work will be more detailed, different composition of PP/PES blends including 95/5, 90/10, 85/15, 75/25 and 70/30 etc will be investigated on base of this research, and the experiments and conclusions relevant to the next research will be published in another paper. Dynamic differential scanning calorimetry (DSC) thermogram provided the necessary data, and the Avrami equation, Ozawa equation and Mo method were employed to obtain relevant kinetics parameters. At last, Kissinger method was applied to calculate the activation energy of crystallization.

Experimental

Raw Materials and Sample Preparation

PP K1005 pellets (MFI is 3g/10min, density is 0.905 g/cm^3) was purchased from Sinopec Beijing Yanshan Chemical Corporation (China) and used without any treatment. PES Ultrason 6020P (M_w=5800, T_g=225°C) was purchased from BASF Co. Ltd (Germany). PP and PES were dried in an oven at 80°C and 120°C for 12h before used. PP and PES were melted extruded by using a twin-screw extruder with a screw diameter of 20 mm and L/D ratio of 34. The screw rate was set at 160 rpm. The barrel of the extruder has seven temperature-control zones and their temperatures were set at 200 - 220 - 275 - 280 - 280 - 275 - 260°C (from hopper to die). The weight ratio of PP/PES is fixed at 80/20.

DSC analysis

Nonisothermal crystallization was carried out in the sample pan of a Perkin-Elmer Diamond Differential scanning calorimeter, instrument's operating temperature were calibrated with indium. The standard process is as follows: the samples (about 5mg) were heated from 20°C to 240°C with heating rate 150°C/min, maintain for 5 min in order to eliminate thermal history, then they were cooled at a constant cooling rates of 5, 10, 15, 20 and 30°C/min, respectively.

Results and discussion

The effects of PES on the crystallization behavior of PP were analyzed through DSC experiments. Figure 1 shows the crystallization thermograms of PP and PP/PES blend at selected cooling rates of 5, 10, 15, 20, and 30°C/min, respectively. The crystallization peak temperature (T_p), the crystallization enthalpy (ΔH_c^0) and the half time of the crystallization ($t_{1/2}$) were listed in Table 1.

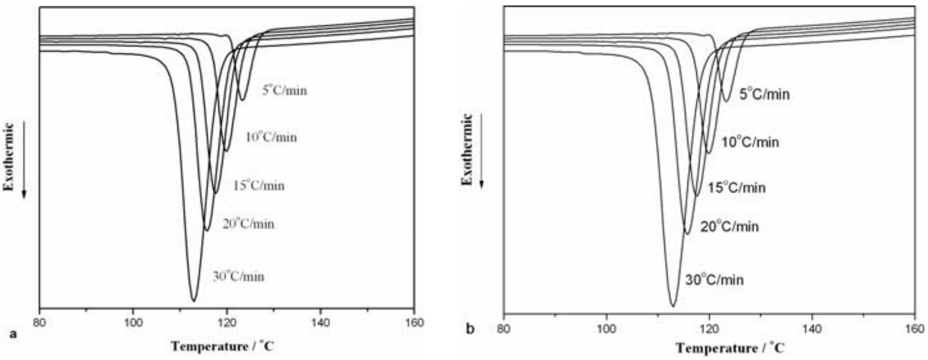

Figure 1. DSC thermograms of (a) PP and (b) PP/PES blend at various cooling rate.

Table 1. Values of the crystallization peak temperature (T_p), the crystallization enthalpy (ΔH_c^0) and the half time of the crystallization ($t_{1/2}$) for the PP and PP/PES blend at various cooling rate.

Sample	Φ(°C/min)$^{(1)}$	T_p (°C)	$-\Delta H_c^0$ (J/g)	$t_{1/2}$ (min)
PP	5	123.30	86.43	0.64
	10	119.86	91.53	0.38
	15	117.52	91.59	0.28
	20	115.68	91.97	0.23
	30	113.00	91.62	0.17
PP/PES	5	121.60	71.73	0.81
	10	119.68	72.10	0.46
	15	116.53	73.55	0.31
	20	114.68	75.08	0.24
	30	112.01	74.07	0.17

(1) Φ: cooling rate.

Figure 1 and Table 1 shows the relationship between T_p and cooling rate (Φ) for PP/PES blend. It was observed that T_p decreases with increasing cooling rate for both PP and PP/PES blend. For example, T_p of PP decreases about 10°C when cooling rate increases from 5 to 30°C/min. At higher cooling rate, because there is not more time to overcome the nucleation energy barrier, crystallization starts at lower temperature. In addition, the nuclei activation is limited and the process of nucleation will consume more time so that the profile of the crystallization peak become wider. Secondly, the presence of PES in PP leads to an apparent decrease in T_p at a given cooling rate. Here, the effect PES content in PP matrix on T_p was not discussed. The result implies that the PES molecules are not effective nucleating agent during the PP spherulites in heterogeneous nucleation process, the PP nucleation was interfered by the presence of PES.

Figure 2 shows the plots of the relative degree of crystallinity (X_t) as a function of time for PP and PP/PES blend at different cooling rates. Here X_t is estimated from Eq. 1:

$$X_t = \frac{\int_{T_0}^{T_t} (dH_c / dT) dT}{\int_{T_0}^{T_\infty} (dH_c / dT) dT} \qquad (1)$$

where T_0, T_t and T_∞ are the initial crystallization temperature, the crystallization temperature at time t and the ultimate crystallization temperature, respectively. The dH_c is the enthalpy of crystallization released during an infinitesimal temperature range dT. The relative degree of crystallinity can also be written as $X(T)$, which is described as a function of temperature. According to different cooling rate (Φ), the temperature parameters can be converted into a timescale by using Eq. 2:

$$t = \frac{T_0 - T_t}{\Phi} \qquad \mathbf{(2)}$$

where T_t is the temperature at crystallization time t. The conversion from temperature to time is performed using a constant cooling rate.

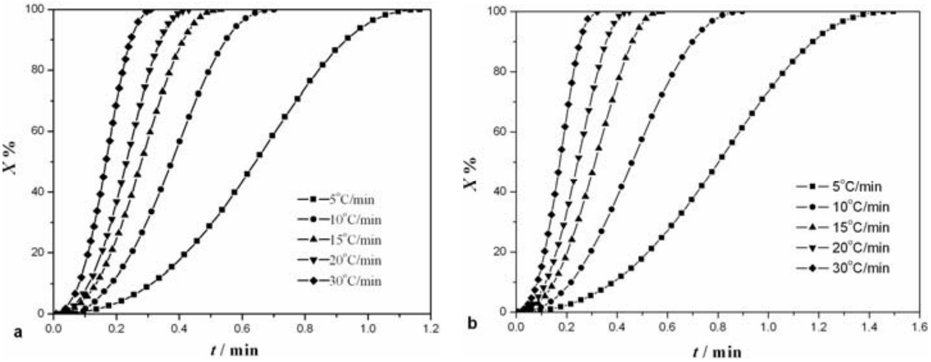

Figure 2. Variation of the relative crystallinity (X_t) with time for nonisothermal crystallization of (a) PP, (b) PP/PES blend.

From these curves, it can be seen that the time of crystallization completion decreased while the cooling rate increased. Furthermore, an important parameter that can be obtained is the half-time of crystallization ($t_{1/2}$), which is the value of the time from the onset of crystallization to the time at which X_t is 50%. The values of $t_{1/2}$ for PP and PP/PES blend are also listed in Table 1. It is clear that the value of $t_{1/2}$ for PP is less than that of PP/PES blend at a given cooling rate, signifying that the addition of PES could decelerate the overall crystallization process. The results can be explained as follows: the PES molecular chain is long and rigid, not like small molecule, do not act as a heterogeneous nucleating agent to facilitate crystallization. Small molecules, or nanoparticles of inorganic compounds, can act as a nucleating agent to decrease the time of polymer crystallization, however, PES hampered the growth of PP spherulites. In general, the common approach that is adopted to analyze the nonisothermal crystallization kinetics is the Avrami equation [15], which can be written as:

$$1 - X(t) = \exp(-kt^n) \qquad \mathbf{(3)}$$

The logarithmic form of Eq. 3 is Eq. 4:

$$\log[-\ln(1 - X(t))] = \log k + n \log t \qquad \mathbf{(4)}$$

where $X(t)$, k, t, n are the relative crystallinity, the rate constant, crystallization time and Avrami exponent, respectively.

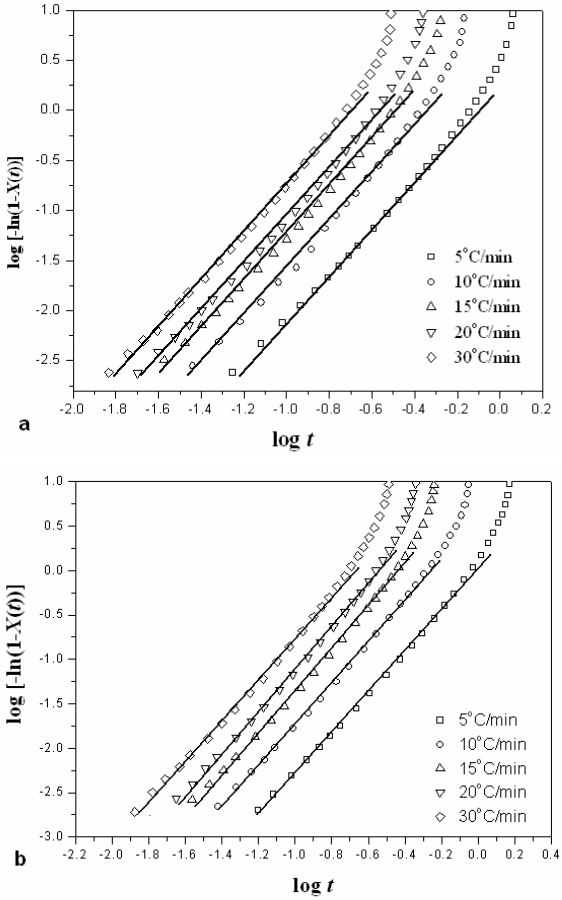

Figure 3. Avrami plots of log [-ln(1-$X(t)$)] versus log t for crystallization of (a) PP and (b) PP/PES blend at various cooling rates.

Figure 3 shows the plots of log[-ln(1-$X(t)$)] versus log t for crystallization of PP and PP/PES blend at various cooling rates. It can be seen that the plots exhibit a poor linear relationship, suggesting that the Avrami analysis does not effectively describe the overall nonisothermal crystallization of PP and PP/PES blend. Each curve shows slight deviation at the end stage of crystallization and exhibits good linear relationship at the beginning of crystallization (from less than 80% for the $X(t)$ values), indicating that the nucleation mechanism and crystal growth geometries were similar for the primary crystallization process at various cooling rates. The deviation was usuall considered to be due to the presence of secondary crystallization, which was caused by the slower crystallization and further perfection of crystals in the later stage. Thus the kinetic data in the early stage were used to estimate the Avrami parameters for nonisothermal crystallization of PP and PP/PES blend. The values of the Avrami parameter exponent n and the rate constant k determined from the slopes and the intercepts of the solid lines (in Figure 3) are listed in Table 2. The average values of the Avrami exponent are n = 2.39 and 2.35 corresponding to PP and PP/PES blend, respectively. That means that the primary crystallization stage for nonisothermal melting process of PP and PP/PES may correspond to a two-dimensional growth of lamellar crystals with thermal nucleation kinetics [16]. In addition, the values of *k* increases with increasing cooling rate for PP and PP/PES blend. This can be explained as the fact that at higher cooling rate, melt crystallization occurs at lower temperature and thus has higher crystallization rate due to higher undercooling. Furthermore, at a given cooling rate, the values of *k* of PP are greater than those of PP/PES blend, indicating higher crystallization rates of PP than those of PP/PES blend.

Table 2. Results of the Avrami Analysis for Nonisothermal Crystallization of PP and PP/PES blend.

Sample	Φ (°C/min)	n	k (min^{-n})
PP	5	2.39	1.90
	10	2.46	7.36
	15	2.34	12.62
	20	2.36	19.95
	30	2.39	46.77
PP/PES	5	2.33	1.09
	10	2.35	4.17
	15	2.35	10.26
	20	2.37	18.79
	30	2.34	39.99

Owing to the nonisothermal character of the process, cooling rate (Φ) is the important factor that needs to be considered. Ozawa modified the Avrami equation based on the mathematical derivation, the equation is given by [17]:

$$1 - X(T) = \exp[-K(T)/\Phi^{m}] \qquad (5)$$

where $X(T)$ is relative crystallinity as function of temperature T, $K(T)$ is the cooling function of temperature that is relevant to nucleus formation, nucleation rate and nucleus growth rate, also called Ozawa crystallization rate constant, m is the Ozawa exponent. Eq. 5 in the logarithmic form can be written as:

$$\log[-\ln(1 - X(T))] = \log K(T) - m\log\Phi \qquad (6)$$

Through selecting a certain temperature to get the data of the degree of conversion at various cooling rate, and plotting the left-hand side of Eq. 7 vs. log Φ, m and log $K(T)$ can be obtained from slope and intercept. Plots based on Eq. 6 of PP and PP/PES are presented in Figure 4. From these curves it can be concluded that the $X(T)$ values calculated at various temperatures decreased with increasing cooling rate at a given temperature. The Ozawa method could successfully describe the nonisothermal crystallization process of PP, owing to the fact that the plots would give a series of lines for PP in Figure 4. However, the Ozawa plots of PP/PES blend show deviation from linearity under some temperatures, especially the curves of 121, 120 119 and 117°C. If a more detailed investigation was made, it was noticed that Ozawa method could correctly describes nonisothermal crystallization when cooling rate was 15, 20, 30°C/min, respectively, whose data correspond to a *y*-axis value of approximately are greater than -1.0. Combining with the discussion of Avrami analysis, in Figure 3, all curves include a curvature when $X(t)$>80%, indicating Avrami analysis does not describe the end stage of crystallization process. But under this condition, Ozawa method can be successfully applied the end stage of the crystallization process for PP/PES blend.

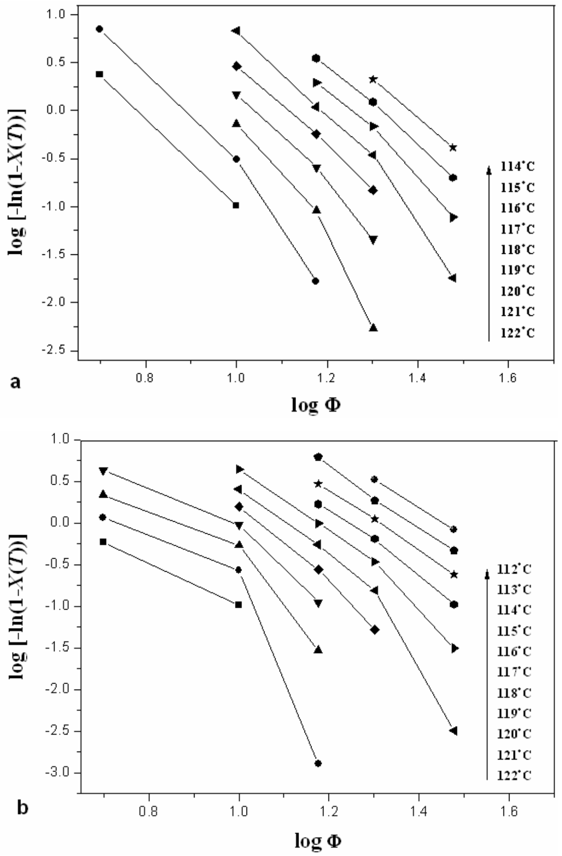

Figure 4. Ozawa plots of log[-ln(1-$X(T)$)] versus log Φ for crystallization of (a) PP, (b) PP/PES blend.

In order to better describe the overall process of nonisothermal crystallization of PP/PES blend, Mo method was tried. By combining the Avrami equation with Ozawa equation, a modified equation was proposed by Zhishen Mo and his coworkers, which is given by [18]:

$$\log\Phi = \log F(T) - \alpha \log t \qquad (7)$$

where $F(T) = [K(T)/Z]^{1/m}$ and $\alpha = n / m$. The kinetics parameter $F(T)$ refers to the value of cooling rate that needs to be selected within a unit of crystallization time when the measured system amounts to a certain degree of crystallinity, and α is the ratio of the Avrami exponent n to the Ozawa exponent m. When selecting a certain relative degree of crystallization, from the plot of $\log\Phi$ versus log t (Figure 5), the values of α and $F(T)$ can be obtain by slopes and intercepts of fitting linear lines. The results are listed in Table 3.

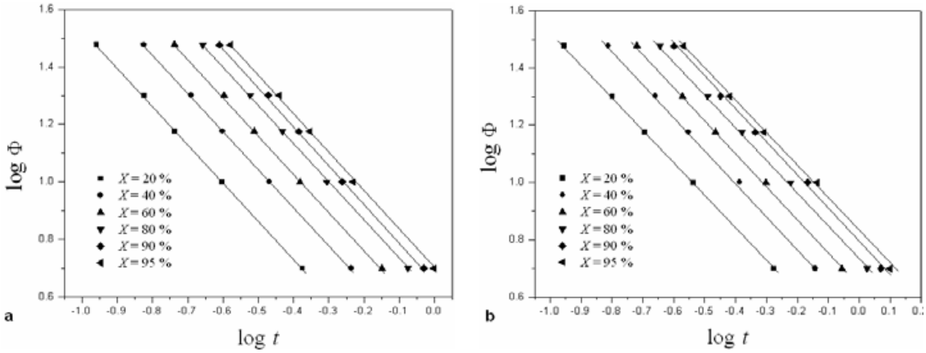

Figure 5. Plots of log Φ versus log *t* for (a) PP, (b) PP/PES blend.

Table 3. Nonisothermal crystallization kinetics parameters for PP and PP/PES blend at different relative degrees of crystallinity by Mo method.

Sample	X_t (%)	log F(T)	α
PP	20	0.197	1.33
	40	0.382	1.33
	60	0.498	1.33
	80	0.595	1.34
	90	0.655	1.35
	95	0.694	1.36
PP/PES	20	0.383	1.15
	40	0.541	1.15
	60	0.634	1.16
	80	0.734	1.16
	90	0.794	1.14
	95	0.828	1.14

It can be seen from Table 3 that the value of α for PP varies from 1.33 to 1.36 and for PP/PES varies from 1.14 to 1.16. The variation in the values of α is very small. The results indicate that the Mo method is successful in describing the nonisothermal process of PP and PP/PES blend. The value of *F*(*T*) increases with the increase of the relative crystallinity, and the *F*(*T*) values of PP are smaller than those of PP/PES blend at a given crystallinity. *F*(*T*) mainly reflects the crystallization facilitation effect of PES on PP matrix. The greater value of *F*(*T*), the slower of the rate for crystallization. When PES is added to PP matrix, blend can achieves the same degree of crystallinity slower than PP. This implies slower kinetics of crystallization, and it is in agreement with our aforementioned discussion that PES hampered the crystallization of PP.

To evaluate the effective energy barrier for nonisothermal crystallization process, the Kissinger method [19] is adopted, too. Kissinger method enables us to determine the activation energy (Δ*E*) for the transport of the macromolecular segments to the growing surface. The equation can be written as below:

$$\frac{d[\ln(\Phi / T_p^2)]}{d(1/T_p)} = -\frac{\Delta E}{R} \qquad \textbf{(8)}$$

where T_p, R, Φ and ΔE are peak temperature, the universal gas constant, cooling rate and the crystallization activation energy, respectively. Figure 6 shows the plots based on the Kissinger method. The value of ΔE can be obtained from the slope of $\ln(\Phi/T_p^2)$ versus $1/T_p$. The values of ΔE are estimated as 227.4kJ/mol for PP and 220.2kJ/mol for PP/PES blend. The addition of PES slightly lowers the activation energy of PP. This can be discussed as follows: the crystallization process of polymers can be divided into two parts: (1) nucleation, which is relate to the free energy barrier and (2) crystal growth whose rate is relate to the activation energy for the transport of crystalline units across the phase. In the present study, the decrease of half time of the crystallization indicates the lower free energy barrier for PP/PES blend compared to PP. However, for PES molecules, there are two mutually opposite effects on the crystallization behavior of PP: nucleation ability and growth retardation, which may be related to feature of rigid molecular chain and dispersion state of PES.

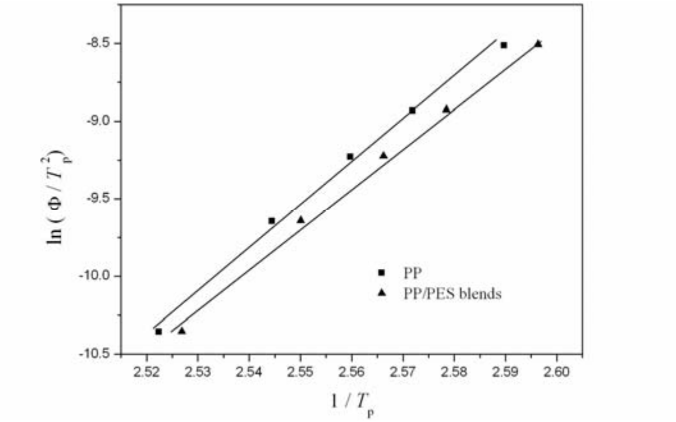

Figure 6. The plots of $\ln(\Phi/T_p^2)$ versus $1/T_p$ of PP and PP/PES blend.

Conclusions

The nonisothermal crystallization kinetics from PP and PP/PES (80/20 wt%) blend were investigated under different cooling rates by means of DSC technique. The Avrami equation, the Ozawa method, and Mo method were used for describing the nonisothermal crystallization behavior. It was found that the Avrami expression was able to effectively describe the early stage of nonisothermal crystallization process for both PP and PP/PES blend. The average values of Avrami exponent n for PP and PP/PES blend are 2.39 and 2.35, respectively, indicating that the primary stage for nonisothermal crystallization for two samples is a two-dimensional growth of lamellar crystals with thermal nucleation kinetics. The Ozawa method can successfully describes the nonisothermal crystallization behavior of PP, but partly effective to PP/PES blend. When Mo method was employed to investigate the nonisothermal crystallization behaviors of PP and PP/PES blend, the values of the kinetics parameter $F(T)$ increases with the increase of the relative crystallinity, meanwhile, the F(T) values of PP are smaller than those of PP/PES blend at a given crystallinity. At last, the activation energy (ΔE) for nonisothermal crystallization was determined using Kissinger method. The result showed that the ΔE value of PP is slightly higher than that of PP/PES blend. Combining the above-mentioned discussion, Two conclusions can be made: (1) Owing to the feature of rigid molecular chain of PES, it does not act as a heterogeneous nucleating agent to facilitate crystallization, and it hampered the growth of PP spherulites. (2) The PP nucleation was interfered by the presence of PES; the addition of PES decelerates the overall crystallization process of PP and leads two opposite effects on the crystallization process of PP: nucleation ability and growth retardation.

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