

# Nonisothermal Crystallization, Melting Behavior, and Morphology of PP/EPPE Blends

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**ABSTRACT:** Nonisothermal crystallization, melting behavior, and morphology of polypropylene (PP)/Easy processing polyethylene (EPPE) blends were studied by differential scanning calorimetry (DSC) and scanning electron microscope (SEM). The results showed that PP and EPPE are miscible, and there is no obvious phase separation in microphotographs of the blends. The modified Avrami analysis, Ozawa equation, and also Mo Z.S. method were used to analyze the nonisothermal crystallization kinetics of the blends. Values of Avrami exponent indicated the crystallization nucleation of the blends is homogeneous, the growth of spherulites is tridimensional, and crystallization

mechanism of PP is not affected much by EPPE. The crystallization activation energy was estimated by Kissinger method. The result obtained from modified Avrami analysis, Mo Z.S. method, and Kissinger methods were well agreed. The addition of minor EPPE phase favored to decrease the overall crystallization rate of PP, showing some dilution effect of EPPE on PP. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 115: 1256–1263, 2010

**Key words:** polypropylene(PP); easy processing polyethylene (EPPE); melting behavior; nonisothermal crystallization kinetics; morphology

## INTRODUCTION

Polypropylene is one of the most widely used polyolefin materials because of its outstanding mechanical property and comparatively low price, but its application in some fields are limited due to its low fracture toughness especially at low temperature and a high notch sensitivity at room temperature. Blending of PP with a dispersed elastomeric phase [e.g., ethylene-propylene–diene rubber (EPDM)] is widely practiced,<sup>1–5</sup> because the rubber can increase the overall toughness of the PP matrix.<sup>6</sup> But the addition of elastomers often takes negative effects on some properties of PP, such as stiffness, hardness, and rheological properties.<sup>7</sup>

The development of metallocene catalysts has led to production of numerous new polyolefin materials, among which EPPE is a new kind of PE material catalyzed with metallocene catalyzer. EPPE is a copolymer of ethylene and other long chain olefins, because of the tactic long branches in the EPPE molecules; its rheological behavior is similar to that of LDPE. At the same time, high tacticity of branches keep it good mechanical property like LLDPE, so it combines good mechanical property and good processability. As a result, its overall properties are superior to those of conventional PE and mPE and it has a wide variety of

applications. Although blending with other polyolefin materials, compare with LDPE, EPPE can endow with good processability and good surface property without lose of mechanical properties. Because of its good mechanical properties, thermal stability, and aging resistance, thus, in comparison with conventional EPDM, mPE (Metallocene-catalyzed polyethylene) elastomer can endow with higher impact strength as a modifier of PP.<sup>8</sup> Moreover, previous work has shown an improved fracture behavior at low temperature and better dynamic properties with an mPE modifier.<sup>9</sup> Because of its better rheological property, EPPE modified PP could have a better rheological property than that of mPE elastomer. It is well-known that the physical properties of semicrystalline polymeric materials strongly depend on their crystallization and microstructure; thus, investigations of the crystallization behavior and morphology of polymer blends are significant both theoretically and practically. In particular, the crystallization behavior during nonisothermal crystallization from melt is of increasing technological importance, because these conditions are the closest to practical industrial conditions. Therefore, it is highly desired to investigate the crystallization behavior and morphology to optimize blends composition, processing technology of EPPE modified PP. However, such detailed investigations have not been reported until now.

In this study, the melting and crystallization behavior of PP/EPPE blends were investigated and the nonisothermal crystallization kinetics of the

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blends were studied with the modified Avrami analysis, Ozawa equation, and Mo Z.S. method. The morphologies and mechanical properties of the blends were also studied to investigate the effect of EPPE on the microstructure of the blends.

## EXPERIMENTAL

### Materials and sample preparation

The PP [type K9020, MFR (230°C/2.16 kg) = 2.46 g/10 min] used in this study is a commercial polymer, supplied by Qilu Petrochemical Co. (China). The EPPE [type GT140, MFR (190°C/2.16 kg) = 0.9 g/10 min] is a production of Sumitomo Chemical Co. (Japan). Sample blending was carried out by melt-blending on a two-roll mill at 180°C for 10 min. The weight ratios of PP in the blends were set at 100%, 90%, 80%, 60%, 40% and 0%. The melt of blends was compressed in an electric-heat press for 3 min at 12 MPa and 180°C and cold pressed for 10 min at 5 Mpa, to give a 4-mm-thick sheet for mechanical property examination.

### Thermal analysis

A Diamond DSC-7 (Perkin-Elmer, USA) apparatus was applied to record the heat flow during the melting and nonisothermal crystallization processes of the samples. All operations were carried out under a nitrogen environment to avoid oxidation. The temperature and melting enthalpy were calibrated with standard indium. All the sample weights were about 9 mg.

For melting behavior, samples were heated from room temperature to 200°C at a rate of 10°C/min. To erase the thermal history, the temperature was held at 200°C for 1 min. And then the samples were cooled down to 30°C at various constant cooling rates of 2.5°C/min, 5°C/min, 7.5°C/min, and 10°C/min. A second run was carried out after the samples were held at 30°C for 1 min.

### Morphology analysis

SEM micrographs were taken on a KYKY 2800B (KYKY Technology Development, China) scanning electric microscope according to the method of Campbell and White,<sup>10</sup> and impact fracture surfaces were examined.

## RESULTS AND DISCUSSION

### Melting and crystallization behavior of PP/EPPE blends

Figure 1 shows the DSC melting heat flow of pure polymers and their blends. The melting temperature

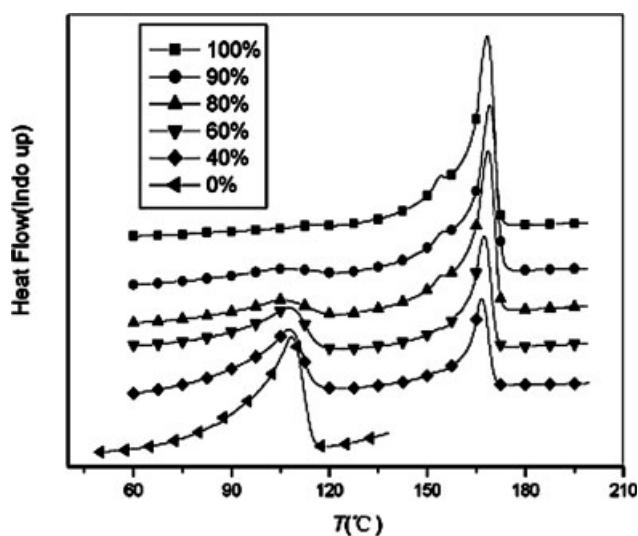


Figure 1 DSC melting curves of PP/EPPE blends at a heating rate of 10°C/min.

of PP ( $T_{m2}$ ) decreased a little with increasing of EPPE content, however, the melting temperature of EPPE ( $T_{m1}$ ) almost unchanged with increasing of PP content, the melting temperature of PP decreased from 168.4°C to 166.6°C with EPPE content increased from 0 to 60%. This observation indicates that there is some interaction between PP and EPPE molecules, which is attributed to the miscibility of PP and EPPE. The melting temperature ( $T_{m2}$ ) of PP in the blends is between 165°C and 170°C. This indicates that the PP, both in the pure state and in the blends, exhibits only  $\alpha$ -crystal structure because the melting temperature of the  $\alpha$ -crystal structure is in the range of 160–176°C.<sup>11,12</sup>

For the pure PP and pure EPPE and their blends which are crystallizable, nonisothermal crystallization were performed from the melt by DSC with various cooling rates of 2.5°C/min–10°C/min. Figure 2 shows the crystallization exotherms for some PP/EPPE blends compared with pure PP and EPPE, respectively (cooling rate: 10°C/min). All DSC traces show two crystallization peaks except those of pure polymers, indicates two crystallizable components exist in the blends. The PP exothermal peaks move to lower temperature, whereas the EPPE exothermal peak moved to higher temperature, means that the interaction of PP and EPPE chains prevented PP from crystallization, and the PP act as nuclei agent while EPPE crystallize, this changes can also be seen in crystallization rate constants.

As an example, Figure 3 shows the typical crystallization exotherms for PP (90%)/EPPE blends at various cooling rates. The exotherm peaks ( $T_p$ ) shifted obviously to lower temperature as the cooling rate increasing (Table I). The decrease of  $T_p$  with a higher cooling rate is due to that the crystallization rate is

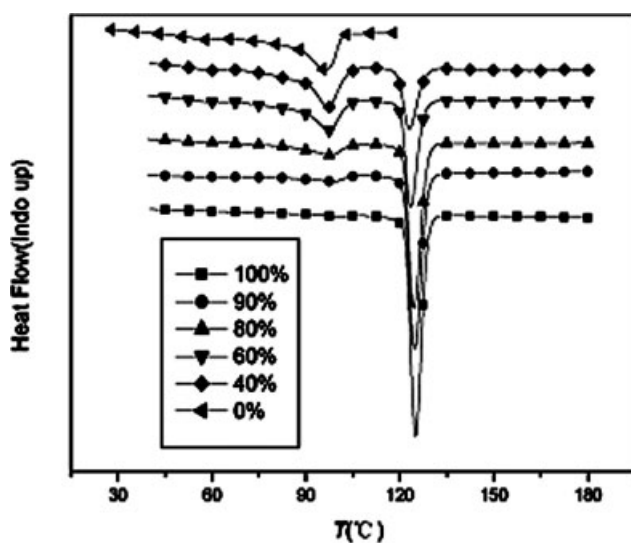


Figure 2 DSC nonisothermal crystallization curves of PP/EPPE blends at a cooling rate of 10°C/min.

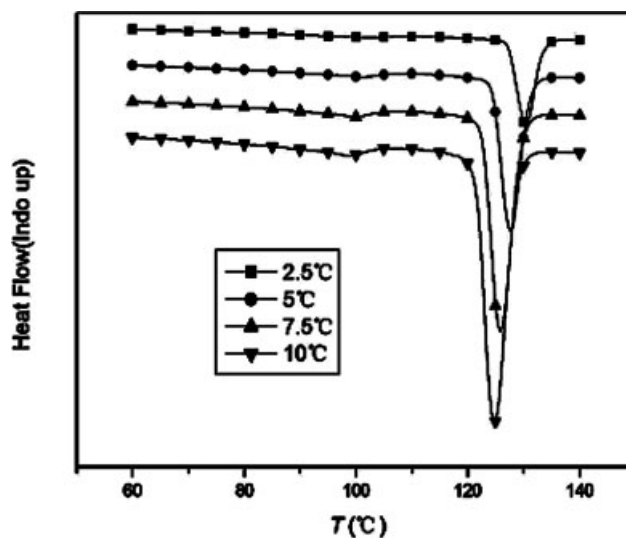


Figure 3 DSC nonisothermal crystallization curves for PP in the PP (90%)/EPPE blends at various cooling rates.

lower than the experimental cooling rate.<sup>13</sup> At a lower cooling rate, PP molecules have enough time to form the necessary nuclei for crystallization and, therefore, come to a higher  $T_p$ , and the crystallization temperature and the crystallinity are correspondingly higher (Table I). The crystallinity of PP can be calculated according to Kirshenbaum et al.,<sup>14</sup> for all the samples, crystallinity of PP ( $X$ ) is defined as follows:

$$X = \frac{\Delta H_c}{187.7 \times PP\%} \quad (1)$$

The 100% crystallization enthalpy of PP is 187.7 (J/g),  $\Delta H_c$  is the crystallization enthalpy of PP in the pure PP and/or the PP/EPPE blends, the values are listed in Table I. From Table I, we can see that the crystallinity of PP/EPPE is lower than that of pure PP because the interaction between molecules pre-

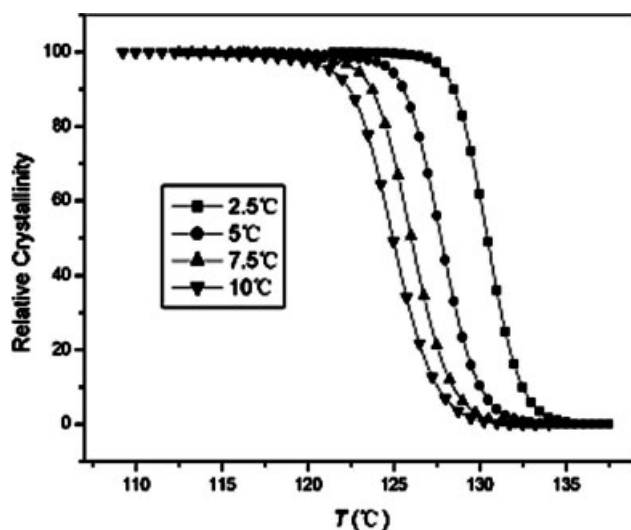
vented the PP molecule from entering the crystal and some PP chains dissolved into the EPPE melt. The crystallinity of PP (90%)/EPPE blends is lower than PP (80%)/EPPE blends because the EPPE had saturated when the content is up to a certain degree.

### Nonisothermal crystallization kinetics

Up to date, several analytical methods have been developed to describe the nonisothermal crystallization kinetics of polymers as follows: (i) modified Avrami analysis,<sup>15–17</sup> (ii) Ozawa equation,<sup>18,19</sup> (iii) Ziabicki analysis,<sup>20,21</sup> and (iv) others,<sup>22–25</sup> such as Mo Z.S. method. In this study, the modified Avrami analysis and Mo Z.S. method are applied to describe the nonisothermal crystallization kinetics of PP/EPPE blends, and the contrastive study was taken.

TABLE I  
Melting Behavior and Avrami Parameters of PP/EPPE Blends

Sample (PP ratio)	$D$ (°C/min)	$n$	$\log k$	$t_{1/2}$ (min)	$t_p$	$\Delta H$ (J/g)	Crystallinity (%)
100%	2.5	5.10	-2.17	2.46	130.6	86.57	46.12
	5.0	5.40	-1.01	1.43	127.9	84.84	45.20
	7.5	5.24	-0.187	1.00	126.3	84.08	44.79
	10	5.65	0.145	0.872	125.2	83.84	44.67
90%	2.5	5.10	-2.39	2.70	130.5	72.48	42.91
	5.0	5.22	-1.16	1.55	127.7	72.27	42.78
	7.5	5.06	-0.304	1.07	125.9	71.65	42.41
	10	4.90	0.027	0.833	124.8	71.59	42.38
80%	2.5	5.31	-2.87	3.21	129.9	68.24	45.44
	5.0	5.37	-1.34	1.65	127.1	67.45	44.92
	7.5	5.39	-0.474	1.14	125.6	66.82	44.50
	10	5.50	0.029	0.921	124.6	66.64	44.38



**Figure 4** Plot of relative crystallinity  $\chi_t$  versus crystallization temperature  $T$  for PP (90%)/EPPE blends at various cooling rates.

The Avrami analysis<sup>17,26,27</sup> has been widely used to describe isothermal crystallization kinetics of polymers as follows:

$$1 - X_t = \exp(-kt^n) \quad (2)$$

where,  $X_t$  is the relative crystallinity,  $k$  is the crystallization rate constant, and  $n$  is the Avrami exponent. Here, the value of Avrami exponent  $n$  depends on the nucleation mechanism and growth dimensions, the parameter  $k$  is a function of the nucleation and the growth rate. The relative crystallinity  $X_t$ , as a function of crystallization time is defined as follows:

$$X_t = \frac{\int_0^t (dH_c/dt)dt}{\int_0^{t_\infty} (dH_c/dt)dt} \quad (3)$$

where,  $dH_c/dt$  is the rate of heat evolution, and  $t_0$  and  $t_\infty$  is the time at which crystallization starts and ends, respectively.

The Avrami equation can be modified to describe nonisothermal crystallization.<sup>15,16,28</sup> For nonisothermal crystallization at a chosen cooling rate, the relative crystallinity  $X_t$  is a function of crystallization temperature. And the crystallization temperature can be converted to crystallization time  $t$  using the following equation<sup>19,21</sup>:

$$t = \frac{T_0 - T}{D} \quad (4)$$

where,  $D$  is the cooling rate.

As an example, Figure 4 shows the relative crystallinity of PP in the PP (90%)/EPPE blends at various cooling rates. All curves in Figure 4 show a reversed sigmoidal shape, indicating a fast primary process during the initial stage and slower secondary process

during the later stage. The plot of  $X_t$  versus  $T$  shifts to the low-temperature region as the cooling rate increases, indicating the crystallization is enhanced as temperature decreases. That is because of the strong temperature dependence on the nucleation and the growth parameters.<sup>29</sup> After the maximum in the heat flow curves has passed, a small fraction of crystallinity develops by slower, secondary kinetics processes. The lower cooling rate provides more fluidity, more diffusivity, and more time at high-temperature for perfect crystallization due to lower relative viscosity, thus inducing much higher crystallinity at lower cooling rates, as shown in Table I.

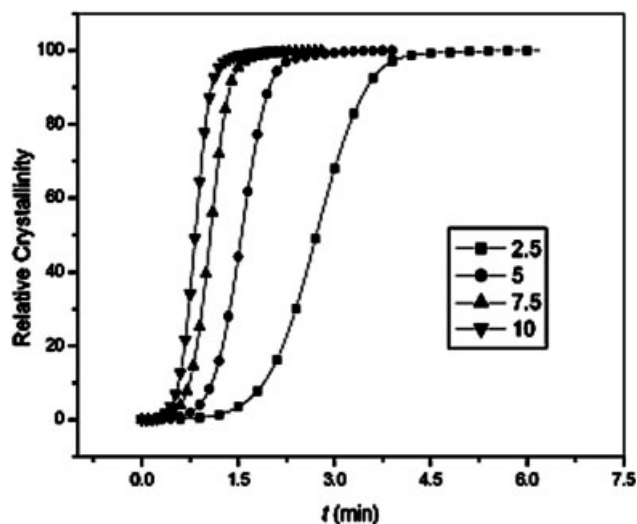
The temperature axis in Figure 4 can be transformed into time scale according to eq. (4), as shown in Figure 5. The sigmoidal shape of the curves suggests the modified Avrami analysis is applicable for nonisothermal crystallization of PP/EPPE blends. Meanwhile, the crystallization half-time  $t_{1/2}$  can be calculated directly from the relative crystallinity versus time plot,<sup>17,30</sup> as shown in Table I.

Rewritten eq. (1) in a double logarithm form the following:

$$\log[-\ln(1 - X_t)] = \log(k) + n \log(t) \quad (5)$$

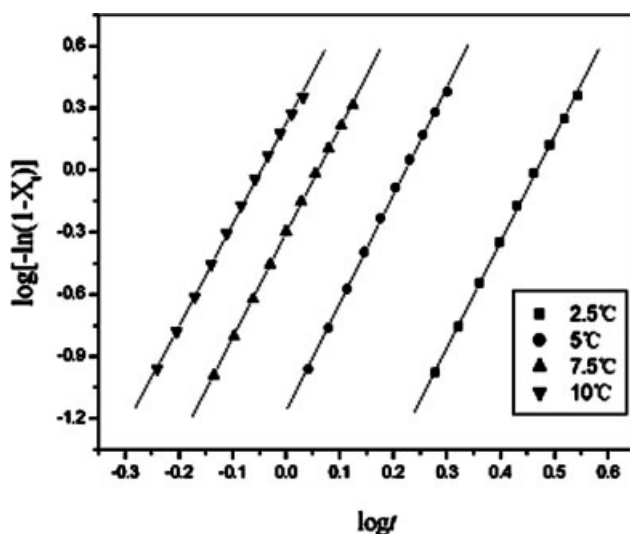
Then, the Avrami parameters can be calculated from the  $\log[-\ln(1 - X_t)]$  versus  $\ln t$ . Here, the crystallization rate of nonisothermal crystallization depends on the cooling rate. Thus, the crystallization rate constant  $k$  should be corrected adequately. Assuming a constant cooling rate, the crystallization rate constant can be corrected as follows<sup>19</sup>:  $\ln k' = \ln k/D$ .

Figure 6 shows the plot of  $\log[-\ln(1 - X_t)]$  versus  $\log t$  for nonisothermal crystallization of PP (90%)/



**Figure 5** Relationship of crystallinity  $\chi_t$  versus crystallization time  $t$  for PP (90%)/EPPE blends at various cooling rates.





**Figure 6** Avrami plot of PP (90%)/EPPE blends for nonisothermal crystallization at various cooling rates.

EPPE blends. All lines in Figure 6 are almost paralleled to each other, shifting to less time with increasing cooling rate. This implies that the nucleation mechanism and crystal growth geometries are similar, although the cooling rates are different. The Avrami parameters were calculated from the plot of  $\log[-\ln(1-X_t)]$  versus  $\log t$ , and the values are listed in Table I. Regardless of the cooling rates, the Avrami exponent  $n$  for the pure PP is in the range of 5.10–5.65, showing homogeneous nucleation mechanism of PP, but the Avrami exponent calculated from nonisothermal kinetics cannot be compared with that of isothermal kinetics. The Avrami exponents of PP/EPPE blends are a little smaller (4.90–5.50) than that of pure PP, showing a little heterogeneous nucleation effect of EPPE on PP, but the effect is negligible.

However, the crystallization rate is dependent upon the blend composition and cooling rates. On one hand, for the pure PP, the crystallization rate constant ( $k$ ) increases with increasing cooling rate. Whereas, the crystallization half-time ( $t_{1/2}$ ) decreases with increasing cooling rate (Table I). Similar trends in both the  $k$  and  $t_{1/2}$  are observed for the PP (90%)/EPPE and PP (80%)/EPPE blends. On the other hand, both the  $k$  and  $t_{1/2}$  are also influenced by the addition of EPPE as follows: that is, at the same cooling rate, the  $\log k$  slightly decreases with the EPPE content increasing, and the  $t_{1/2}$  adversely affected. Thus, the crystallization rate is decelerated with introduction of EPPE in PP, which is due to the interaction of EPPE and PP prevented the PP chains from approaching to the growing PP nuclei at higher temperature, then the crystallization ability of PP molecules in the blends is decreased, compared with that in pure PP, and then the crystallization rate

decreases. Meanwhile, because of the interaction of PP and EPPE molecules, some PP molecules dissolved into the EPPE melt and then come to a lower crystallinity (Table I).

Ozawa equation<sup>18</sup> is another important theory for nonisothermal crystallization kinetics, which is expressed as follows:

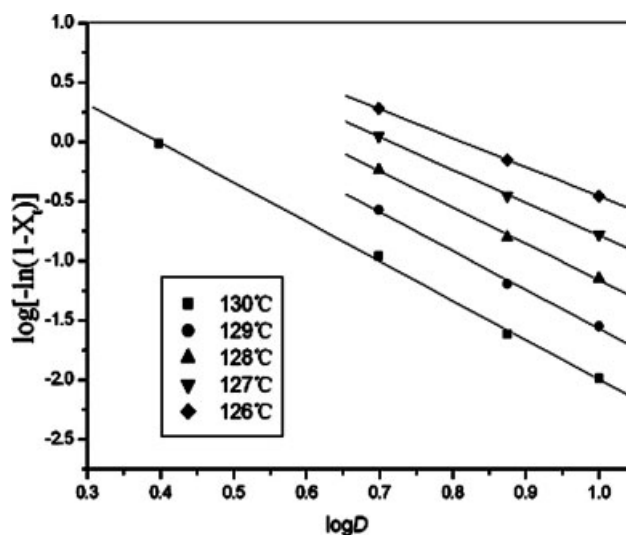
$$1 - C(T) = \exp[-K(T)/D^m] \quad (6)$$

where,  $D$  is cooling rate,  $C(T)$  is the relative crystallinity at given temperature  $T$ ,  $K(T)$  is the growth rate constant, and  $m$  is the Ozawa exponent. According to Ozawa equation, we can get the plot of logarithm of  $1-C(T)$  versus logarithm of  $D$ , see Figure 7. From Figure 7, we see that within experimental cooling rate, straight lines show that Ozawa method can be applied to deal with the PP/EPPE blends system,<sup>31</sup> the point of 2.5°C/min are not shown on the line because when the sample with 10°C/min begin to crystallize, the sample at 2.5/min has finished the crystallization process. The Ozawa exponents are listed in Table II, the difference between the Ozawa exponent and Avrami exponent are because the Avrami analysis did not take cooling rate into account.

For comparison, a new simple method which was proposed by Mo and coworkers,<sup>22</sup> is expressed as follows:

$$\log D = \log F(T) - a \log t \quad (7)$$

where,  $F(T) = [K(T)/k]^{1/m}$  refers to the cooling rate value, which must be chosen within unit crystallization time when the measured system amounts to a certain relative crystallinity, then the  $F(T)$  value has a definite physical and practical meaning, that is, at



**Figure 7** Plots of  $\ln[-\ln(1-C(T))]$  versus  $\ln D$  for PP (90%)/EPPE blends at various temperatures based on the Ozawa analysis.

**TABLE II**  
Crystallization Parameters of PP/EPPE Blends Based on Ozawa Equation

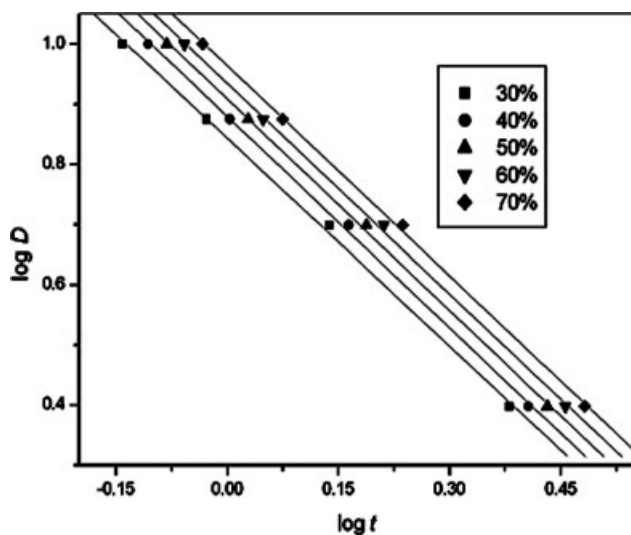
Sample (PP ratio)	$T$ (°C)	$m$	$\log K(T)$
100%	126	2.26	2.64
	127	3.02	2.68
	128	3.30	2.18
	129	3.49	1.95
	130	3.38	1.42
	126	2.44	1.98
90%	127	2.76	1.98
	128	3.04	1.88
	129	3.25	1.69
	130	3.31	1.31
	126	2.19	1.69
	127	2.47	1.63
80%	128	2.71	1.49
	129	2.72	1.12
	130	2.99	0.95

**TABLE III**  
Crystallization Parameters of PP/EPPE Blends Based on Mo Methods

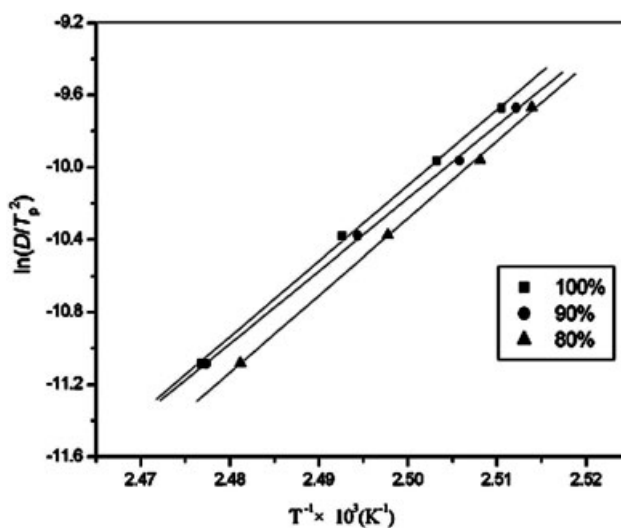
Sample (PP ratio)	$X_t$ (%)	$\log F(t)$	$a$	$E_a$ (kJ/mol)
100%	30	0.823	1.25	-347.4
	40	0.859	1.26	
	50	0.889	1.25	
	60	0.915	1.24	
	70	0.942	1.24	
	30	0.844	1.15	
90%	40	0.880	1.17	-334.0
	50	0.909	1.17	
	60	0.935	1.17	
	70	0.964	1.16	
	30	0.890	1.10	
	40	0.920	1.10	
80%	50	0.947	1.09	-354.4
	60	0.973	1.09	
	70	0.994	1.09	

a certain relative crystallinity, a high value of  $F(T)$  means a high cooling rate is needed to reach this crystallinity in a unit time, which reflects the difficulty of its crystallization process;  $a$  is the ratio of the Avrami exponent  $n$  to the Ozawa exponent  $m$  ( $a = n/m$ ). According to eq. (7),  $\log F(T)$  and  $a$  can be determined from the slope and intercept of plot of logarithm cooling rate versus logarithm time at different relative crystallinity  $X_t$ , respectively. Figure 8 presents the result of PP (90%)/EPPE blends according to eq. (7) at 30, 40, 50, 60 and 70% relative crystallinity. The values of  $F(T)$  and  $a$  for all the samples are listed in Table III. The  $F(T)$  values increase with increasing of relative crystallinity for the same blends. The values of  $a$  are almost a constant for a given composition at different relative crystallinity, this indicates the new method is suc-

cessful for describing the nonisothermal crystallization process of PP/EPPE blends. However, at the same relative crystallinity, the  $F(T)$  values of PP are lower than that of PP/EPPE blends, showing a low cooling rate is needed to get a certain relative crystallinity within unit crystallization time, implying a higher crystallization rate of that of PP than PP/EPPE blends. As for pure PP, the  $a$  values are around 1.25, shows the divergence of Ozawa exponent and Avrami exponent, but that of the PP/EPPE blends are lower, the Ozawa exponents of PP/EPPE blends are around 1.17 and 1.10, respectively (Table III). This is another proof that the EPPE affected the crystallization behavior of PP. And there are some differences between Avrami exponent and Ozawa exponent because the Avrami exponent did not take cooling rate into account.



**Figure 8** Mo plot for PP in the PP (90%)/EPPE blends for nonisothermal crystallization at different relative crystallinity.



**Figure 9** Kissinger plot of  $\ln(D/T_p^2)$  versus  $1/T_p$  of PP/EPPE blends for nonisothermal crystallization with different EPPE content.

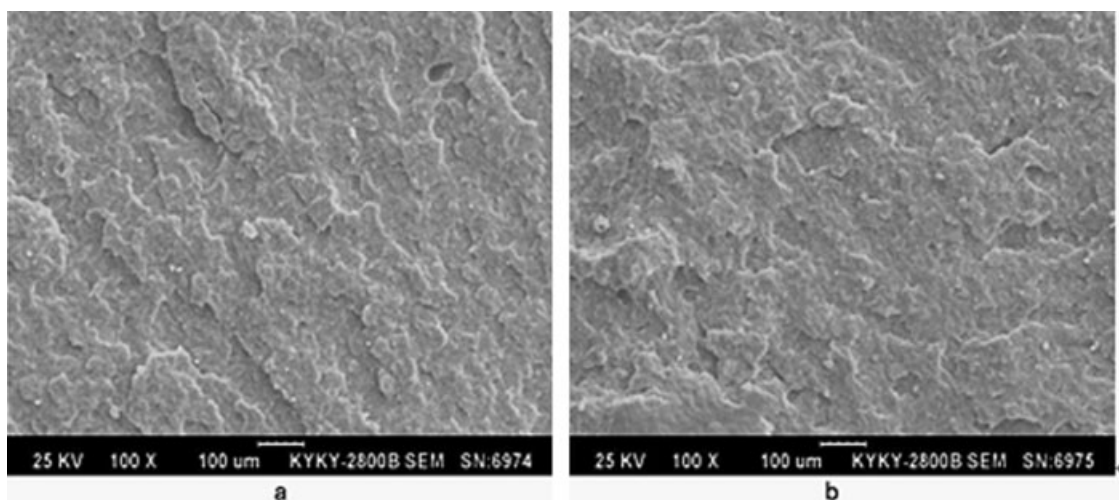


Figure 10 SEM micrographs of PP/EPPE blends. (a)PP and (b)PP (90%)/EPPE.

For nonisothermal crystallization, the crystallization activation energy  $E_a$  can be estimated from the variation of crystallization peak temperature  $T_p$  with cooling rate  $D$  by the Kissinger approach.<sup>32</sup>

$$\frac{d[\ln(D/T_p^2)]}{d(1/T_p)} = -\frac{E_a}{R} \quad (8)$$

where,  $R$  is the universal gas constant.

The Kissinger plot, that is the plot of  $\ln(D/T_p^2)$  versus  $1/T_p$  for PP/EPPE blends, are shown in Figure 9. The  $E_a$  is estimated to be  $-347.4$  kJ/mol for pure PP,  $-334.0$  kJ/mol for the PP (90%)/EPPE blends, and  $-354.4$  kJ/mol for PP (80%)/EPPE blends (Table III). In comparison, the  $E_a$  of the pure PP is similar that of the PP/EPPE blends. The similarity of crystallization activation indicates that the temperature sensitivity of crystallization rate of the blends is similar to that of pure PP. These are because the miscibility of PP and EPPE make the EPPE phase well-dispersed in PP phase and then the crystallization mechanism is hardly affected.

#### Morphology analysis and mechanical property

It is well-known that the properties of materials greatly depend on their morphological structure. For polymer blends or composites, the dispersion of the components is extremely important. A series of SEM micrographs of the impact fracture surfaces obtained during notched impact testing of PP/EPPE blends are shown in Figure 10, which demonstrates clearly that the EPPE uniformly dispersed in the PP matrix and no phase separation in the photograph. This is a good proof to show that the PP and the EPPE are well miscible. The good miscibility of PP and EPPE

is because the PP used in this research is polymerized in sequential reactor with 8% weight ratio of ethylene as comonomer, and the PE segment in PP act as compatibilizer of PP chains and EPPE chains. Figure 11 shows the mechanical properties of the PP/EPPE blends; from Figure 11, we can see that the tensile strength of the blends decreased with increasing of EPPE weight ratio, whereas the impact strength increased and then decreases. This indicates that the EPPE can improve the impact strength in a little extent, but the extent is limited, when the EPPE content is 20% the impact strength increased 22%. This because the good miscibility of the two components prevented the formation of "core-shell" structure and the "core-shell" structure is the ideal structure for impact modification.

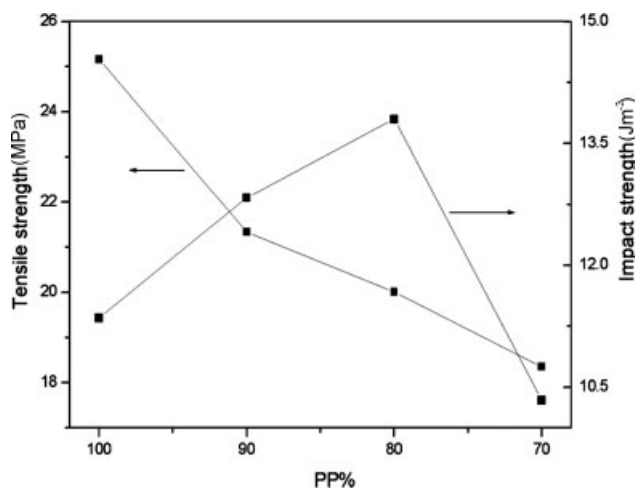


Figure 11 Mechanical properties of the PP/EPPE blends.

## CONCLUSIONS

The PP/EPPE blends, prepared by conventional melt-blending method, were investigated for their melting behavior, crystallization kinetics, and morphology. (1) The study of melting and nonisothermal crystallization behavior shows that PP and EPPE are miscible because the PP is a copolymer with ethylene as comonomer. (2) Nonisothermal crystallization kinetics of the blends was investigated fairly well by modified Avrami analysis, Ozawa equation, and Mo Z.S. method. The results show that the nucleation mechanism of this system is homogeneous, and the crystallization mechanism and crystallization activation energy of the PP are not affected much by EPPE. (3) The SEM observations indicate that EPPE phase is uniformly dispersed in the PP matrix because of their miscibility, and the impact strength of PP increased in a little degree by addition of EPPE.

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