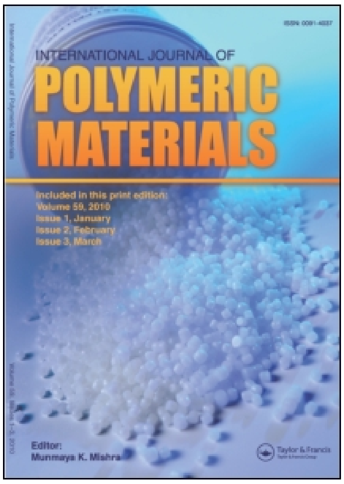

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NONISOTHERMAL CRYSTALLIZATION KINETICS AND MECHANICAL PROPERTIES OF PP/NANO-SIO$_2$ COMPOSITES

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The nonisothermal crystallization kinetics of polypropylene (PP)/nano-SiO$_2$ composites was studied by means of differential scanning calorimetry (DSC). The modified Avrami theories by Jeziorny, Ozawa, and Mo were used to analyze the data of DSC. The results showed that both the Jeziorny and Mo methods could describe this system very well, but the Ozawa analysis failed. The activation energy was evaluated by the Kissinger method. It was found that the crystallization activation energy of PP was higher than that of PP/nano-SiO$_2$ composites. The determined results of mechanical properties showed that the addition of nano-SiO$_2$ increased the mechanical properties of the PP. Micrographs of Polarized optical micrograph (POM) further demonstrated that nano-SiO$_2$ could toughen the PP.

Keywords: polypropylene, nano-SiO$_2$, nonisothermal crystallization kinetics, mechanical property

INTRODUCTION

Polypropylene (PP) is one of the most widely used polyolefin polymers, but its application in some fields is limited due to its low fracture toughness at low temperature and a high notch sensitivity at room temperature. Compounding PP with a dispersed elastomeric phase (e.g., ethylene-propylene-diene rubber [EPDM]) is widely practiced [1–5], because the rubber can increase the overall toughness of the PP matrix [6]. But the addition of elastomers often has negative effects on some properties of PP, such as stiffness and hardness [7].

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The development of nano-technology had produced numerous new materials, among which nano-materials are extremely attractive to both the rubber and plastics industries [8–10]. At this scale, nanoparticle are characterized by small size, large specific area, high surface energy, big proportion of atoms situated in the surface, and high activity [11], which may improve dramatically the physical and mechanical macroscopic properties of polymeric composites. The polymer nanocomposites exhibit high heat distortion temperature, enhanced flame resistance, greater modulus and strength, and a decreased thermal expansion coefficient [12–14], and so on.

Composites of PP/nano-SiO_2 have attracted broad attention because of their important performance and economical value. Several researchers have investigated the mechanical properties of PP/nano-SiO_2 composites. Rong et al. [15] reported a kind of nano-SiO_2/PP composities prepared by conventional compounding technique, in which the nano-particles were grafted beforehand by irradiated polystyrene and the tensile properties were improved. Masao et al. [16] examined the tensile yield stress of PP composites filled with ultrafine SiO_2 particles, and found that the smaller particle size of SiO_2 is, the stronger the tensile strength of the composites under the same loading level.

Up to now, almost all studies of PP/nano-SiO_2 composites concentrated mainly on the physical properties, whereas crystallization kinetics of PP/nano-SiO_2 composites were not found in the authors' literature survey. In order to obtain high-performance polymeric materials, investigation of the nonisothermal crystalliation kinetics is significant both theoretically and practically. Therefore, in this article, nonisothermal crystallization kinetics was studied. In addition, mechanical properties were measured in order to provide useful information for the application of the composites.

EXPERIMENTAL

Materials

The PP (type T30S, $d = 0.901\,g/cm^3$, melting flow rate (230°C/2.16 kg) = 3.88 g/10 min) provided by Daqing Petrochemical Co., China, was used as matrix in this work; The nano-SiO_2 (type A-200) was supplied by Shenyang Chemical Co., Ltd, with an average primary particle size of 12 nm and a specific area of 200 m^2/g.

Preparation of PP/nano-SiO_2 Composites

Blend samples were prepared by melt-blending on a two-roll mill at 176°C for 10 min. To enhance the compatibility of PP and nano-SiO$_2$, an Aluminum-Titanium Compound Coupling Agent (OL-AT1618) was used. The composite melts were compressed for 5 min at 16 Mpa and 176°C in electric-heat curing press, and cold pressed for 10 min at 5 Mpa, to give a 4-mm-thick sheet.

Thermal Analysis

Thermal analysis was made on a CDR-4P DSC apparatus (made in Shanghai, China) with samples weight about 7.5–7.8 mg. All the operations were carried out under a nitrogen environment. The temperature and melting enthalpy were calibrated with standard indium. Before the data were gathered, the samples were heated to 210°C and held in the molten state for 5 min in order to eliminate the influence of thermal history. Then the samples were cooled at various constant rate: 2.5, 5, 10, and 20°C/min, respectively. The exothermic crystallization peak was recorded as a function of temperature.

Mechanical Testing

Tensile test was performed by using an electronic tensile tester. Measurement was carried out at room temperature and 50% relative humidity, with a tensile speed of 10 mm/min. The notched impact strength was measured by XCJ-40 testing machine at the same conditions. The reported mechanical properties were the mean values of 5–7 specimens.

RESULTS AND DISCUSSION

Crystallization Behavior of PP/nano-SiO$_2$ Composites

The crystallization exotherms of the composites at various cooling rates are presented in Figure 1. From these curves, some useful data can be obtained for describing their nonisothermal crystallization behavior, such as the peak temperature (T_p), which is given in Table 1. First, it is obvious that the crystallization peak shifts to lower temperature as the cooling rate increases, which means that the supercooling degree increases and T_p decreases. When the specimens are cooled fast, the motion of PP molecules is not able to follow the cooling temperature, thus retarding the crystallization. Second, at a given cooling rate, T_p of PP/nano-SiO$_2$ composites is higher than that of pure PP, as seen in Table 1. It means that the addition of nano-SiO$_2$ into PP increases the crystallization rate of PP. This may be attributed to the high specific surface energy of nano-SiO$_2$ making the nano-SiO$_2$

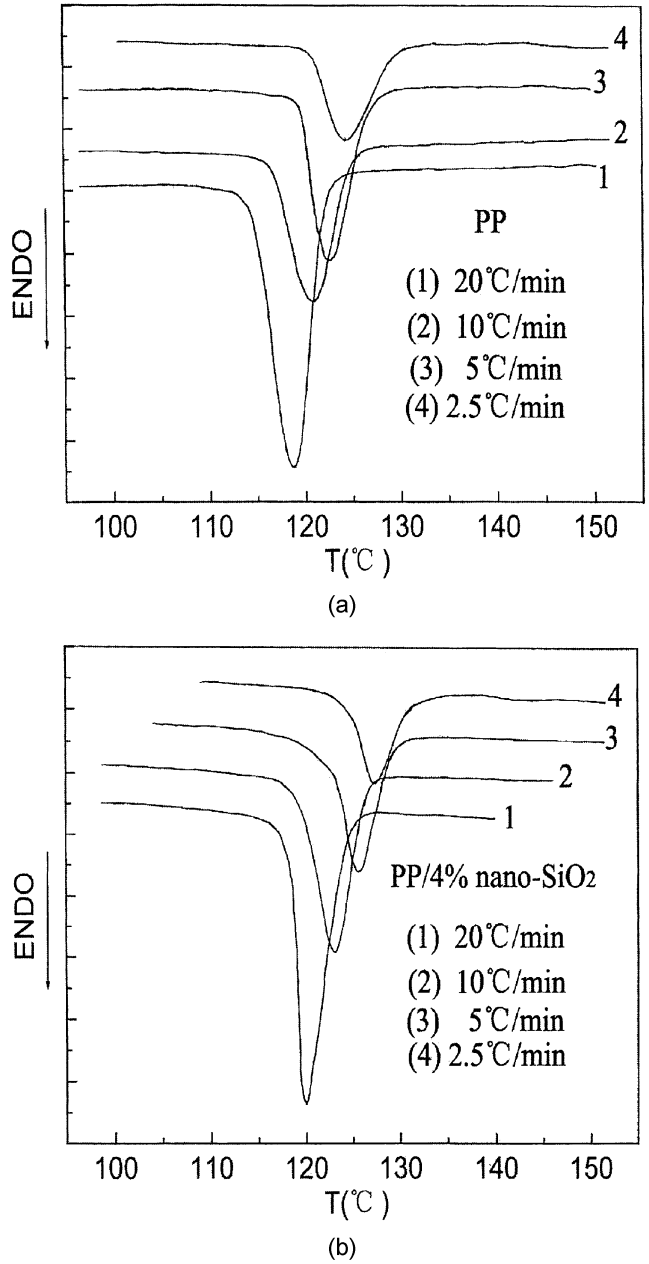


FIGURE 1 DSC thermograms of PP/nano-SiO_2 composites. (a) pure PP, (b) 4 wt% nano-SiO_2.

TABLE 1 Parameters of PP/nano-SiO_2 Composites During Nonisothermal Crystallization Process

Sample	D (°C/min)	n	Z_c	$t_{1/2}$ (min)	T_p (°C)	X_t (%)
0%	2.5	4.24	0.09	3.81	124.4	42.39
	5.0	4.05	0.49	2.25	122.4	39.26
	10	4.01	0.86	1.29	120.5	40.69
	20	3.89	1.04	0.76	118.2	41.89
4%	2.5	3.14	0.21	3.10	126.8	46.92
	5.0	3.41	0.56	2.15	125.4	45.34
	10	4.58	0.88	1.24	122.9	43.72
	20	4.58	0.93	0.68	120.0	44.27
8%	2.5	3.58	0.17	3.14	128.7	46.00
	5.0	3.77	0.51	2.22	125.8	45.44
	10	4.55	0.85	1.30	123.9	45.53
	20	4.87	1.07	0.71	121.2	43.38

easily absorb the PP molecules, causing the crystallization of PP molecules to occur at higher temperature. This phenomenon demonstrates the nucleation effect of nano-SiO_2.

The relative crystallinity (X_t), as a function of temperature, is defined as follows [17]:

$$X_t = \frac{\int_{T_0}^{T}(dH_C/dT)dT}{\int_{T_0}^{T_\infty}(dH_C/dT)dT} \tag{1}$$

where T_0 and T_∞ are the temperature at which crystallization starts and ends, respectively. Figure 2 shows the relationship between relative crystallinity and temperature of PP/4 (4 wt% nano-SiO_2) composites at different cooling rates. Using the equation $t = (T_0 - T)/D$ [17] (where T is the temperature at crystallization time t, and D is the cooling rate), the temperature scale can be transformed into time scale, then eraltive crystallinity as a function of time will be obtained (see Figure 3). As seen from Figure 3, the higher the cooling rate, the less the time for completing the crystallization. The half-time ($t_{1/2}$) of nonisothermal crystallization of PP/nano-SiO_2 composites can be obtained from Figure 3 and the values are listed in Table 1. It is obvious that the values of $t_{1/2}$ decrease with increasing cooling rate. However, at a given cooling rate, the $t_{1/2}$ value of the PP/nano-SiO_2 composites is lower than that of pure PP, meaning that the addition of nano-SiO_2 can accelerate the overall crystallization rate.

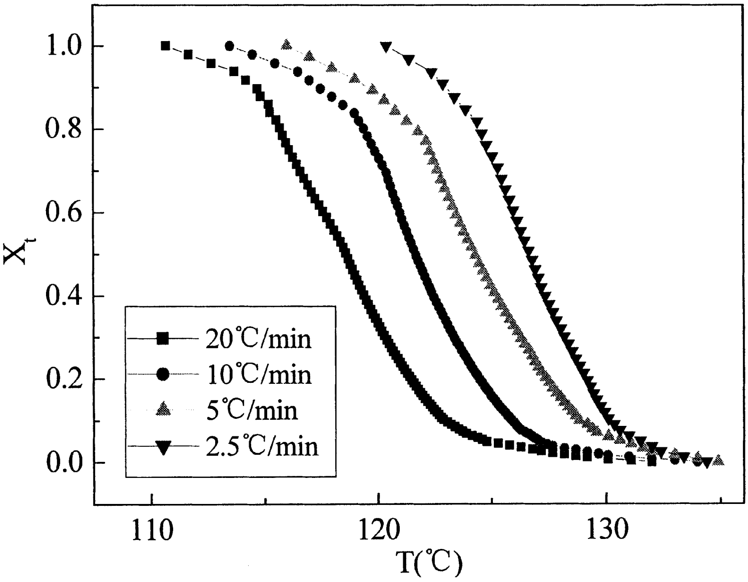


FIGURE 2 Plot of X_t vs. T for crystallization of PP/(4 wt%) nano-SiO$_2$ composites.

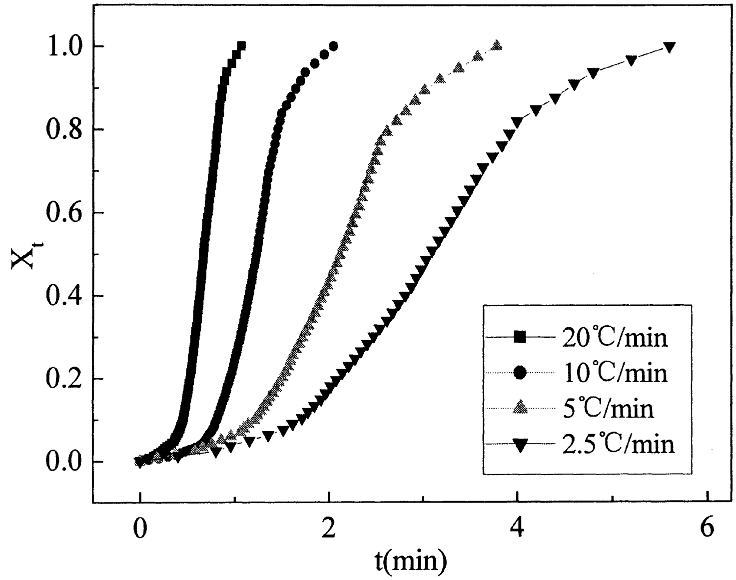


FIGURE 3 Plot of X_t vs. t for crystallization of PP/(4 wt%) nano-SiO$_2$ composites.

In addition, sample's absolute crystallinity (X_{totle}) is defined as the following:

$$X_{totle} = \left(\frac{\Delta H_f}{\Delta H_f^0}\right) \tag{2}$$

where ΔH_f and $\Delta H_f{}^0$ are the melting enthalpies of PP sample and 100% crystallization PP, respectively, $\Delta H_f{}^0 = 209 J/g$ [18]. The results are listed in Table 1. The sample crystallinity decreases with increasing cooling rate, and at the same cooling rate, the crystallinity increases with increasing nano-SiO_2 content.

Nonisothermal Crystallization Kinetics of PP/nano-SiO$_2$ Composites

Several methods may be used to describe the nonisothermal crystallization kinetics of polymers, such as Ozawa [19], Ziabicki [20], Mandelkern [21], and others. In this article the modified Avrami theories by Jeziorny [22], Ozawa [19], and Lu et al. [23] were used to analyze the DSC data of PP/nano-SiO_2 composites, and the contrastive study was also taken.

According to the Avrami equation, the relative crystallinity X_t at a crystallization time t is expressed as follows:

$$1 - X_t = \exp(-Z_t t^n) \tag{3}$$

Where n is the Avrami exponent, which depends on the type of nucleation and growth dimension; the parameter Z_t is an overall crystallization rate that involves both nucleation and growth rate parameters. Since Eq. 3 can be rewritten as: $\ln[-\ln(1 - X_t)] = \ln(-Z_t) + n \ln(t)$, n and Z_t can be evaluated from the slope and intercept of the plots of $\ln[-\ln(1 - X_t)]$ vs. $\ln t$ for each cooling rate, respectively (see Figure 4). Considering the effect of cooling rate, Jeziorny presented the corrected Z_c as the parameter for characterizing the kinetics of nonisothermal crystallization:

$$\ln(-Z_c) = \frac{\ln(-Z_t)}{D} \tag{4}$$

The Avrami exponent n, and the crystallization rate constant Z_c are also listed in Table 1. The n of PP/nano-SiO_2 composites varies in the

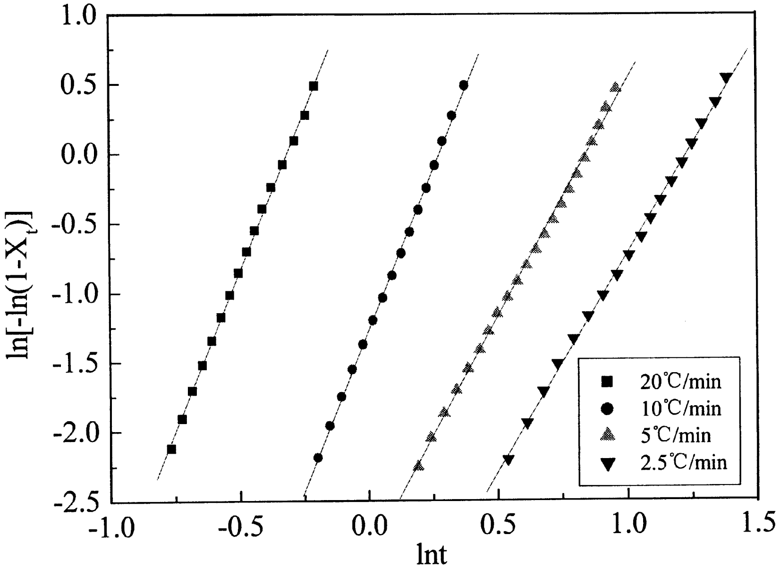


FIGURE 4 Plot of ln[$-$ln(1 $-X_t$)] vs. *lnt* for crystallization of PP/(4 wt%) nano-SiO$_2$ composites.

range of 3.14–4.87, indicating that a typical three-dimension growth of spherulite occurs in the nonisothermal crystallization process. The crystallization rate constant, Z_c, of PP/nano-SiO$_2$ composites increases with increasing the cooling rate, which means that there is an increase in the nucleation rate and growth rate with increasing cooling rate. Whereas, at the same cooling rate, the Z_c of PP/nano-SiO$_2$ composites is higher than that of pure PP, indicating that the spherulite's nucleation rate and growth rate also increase with the addition of nano-SiO$_2$.

Ozawa extended the Avrami equation to the nonisothermal condition. Assuming that the nonisothermal crystallization is the result of infinitesimally small isothermal crystallization steps, the following equation was derived [24]:

$$1 - X_t = \exp[-K(T)/D^m] \tag{5}$$

where $K(T)$ is the function of cooling rate and m is the Ozawa exponent, which is dependent on the dimension of the crystal growth. From plots of ln[$-$ln(1 $-X_t$] vs. ln D at a given temperature, a series of parallel lines should be obtained.

Using Ozawa's method, the results of the nonisothermal crystallization kinetics of PP/nano-SiO_2 composites are shown in Figure 5. It can be seen that the Ozawa method does not produce accurate analysis for the nonisothermal crystallization kinetics of PP/nano-SiO_2 composites, because straight parallel lines can not be obtained. Two main factors can be responsible for the failure of the Ozawa model: first, at a given temperature, the crystallization process at different cooling rates is at a different stage, that is, the lower cooling rate process is at the end of the crystallization process, whereas at the higher cooling rate, the crystallization process is at an earlier stage. Then the change of the slope with temperature means that the parameter *m* is not a constant during crystallization, indicating that Ozawa's approach is not a good method to describe the nonisothermal crystallization process. The second reason may be that the Ozawa exponent can change with the cooling rate, crystallization temperature, and the transformed volume fraction.

Recently, a new method, developed by Mo, was also employed to describe the nonisothermal crystallization for comparison. For the nonisothermal crystallization process, the crystallinity is related to both the cooling rate *D* and the crystallization time *t*. At a fixed

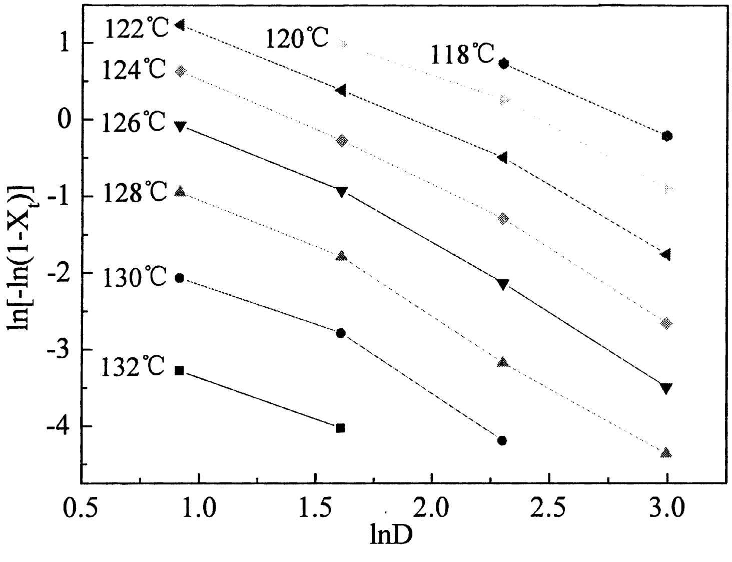


FIGURE 5 Ozawa plot of $\ln[-\ln(1-X_t)]$ vs. $\ln D$ for crystallization of PP/(4 wt%) nano-SiO_2 composites at different crystallization temperatures.

crystallinity, combining the Avrami equation and the Ozawa equation can produce the relationship between D and t:

$$\ln Z_t + n \ln t = \ln K(T) - m \ln D \tag{6}$$

And by rearrangment:

$$\ln D = \ln F(T) - a \ln t \tag{7}$$

Where $F(T) = [K(T)/Z_t]^{1/m}$ refers to the cooling rate value, which must be chosen within unit crystallization time when the measured system amounts to a certain relative crystallinity; a is the ratio of the Avrami exponent n to the Ozawa exponent m (a = n/m). It can be seen that $F(T)$ has a definite physical and practical meaning. According to Eq. 7, at a given relative crystallinity, plotting ln D vs. ln t Results in a linear relationship between ln D and ln t (Figure 6), The results of the kinetic parameter $F(T)$ and a are estimated from the intercept and slope of the line and are presented in Table 2. From Table 2, it can be seen that $F(T)$ systematically increases with increasing relative crystallinity, and indicates that the required cooling rate for attaining a certain relative crystallinity in unit crystallization times increased.

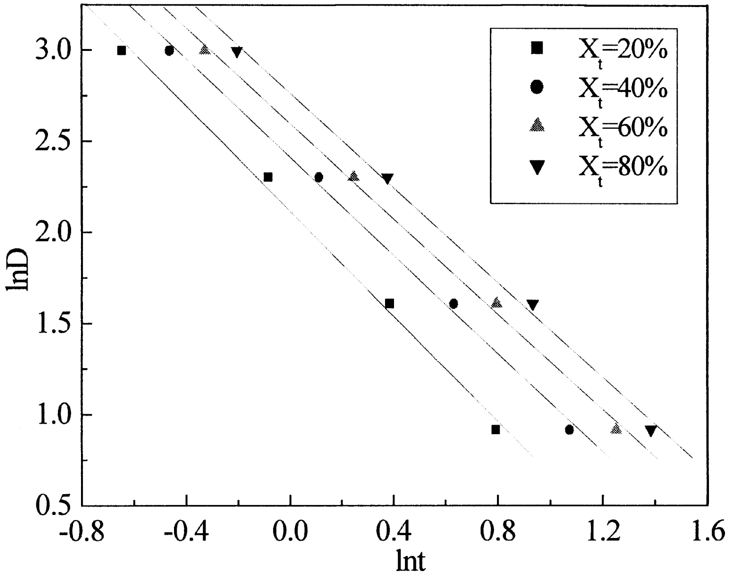


FIGURE 6 Plot of InD vs. Int of PP/(4 wt.%) nano–SiO$_2$ composites.

TABLE 2 Values of *F*(*T*), *a*, and ΔE for Crystallization of PP/nano-SiO$_2$ Composites

Sample	X_t (%)	*F(t)*	*a*	ΔE(kJ/mol)
PP	20	9.046	1.323	442.38
	40	12.44	1.300	
	60	15.09	1.284	
	80	18.99	1.326	
4%	20	8.324	1.441	403.19
	40	11.18	1.346	
	60	13.45	1.307	
	80	15.88	1.297	
8%	20	8.974	1.445	372.55
	40	11.96	1.380	
	60	13.99	1.322	
	80	16.43	1.296	

Moreover, it also can be seen that the required cooling rate of PP is higher than that of PP/nano-SiO$_2$ composites for attaining the same relative crystallinity, which shows that the crystallization rate of PP/nano-SiO$_2$ composites is faster than that of pure PP. Meanwhile, from Figure 6, it is clearly seen that there is a good linear relationship between $\ln D$ and $\ln t$, which suggests that this method is successful in describing the nonisothermal crystallization process of PP/nano-SiO$_2$ composites.

In addition, Kissinger [25], based on the following equation, proposed a method, which is often used in evaluation of activation energy at different cooling rates:

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

where R is the universal gas constant and ΔE is the activation energy of crystallization. From the slope of the plot $\ln(D/T_p^2)$ vs. $1/T_p$ (Figure 7), the crystallization activation energy of PP and PP/nano-SiO$_2$ composites are determined (see Table 2). The results show that the activation energy of PP/nano-SiO$_2$ composites is lower than that of pure PP, indicating that the addition of nano-SiO$_2$ decreases the crystallization activation energy of PP, which is attributed to the strong interaction between PP and nano-SiO$_2$, making the energy of chain segment

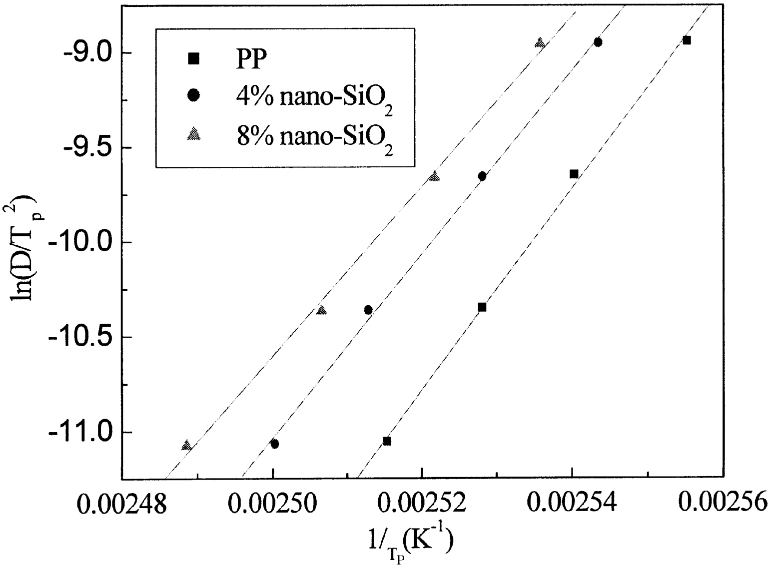


FIGURE 7 Plot of In(D/T_p^2) vs. $1/T_p$ of PP/nano-SiO_2 composites.

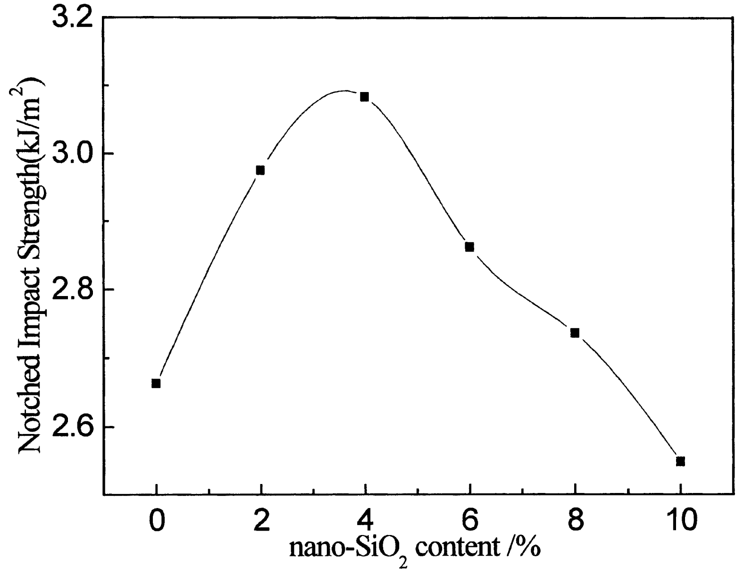


FIGURE 8 Notched impact strength of PP/nano-SiO_2 composites.

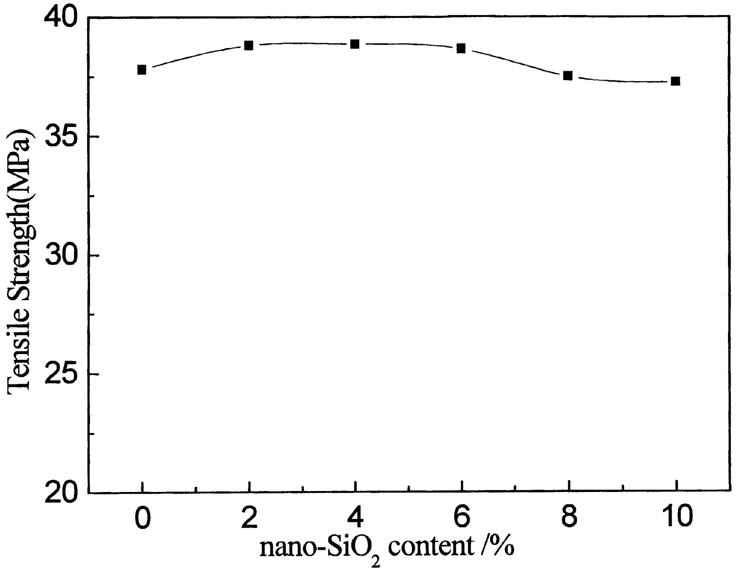


FIGURE 9 Tensile strength of PP/nano-SiO_2 composites.

arrangement of PP decrease during the nonisothermal crystallization process.

Mechanical Properties of PP/nano-SiO_2 Composites

The relationship between the notched impact strength and the content of nano-SiO_2 is shown in Figure 8. The impact strength of composites increased when 2 wt% nano-SiO_2 was added. The maximum impact strength was achieved when the content of nano-SiO_2 was 4 wt%. When the addition of nano-SiO_2 was over 4 wt%, the impact strength of the composites decreased with increasing nano-SiO_2 content. The variation of the tensile strenght of the composites is little, as shown in Figure 9.

Figure 10 shows the micrographs of POM of the PP/nano-SiO_2 composites. The pure PP reveals well-defined spherulite morphology. With the addition of 2 wt% nano-SiO_2, the dimension of the PP spherulite is decreased. When the nano-SiO_2 content increased to 4 wt%, the size of the spherulite is much smaller compared to that of pure PP, as shown in Figure 10c. The much smaller size of the spherulites may be responsible for the increased toughness.

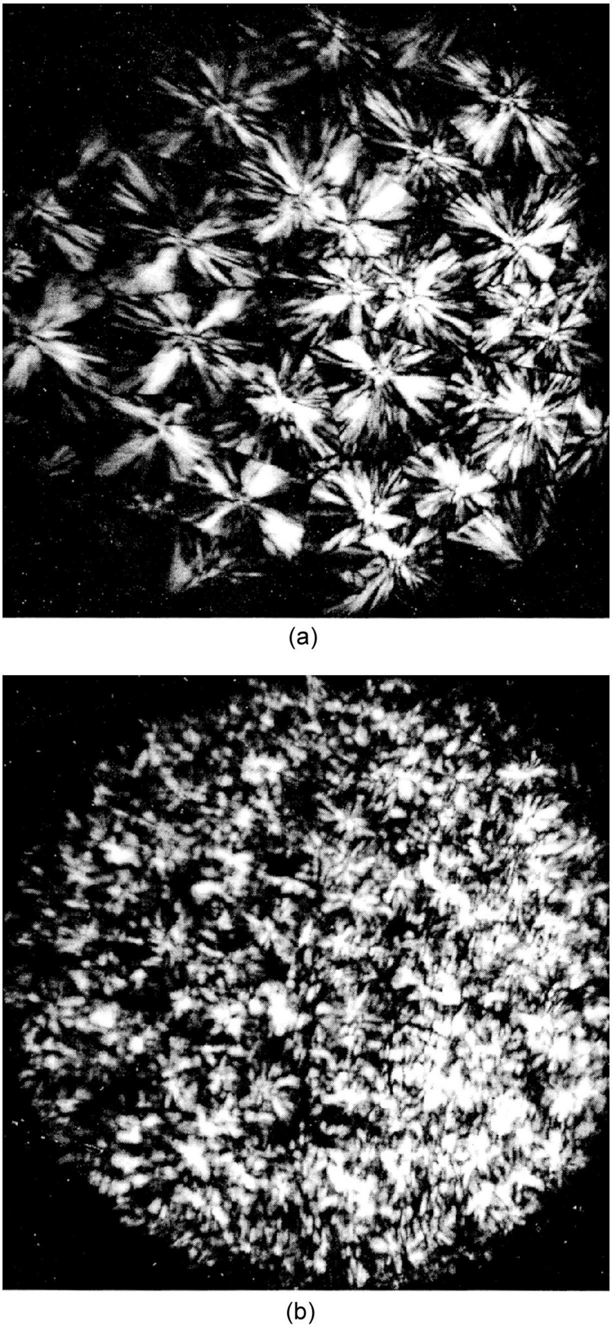
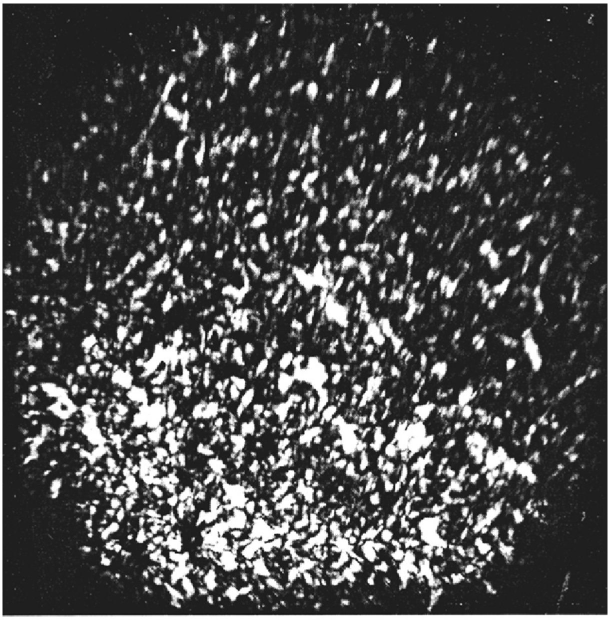


FIGURE 10 POM micrographs of PP/nano-SiO_2 composites. (a) pure PP, (b) 2 wt% nano-SiO_2, (c) 4 wt% nano-SiO_2.



(c)

FIGURE 10 (*Continued*).

CONCLUSIONS

1. The Ozawa analysis failed to provide an adequate description to the nonisothermal crystallization of PP/nano-SiO$_2$ composites. However, the Avrami analysis modified by Jeziorny and a method developed by Mo were successful.
2. The addition of nano-SiO$_2$ resulted in changing both crystallization nucleation and growth during the crystallization process of PP. The values of half-time ($t_{1/2}$) and the parameter (Z_c) showed that the crystallization rate of PP/nano-SiO$_2$ composites is faster than that of pure PP. The crystallization activation energy of PP/nano-SiO$_2$ composites is lower than that of pure PP. The results show that the addition of nano-SiO$_2$ accelerates the overall nonisothermal crystallization process of PP.
3. Due to the decreased spherulite dimension and increased physical entanglement crosslink with the addition of nano-SiO$_2$, the results of mechanical properties of PP/nano-SiO$_2$ composites are superior to pure PP. POM micrographs further demonstrate that nano-SiO$_2$ effects the toughening of PP.

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