Non-isothermal crystallization of HDPE/nano-SiO$_2$ composite

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The kinetics of non-isothermal crystallization of high density polyethylene/nano-scale silicon dioxide (HDPE/nano-SiO$_2$) composite was investigated by means of differential scanning calorimetry at various cooling rates. Several theoretical models were applied to describe the process of non-isothermal crystallization. The results showed that the Avrami analysis modified by Jeziorny or by Mo's treatment could describe the non-isothermal crystallization of the composite very well, but the Ozawa analysis did not give an adequate description. The Avrami exponent n of HDPE/nano-SiO$_2$ composite is slightly larger than that of HDPE. The values of half-time $t_{1/2}$ and Z_c showed that the crystallization rate increased with increasing cooling rates for both HDPE and HDPE/nano-SiO$_2$ composite, but the crystallization rate of HDPE/nano-SiO$_2$ composite was faster than that of HDPE. The activation energies were estimated to be 166.3, 206.2, 251.1 and 266.0 kJ/mol for non-isothermal crystallization of pure HDPE and HDPE/nano-SiO$_2$ composites with different SiO$_2$ loadings of 1%, 3%, and 5% respectively. © *2003 Kluwer Academic Publishers*

1. Introduction

High density polyethylene (HDPE) is an important polymer with high-tonnage production due to its superior mechanical and physical properties. However its toughness, weather resistance, processability and environmental stress cracking resistance are not good enough, which have limited its application in many high-tech fields. One measure to improve the properties is to reinforce with some fillers to form a composite [1–6]. In this presentation the project studied is the composite of HDPE with nano-scale silicon oxide (nano-SiO$_2$) powder filler.

The crystallization behavior of polymer is a basic problem in polymer physics. Especially the filler in a polymer will affect the crystallization behavior of the polymer-based composites very much [7–9] because the filler may adsorb the polymer molecules and act as crystal nuclei. Usually research on the polymer crystallization process is limited to idealized conditions such as isothermal crystallization with constant external conditions; therefore, the theoretical analysis is relatively easy, and the problems concerning cooling rates and thermal gradients within the specimens can be avoided. However, to be relevant to industrial processing, it is desirable to study the crystallization of nanocomposites under non-isothermal conditions because the isother-

mal crystallization conditions are rarely met during the practical processing.

The crystallization studies on HDPE with nano-filler have been reported by several authors. Zheng [9] investigated the crystallization behavior of rare earth neodymium-iron-boron (NdFeB) magnetic powder/high density polyethylene composite. The results showed there was a remarkable heterogeneous nucleation effect of NdFeB on the HDPE matrix. Huang [10] explored HDPE reinforced and toughened by nano-CaCO$_3$. HDPE can be reinforced and toughened by the adhesion force between nano-CaCO$_3$ and HDPE matrix even when the surface of nano-CaCO$_3$ particles is untreated. He [11] prepared HDPE/nano-SiO$_2$ composites by a new dispersing method, using avibrational mill to disperse the nano-SiO$_2$ into HDPE. The composite exhibited excellent abrasive performance. As to our knowledge, there is no report about the isothermal and non-isothermal crystallization behavior of HDPE/nano-SiO$_2$ composites. In our previous work [8], we successfully prepared polypropylene/montmorillonite (PP/Mont.) nanocomposites and studied the non-isothermal crystallization of the nanocomposite based on the Avrami analysis modified by Jeziorny and a method developed by Mo's group. In this article, we report

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the crystallization kinetics of HDPE/nano-SiO₂ composite. Several non-isothermal crystallization kinetic equations were employed to deal with the non-isothermal crystallization data. The kinetic parameters like the Avrami exponent and the activation energy were evaluated from the data based on differential scanning calorimetry (DSC) crystallization exotherms for the original HDPE and the HDPE/nano-SiO₂ composites.

2. Experimental
2.1. Materials
SiO₂ filler with the size of 16 nm was provided by Zhoushan Mingri Nano-materials Co. Having been dried in 110°C for 4 hours, the surface of the SiO₂ filler was covered by silane coupling agent (Kh560), which was purchased from Nanjing Shuguang Chemical Co., before use. the HDPE (Hizex 7000F) used was a product of Mitsui Chemicals Co., Japan with the melt index of 0.04 g/10 min and was used without any treatment.

2.2. Preparation of HDPE/nano-SiO₂ composite
The HDPE and nano-SiO₂ filler covered with silane coupling agent were mixed in a roller at 418–423 K for 10–15 min. The resulting sheet was compression molded at 433 K for 5 min into a plate with a thickness of 2 mm, and kept at in room temperature until conducting the measurements.

2.3. Non-isothermal DSC analysis
The non-isothermal crystallization kinetics of HDPE/nano-SiO₂ composite in the cooling mode from the molten state (melt crystallization) was carried out on a Perkin-Elmer DSC Pyris-1 in nitrogen atmosphere. The temperature and energy readings were calibrated with indium at each cooling rate used in the measurement. The raw sample of 7–10 mg was heated first up to 433 K rapidly and kept for 5 min in the cell in order to eliminate the thermal history of the sample and destroy any nuclei that might act as seed crystals. Then the sample was cooled down to 323 K at five different cooling rates of 2, 5, 10, 20 and 40 K/min, respectively. The exothermic crystallization peak was recorded as a function of temperature, and the change of enthalpy was recorded at the same time.

3. Results and discussion
3.1. Crystallization behavior of HDPE/nano-SiO₂ composite
The crystallization exotherms of the original HDPE and the HDPE/nano-SiO₂ composite at five cooling rates of 2, 5, 10, 20 and 40 K/min are shown in Fig. 1. Some useful kinetic parameters can be read from the curves directly. They are the peak temperature, T_p, the relative degree of crystallinity X_t, starting crystallization temperature T_{on}, crystallization enthalpy ΔH_c and half crystallization time, $t_{1/2}$, which are listed in Table I. The effect of the different cooling rates is following: the faster the cooling rate, the lower the temperature range at which the crystallization occurs, at slower cooling rate, there is sufficient time to activate nuclei at higher temperature. On the contrary, at faster cooling rates, the activation of nuclei occurs at lower temperature. Consequently, crystallization nucleates at higher temperatures when the polymer samples are cooled at a slower scanning rate. The peak temperature T_p shifts to lower temperature with an increasing cooling rate for both he original HDPE and the HDPE/nano-SiO₂ composite. For a given cooling rate, T_p of the HDPE/nano-SiO₂ composites is slightly higher than that of the original HDPE, indicating that the addition of SiO₂ nano-particles into HDPE increases the crystallization rate of HDPE. The crystallization enthalpy ΔH_c has the same variation tendency as the cooling rate increases, but shifts to lower values when the SiO₂ loading in the composites increases. This means that the crystallization of HDPE/nano-SiO₂ composites becomes more imperfect than the original HDPE. The half crystallization time $t_{1/2}$ decreased with increasing cooling rate and SiO₂ loading in nanocomposites. The SiO₂ nano-particles have a remarkable heterogeneous nucleation effect on the HDPE matrix, and speed of the process of crystallization of HDPE.
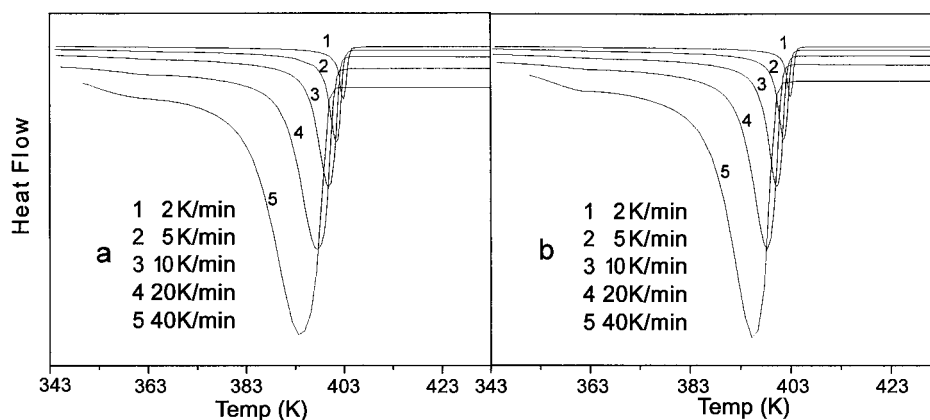

Figure 1 DSC thermograms of non-isothermal cold crystallization for the original HDPE (a) and HDPE/nano-SiO₂ composite with 3% loading of SiO₂ (by weight) (b).

TABLE I Values of the T_{peak}, $t_{1/2}$, ΔH_c, n and Z_c at various cooling rates

Samples	ϕ(K/min)	T_{peak} (K)	T_{onset} (K)	$t_{1/2}$ (S)	ΔH(J/g)	n	Z_c
Origin HDPE	40	383.8	390.3	15.5	175.6	2.8	1.27
	20	387.8	392.0	21.6	179.9	2.9	1.51
	10	389.9	392.5	28.4	183.1	3.3	1.64
	5	391.6	393.4	50.2	183.9	3.4	1.75
	2	393.1	394.3	84.7	190.5	3.2	0.30
HDPE/nano-SiO$_2$	40	385.4	390.4	12.2	171.6	2.9	1.12
(1% by wt)	20	388.5	391.6	15.3	180.2	2.8	1.51
	10	390.4	392.5	24.7	179.5	3.1	1.78
	5	391.8	393.4	35.7	182.4	3.1	1.61
	2	393.1	394.3	71.3	189.2	3.1	0.65
HDPE/nano-SiO$_2$	40	386.7	390.7	11.4	171.4	2.9	1.32
(3% by wt)	20	389.1	391.6	15.6	179.3	3.4	1.64
	10	390.9	392.7	20.8	172.8	3.2	1.95
	5	392.0	393.3	21.8	176.5	3.2	1.79
	2	393.2	394.2	33.3	185.2	3.4	0.17
HDPE/nano-SiO$_2$	40	386.9	390.5	11.6	168.9	3.6	1.43
(5% by wt)	20	389.3	391.4	15.2	171.2	3.6	1.76
	10	390.8	392.6	22.6	174.1	3.3	1.92
	5	392.0	393.3	51.5	170.7	3.3	1.89
	2	393.2	394.3	65.1	180.2	3.2	0.41

3.2. Non-isothermal crystallization kinetics of HDPE/nano-SiO$_2$ composite

Several methods [12] of describing the crystallization kinetics are based on the Avrami equation,

$$1 - X_t = \exp\left(-Z_t t^n\right) \qquad (1)$$

where X_t is a relative degree of crystallinity, a function of crystallization temperature T, the exponent n is a mechanism constant depending on the type of nucleation and growth process parameters; and parameter Z_t is a composite-rate constant involving both nucleation growth rate parameters. One approach adopted here is Jeziorny's modified Avrami method, which allows direct applicator of the Avrami analysis to the data obtained from the non-isothermal crystallization thermograms. Using Equation 1 in double-logarithmic form

$$\ln[-\ln(1 - X_t)] = \ln Z_t + n \ln t \qquad (2)$$

Plotting $\ln[-\ln(1 - X_t)]$ against in t for each cooling rate, a straight line is obtained with the data at a lower degree of crystallinity in the linear regression only (Fig. 2). Thus two parameters n and Z_t are obtained from the plots. It should be taken into account that in non-isothermal crystallization, the values of the n and Z_t do not have the same physical significance as in isothermal crystallization, due to the fact that the temperature changes constantly under non-isothermal conditions. It affects the rates of both nuclei formation and spherulite growth since they are temperature dependent. In this case, n and Z_t might be only considered as two adjustable parameters to fit the data. Although the physical meaning of n and Z_t cannot be related to the isothermal case in a simple way, Equation 1 provides further insight into the kinetics of non-isothermal crystallization.

Considering the non-isothermal character of the process investigated, Jeziorny [13] proposed the following form of the parameter characterizing the kinetics of
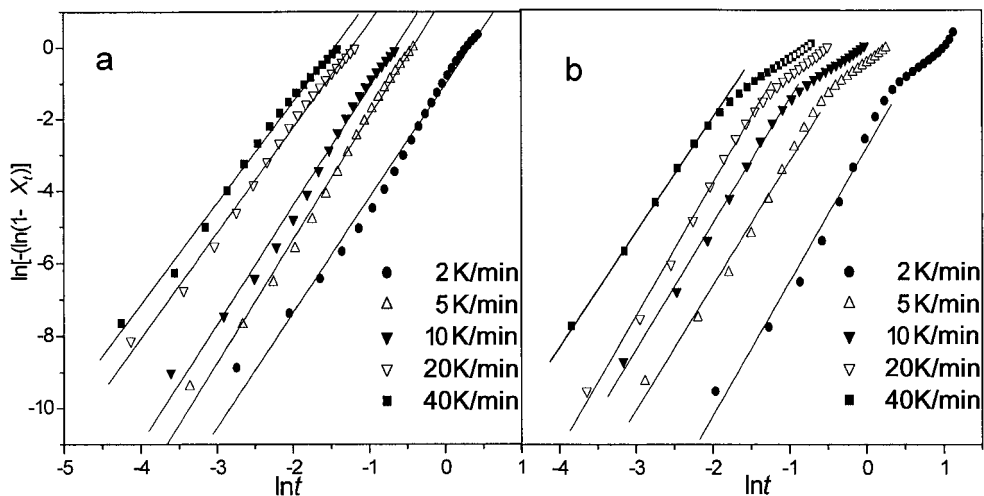
Figure 2 Plots of $\ln(-\ln(l - X_t))$ versus $\ln t$ for crystallization of the original HDPE (a) and HDPE/nano-SiO$_2$ composite with 3% loading of SiO$_2$ (by weight) (b).

non-isothermal crystallization

$$\ln Z_c = \ln Z_t / \phi \qquad (3)$$

where Z_c is the corrected kinetic rate constant; ϕ is cooling rate. The results obtained from the Avrami plots and Jeziorny method are summarized in Table I as well. The Avrami exponents n are non-integer and range from 2.8 to 3.4 for the original HDPE, which is consistent with the results of Gupta [14], and from 2.9 to 3.6 for HDPE/nano-SiO$_2$ composites. The n values for HDPE/nano-SiO$_2$ composites are slightly larger than that of the original HDPE at the same cooling rate, indicating that the nano-particles of SiO$_2$ act as a nucleating agent for the HDPE matrix. The Z_c values of HDPE/nano-SiO$_2$ composites are, as expected, higher than that of the original HDPE at the same cooling rate.

The alternative approach adopted here is the Ozawa equation. Assuming that the non-isothermal crystallization process is the result of an infinite number of the small isothermal crystallization steps, the following equation has been derived [15]:

$$1 - X_t = \exp[-K(T)/\phi^m] \qquad (4)$$

where $K(T)$ is the function of cooling rate; m is the Ozawa exponent that depends on the dimension of crystal growth. Taking the double-logarithmic form

$$\ln[-\ln(1 - X_t)] = \ln K(T) - m \ln \phi \qquad (6)$$

Studying the process at different cooling rates and plotting $\ln[-\ln(1-X_t)]$ against $\ln \phi$ at a given temperature, a straight line should be obtained if the Ozawa method is valid. And parameters of m and $K(T)$ can be determined from the slope and intercept, respectively.

Fig. 3 shows the results for the original HDPE and the HDPE/nano-SiO$_2$ composites according to Equation 6 of the Ozawa method. The non-linear dependence of $\ln[-\ln(1 - X_t)]$ upon $\ln \phi$ shows that the Ozawa equation is not suitable to describe the non-isothermal crystallization in the HDPE and HDPE/nano-SiO$_2$ composite. The curvature in Fig. 3 prevents an accu-

rate analysis of the non-isothermal crystallization data. For polyethylene and its composites the crystallization is complicated due to an additional slow process, referred to as secondary crystallization, which is considered to involve improvement of the crystalline order. The secondary effect for polyethylene crystallization is sometimes greater than 40% of the total [16] and may be for this reason the Ozawa equation is not fulfilled.

In order to understand the crystallization behavior deeply, a method proposed by Mo's group more recently [14, 15] is introduced to describe the non-isothermal crystallization of the original HDPE and the HDPE/nano-SiO$_2$ composite. For the non-isothermal crystallization process, physical variables relating to the process are the degree of crystallization X_t, cooling rate ϕ, and crystallization temperature T. By combining Ozawa and Avrami equations, Mo developed the following equations,

$$\ln Z_t + n \ln t = \ln K(T) - m \ln \phi \qquad (7)$$

or its rewritten form

$$\ln \phi = \ln F(T) - a \ln t \qquad (8)$$

where $F(T) = [K(T)/Z_t]^{1/m}$, m is the Ozawa exponent, and a is the ratio between the Avrami exponent n and the Ozawa exponent $m (a = n/m)$. $F(T)$ refers to the value of the cooling rate chosen at unit crystallization time, when the system has a defined degree of crystallinity. According to Equation 8, for a given relative degree of crystallinity, the plot $\ln \phi$ versus $\ln t$ gives a straight line (as shown in Fig. 4) with $\ln F(T)$ as the intercept and a as the slope (as shown in Table II). It is shown that $F(T)$ systematically increases with a rise in the relative degree of crystallinity, and the values of a decrease with an increasing relative degree of crystallinity. The $F(T)$ vales of the original HDPE are larger than those of HDPE/nano-SiO$_2$ composites and the values of a of the original HDPE are lower than those of HDPE/nano-SiO$_2$ composites at the same relative degree of crystallinity. It is clear that this method is successful in describing the non-isothermal process
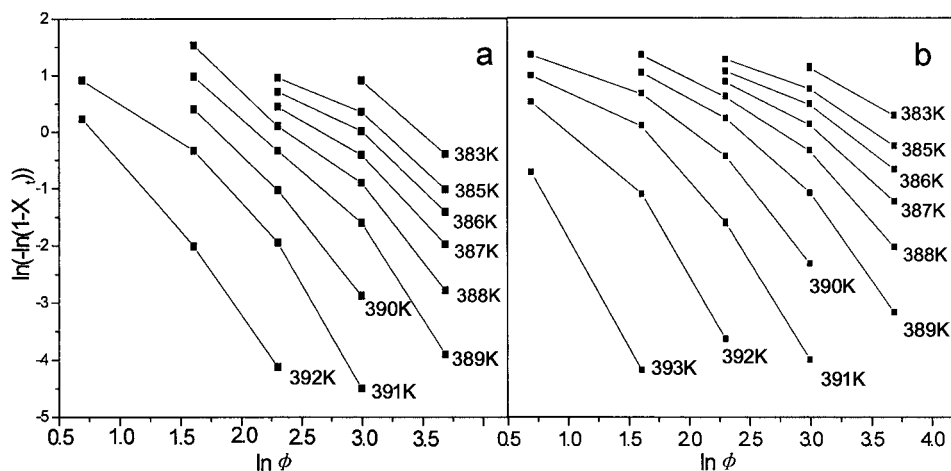

Figure 3 Ozawa plots of $\ln(-\ln(1 - X_t))$ versus $\ln \phi$ for crystallization of the original HDPE (a) and HDPE/nano-SiO$_2$ composite with 3% loading of SiO$_2$ (by weight) (b).
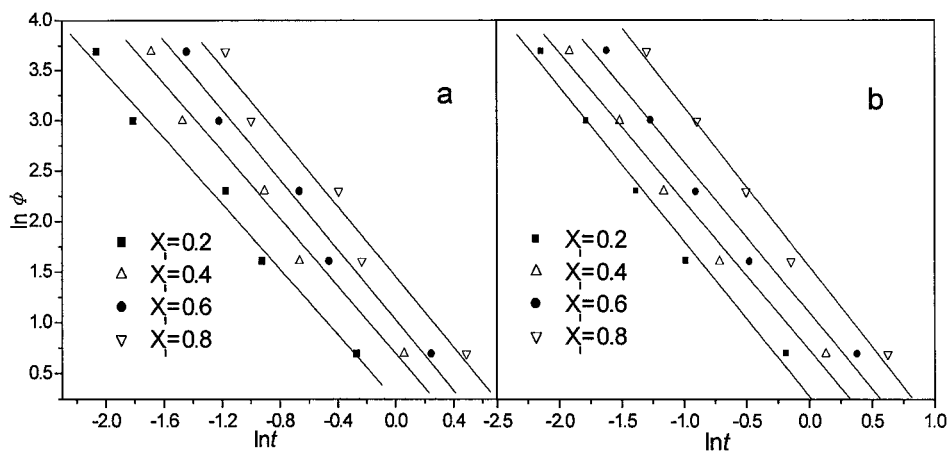
Figure 4 Plots of ln ϕ versus ln t for crystallization of the original HDPE (a) and HDPE/nano-SiO$_2$ composite with 3% loading of SiO$_2$ (by weight) (b).

of the original HDPE and the HDPE/nano-SiO$_2$ composites, as it did also in PP/Mont nanocomposites [7] and POM/Mont nanocomposites [8].

In addition, the approach often used for evaluation of activation energy at different cooling rates was proposed by Kissinger [19], based on the following equation:

$$d[\log n(\phi/T_p^2)]/d(1/T_p) = -\Delta E/R \qquad (9)$$

where R is the universal gas constant and ΔE the activation energy for crystallization. The slopes of plots of $\log(\phi/T_p^2)$ against $1/T_p$ were used to determine (Fig. 5), the activation energies of non-isothermal melt crystallization of HDPE and HDPE/nano-SiO$_2$ composites with the SiO$_2$ loadings of 1%, 3% and 5% (by weight) as 166.3, 206.2, 251.1 and 266.0 kJ/mol, respectively. They increase with increasing SiO$_2$ loading in the composite. The nano-SiO$_2$ particles have double functions in the HDPE matrix. Acting as a nucleating agent, the SiO$_2$ nano-particles accelerate the process of non-isothermal crystallization, which can be proven by the results of the half crystallization time ($t_{1/2}$) and the parameters of non-isothermal
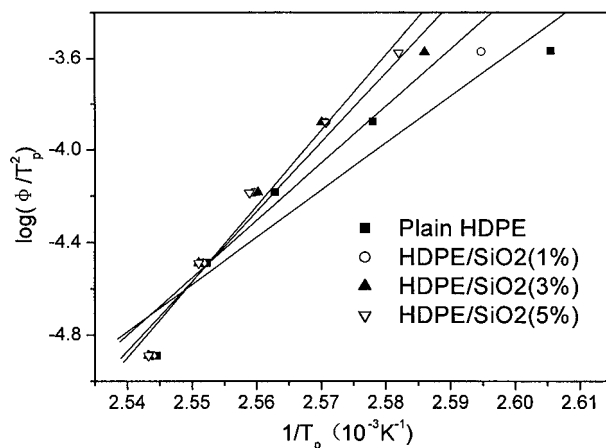

Figure 5 Plots of log (ϕ/T_p^2) versus l/T_p for the original HDPE and HDPE/nano-SiO$_2$ composites.

crystallization. Another function is that the nano-SiO$_2$ particles can easily adsorb the polyethylene molecular segments, this then blocks the movement of molecular segments and makes crystallization difficult. Therefore the segments need more energy to rearrange, and results in increasing of the activation energies of non-isothermal melt crystallization. The fact that activation energies increase with increasing of SiO$_2$ loading in the HDPE/nano-SiO$_2$ composite is different from the behaviour of PP/Mont [7]. The reason comes from the flexibility of the backbone of the polymer. The HDPE chain is more flexible than that of PP, and there are no —CH$_3$ groups hanging from the HDPE backbone, which lessen the adsorption of nano-SiO$_2$ particles to polymeric chains due to steric hindrance. A similar result is also found in the PEO/SiO$_2$ composite [20]. The crystallization behavior of the HDPE/nano-SiO$_2$ composite is confined crystallization like that of the PEO/SiO$_2$ system. The process of non-isothermal crystallization becomes imperfect. Fig. 6 shows the melt DSC thermograms (20 K/min) of HDPE/nano-SiO$_2$ composites with different SiO$_2$ loadings after melt crystallization at the same cooling rate. The peak temperatures decrease with increasing SiO$_2$ loading, and this also indicates that the process of non-isothermal crystallization of HDPE/nano-SiO$_2$ composite is more imperfect than the original HDPE.

TABLE II Nonisothermal crystallization kinetic parameters based on Mo's treatment and Kissinger's method

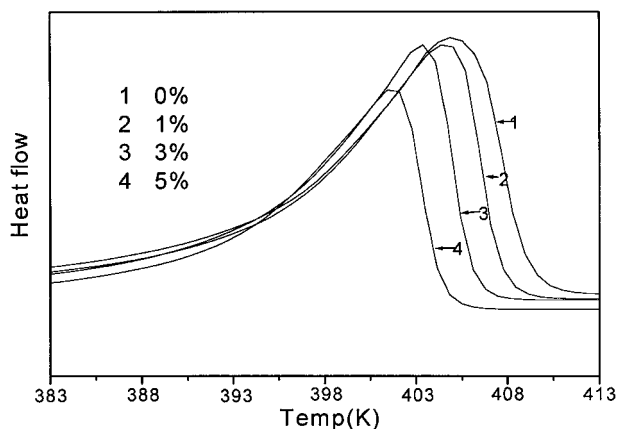| Sample	X_t (%)	$F(T)$	a	ΔE (kJ/mol)
Origin HDPE	20	1.72	1.62	166.3
	40	4.96	1.67	
	60	10.7	1.73	
	80	28.6	1.74	
HDPE/nano-SiO$_2$	20	2.67	1.43	206.2
(1% by wt)	40	5.33	1.59	
	60	11.3	1.67	
	80	39.4	1.65	
HDPE/nano-SiO$_2$	20	2.41	1.52	251.1
(3% by wt)	40	5.45	1.47	
	60	12.7	1.49	
	80	36.1	1.58	
HDPE/nano-SiO$_2$	20	1.74	1.52	266.0
(5% by wt)	40	3.54	1.60	
	60	9.85	1.70	
	80	37.8	1.69	

Figure 6 Melt DSC thermograms (20 K/min) of HDPE/nano-SiO$_2$ composites with various SiO$_2$ loading.

4. Conclusion

Non-isothermal crystallization of HDPE/nano-SiO$_2$ composites shows different rate-dependent characteristics. The Ozawa equation, when applied to this system, failed to provide an adequate description of the non-isothermal crystallization. The Avrami equation modified by Jeziorny's method and Mo's treatment are successful for describing the non-isothermal crystallization process of HDPE/nano-SiO$_2$ composites. The half-time $t_{1/2}$ and the kinetic parameters showed that the crystallization rate of HDPE and HDPE/nano-SiO$_2$ composites increased with increasing cooling rates, but the crystallization rate of HDPE/nano-SiO$_2$ composites is faster than that of HDPE at a given cooling rate. By using the method proposed by Kissinger, activation energies have been evaluated to be 166.3, 206.2, 251.1 and 266.0 kJ/mol for non-isothermal crystallization of HDPE and HDPE/nano-SiO$_2$ composites with SiO$_2$ loadings of 1%, 3% and 5% (by weight), respectively.

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