Study on Crystallization Kinetics of LDPE Filled with CaCO$_3$ of Different Size and Size Distribution

Jun Zhang,[1] Jue Fang,[1] Bing Han,[2] Ninglin Zhou,[1] Juan Wu,[1] Zhen-Mao Ma,[1] Hong Mo,[1] Jian Shen[1,3]

[1]Jiangsu Engineering Research Center for Biomedical Function Materials, College of Chemistry and Environment Science, Nanjing Normal University, Nanjing 210097, People's Republic of China
[2]College of Materials Science and Engineering, Nanjing Institute of Technology, Nanjing 211167, People's Republic of China
[3]Research Center of Surface and Interface Chemistry and Chemical Engineering Technology, Nanjing University, Nanjing 210093, People's Republic of China

ABSTRACT: The thermoplastic filled with the different size distribution fillers was a new method for improving processability of thermoplastic composites. In our former study, we found that the melt torque of low-density polyethylene (LDPE) composites, which were filled with 30 wt % the effective size distribution CaCO$_3$, evidently decreased. In this article, two sizes of CaCO$_3$, 600 meshes and 2500 meshes, were blended by different proportions and were filled into LDPE matrix with 30 wt %. Crystal process, isothermal crystallization kinetics, and nonisothermal crystallization kinetics of a series of composites were characterized by differential scanning calorimeter (DSC). The results showed that composites filled with the effective size distribution CaCO$_3$ leaded to the lower melting and crystallization temperature, the more wide crystallization temperature area, while their the crystallization rate constant (k) of isothermal crystallization kinetics decreased and their Avrami exponents (n) and crystallization half-life ($t_{1/2}$) of isothermal crystallization kinetics increased compared with those of the composites filled with the single size CaCO$_3$. Nonisothermal crystallization kinetics had the similar results. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 120: 3490–3500, 2011

Key words: low density polyethylene; CaCO$_3$; different size and size distribution; crystallization kinetics; torque

INTRODUCTION

Polymer/filler composites have lots of improved properties compared with the neat polymer, such as better mechanical properties, higher stability, and reduced thermal expansion coefficient. Low-density polyethylene (LDPE) is currently the most widely used commercial polymer due to its superior mechanical and physical properties.

In crystalline polymer/filler composites, the crystal morphology, crystallinity, and the melting temperature are the most important factors in determining mechanical and physical properties of final products.[1] The crystallization of these polymers is often influenced not only by processing condition but also by the final products.

The abilities of particle fillers to act as nucleating agents and modify the crystalline matrix of polymers have significant effects on the crystalline structure, crystalline phase, and crystallization process of polymers.[2–16] The different size and size distribution fillers can lead to the different nucleation effects of nucleating agents and the modification of crystalline matrix of polymers.[17]

In our former study, we found that the melting viscosity of polymer composites, which were filled with the different efficient size and size distribution fillers, evidently decreased.[18] The melting viscosity of polymers can affect extensively the crystallization behavior of the polymer composites. The lower the melting viscosity of polymer composites is, the slower the nucleation rate and quicker crystal growth rate is.[19]

In this article, we investigated the crystal morphology and isothermal and nonisothermal crystallization kinetics of LDPE filled with the different size and size distribution CaCO$_3$. Our research was focused on the kinetics of the nucleation and crystal growth of the LDPE composites filled with different size and size distribution CaCO$_3$.

TABLE I
Size and Characteristics of CaCO₃ Used as Fillers

Size of CaCO₃ (mesh)	CaCO₃ content (%)	Top cut (98%) (μm)	Mean particle size (d50%) (μm)	D(3, 2) (μm)
600	≥98.0	25.7	5.4	3.71
2500	≥98.0	8	1.7	1.96

EXPERIMENTAL

Materials

The unfilled LDPE used as matrix was provided by Yangtze Chemical Ind. Ltd.(Nanjing China). The different sizes CaCO₃ samples used as fillers, i.e., 600 meshes and 2500 meshes were provided by Nanjing OMYA Fine Chemical Ind. (Nanjing, China). The size distribution of CaCO₃ samples were measured with LS-CWM (2) laser particle sizer, which was provided by OMEC Co. (Zhuhai China). The characteristics and size of fillers are given in Table I.

Samples preparation

Stearic acid (1 g) and CaCO₃ (50g) were added to a suspension of cyclohexane, stirred at 50°C for 2 h, then filtered off, washed thoroughly with cyclohexane, and dried in a vacuum to gain the activated CaCO₃.

The different sizes CaCO₃ was blended with different percentages and filled into LDPE matrix at 30 wt %. Table II listed the proportions of 600 and 2500 mesh CaCO₃ in the filled mixture. The LDPE and CaCO₃ were blended on a haake rheomix 557-5501 twin screw extruder, which was provided by Thermo Electron Corp. (U.S.). In the extrusion step, barrel temperatures were set at 160, 170, 180, 180°C and a screw speed of 50 rpm was used.

Measurement of DSC

The melting and crystalline behaviors of pure PE and Samples 1–6 were measured with Perkin–Elmer DSC-7. First, Samples 1–6 were heated from the room temperature to 150°C, and held at 150°C for 10 min to eliminate all the thermal histories in the materials. Second, the samples were cooled down to 50°C at the cooling rate of 10°C/min to get their crystalline characteristics. Last, the samples were

TABLE II
Different Size Distribution CaCO₃ of Samples of Blending of 600 and 2500 Mesh Filler

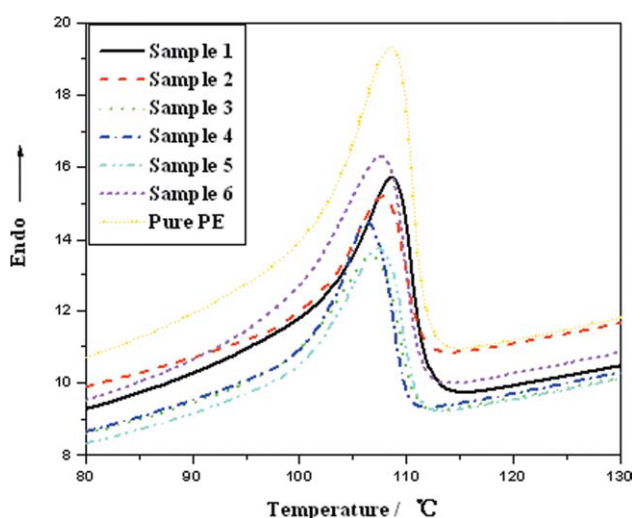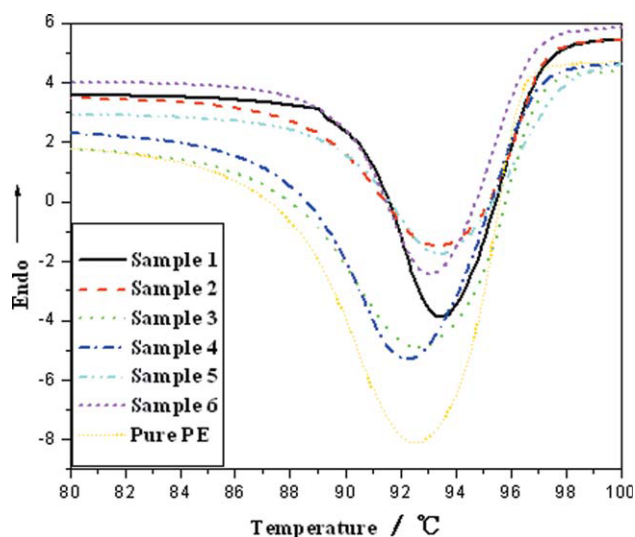| Sample	1	2	3	4	5	6
600 mesh (%)	0	20	40	60	80	100
2500 mesh (%)	100	80	60	40	20	0

Figure 1 Melting curves of pure PE and Samples 1–6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

Figure 2 Crystallization curves of pure PE and Samples 1–6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE III
DSC Results of Pure PE and Samples 1–6 (10 K/min)

Sample	1	2	3	4	5	6	PE
T_m	108.6	107.8	106.7	106.2	107.5	107.7	108.7
T_c	93.5	93.3	92.5	92.1	93.5	93.2	92.6
ΔT	15.1	14.5	14.2	14.1	14	14.5	16.1
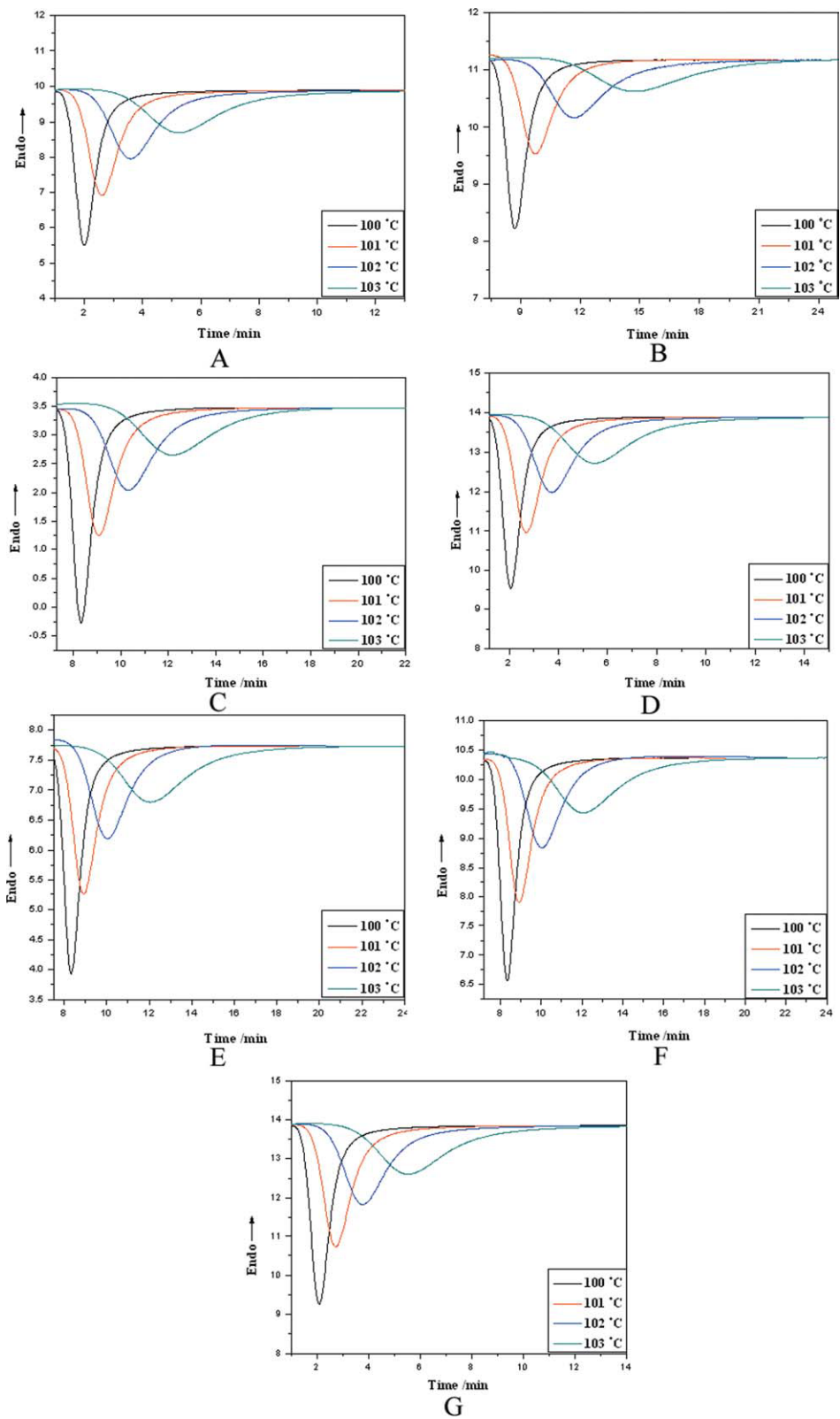
Figure 3 The isothermal crystallization curves of Samples 1–6 and pure PE at various temperatures (100, 101, 102, and 103°C) (A) Sample 1; (B) Sample 2; (C) Sample 3; (D) Sample 4; (E) Sample 5; (F) Sample 6; (G) pure PE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
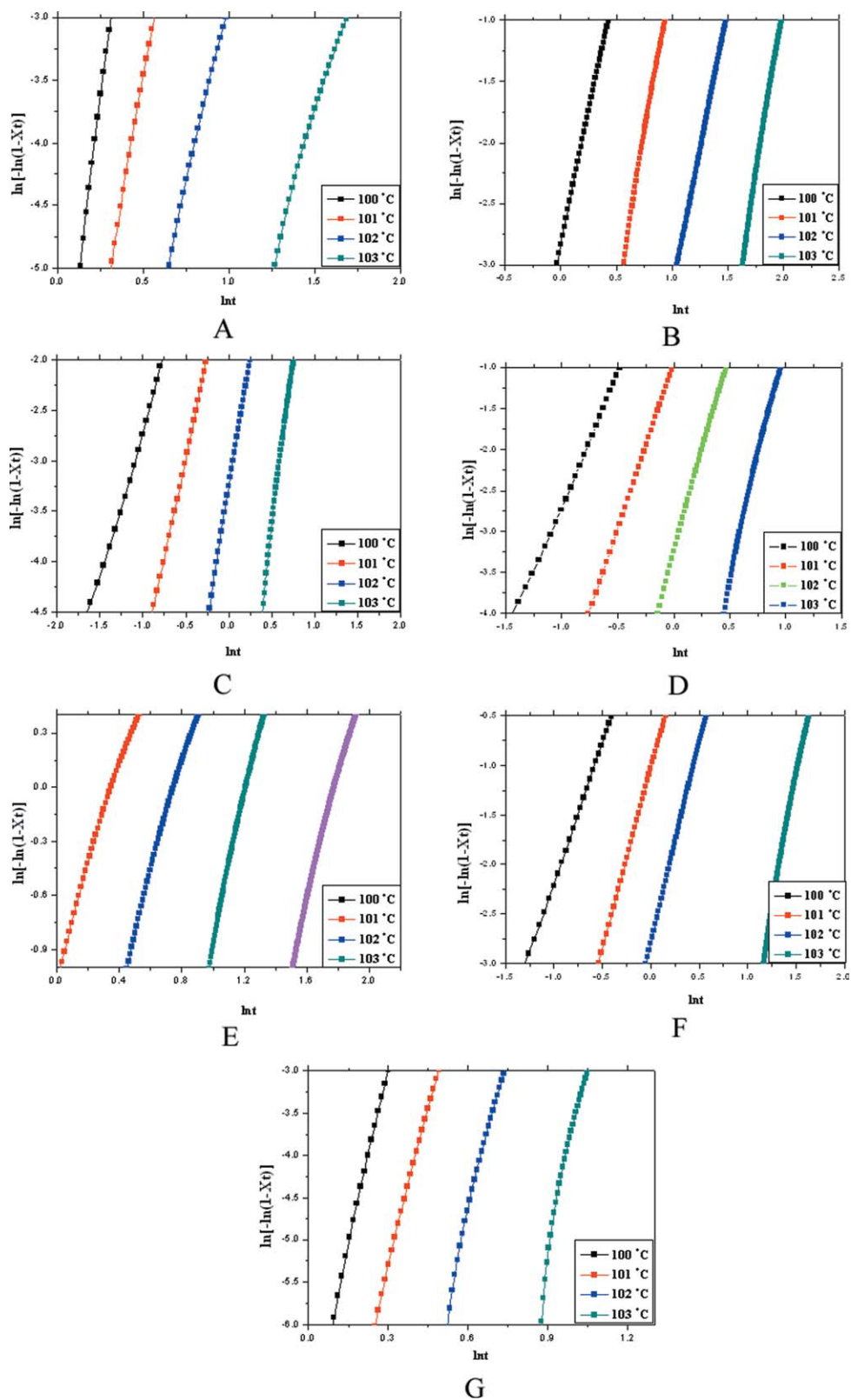
Figure 4 Plots of ln[−ln(1 − X_t)] versus lnt for Samples 1–6 and pure PE (A) Sample 1; (B) Sample 2; (C) Sample 3; (D) Sample 4; (E) Sample 5; (F) Sample 6; (G) pure PE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE IV
Isothermal Crystallization Kinetic Parameters of Pure PE and Samples 1–6

	Sample	PE	1	2	3	4	5	6
100°C	n	2.05	2.15	2.20	2.42	2.57	2.27	2.20
	K (s^{-n})	3.24×10^{-4}	6.25×10^{-4}	5.78×10^{-5}	3.07×10^{-5}	4.25×10^{-5}	4.23×10^{-4}	5.07×10^{-4}
	$t_{1/2}$ (s)	42.1	24.2	71.5	62.9	43.6	26.0	26.6
101°C	n	2.01	2.22	2.47	2.50	2.62	2.22	2.34
	K (s^{-n})	2.34×10^{-4}	3.45×10^{-4}	8.94×10^{-6}	2.25×10^{-5}	2.57×10^{-5}	7.86×10^{-5}	1.58×10^{-4}
	$t_{1/2}$ (s)	53.3	30.8	95.4	62.4	49.1	59.8	36.0
102°C	n	2.05	2.34	2.59	2.74	2.89	2.57	2.46
	K (s^{-n})	4.45×10^{-5}	2.55×10^{-5}	2.12×10^{-6}	9.84×10^{-7}	8.01×10^{-7}	1.21×10^{-5}	1.98×10^{-5}
	$t_{1/2}$ (s)	110.9	78.6	134.6	136.3	113.3	71.1	70.3
103°C	n	2.11	2.54	2.95	2.88	3.11	2.67	2.62
	K (s^{-n})	6.67×10^{-6}	2.47×10^{-6}	1.58×10^{-7}	1.37×10^{-7}	5.02×10^{-8}	1.35×10^{-6}	1.79×10^{-6}
	$t_{1/2}$(s)	238.7	139.6	210.3	212.6	197.5	137.6	135.8

heated to 150°C at the heating rate of 10°C/min to get their melting characteristics. All the operations were performed under nitrogen flow. Sample weight is in the range of 4–5 mg.

During the isothermal crystallization kinetic measurements, the samples were heated from room temperature to 150°C at the heating rate of 50°C/min, and held at 150°C for 10 min to eliminate all the thermal histories in the materials. Then, the samples were cooled rapidly down at the cooling rate of 50°C/min to the crystallization temperatures 100, 101, 102, and 103°C, respectively, and held at these temperatures for the entire crystallization process.

During the nonisothermal crystallization kinetic measurements, the samples were heated from the room temperature to 150°C at the heating rate of 50°C/min, and held at 150°C for 10 min to eliminate all the thermal histories in the materials. Then, the samples were cooled down to crystallize at the selected constant rates (from 5 to 40°C/min). All the operations were performed under a nitrogen purge. Sample weight was in the range of 4–5 mg.

Measurement of equilibrium torque

Equilibrium torque of Samples 1–6 were measured in a Haake torque rheometer (Polylab 600) which was provided by Thermo Electron Corp. (Waltham, M.A. U.S.). The measure temperature was 180°C and the rotor speed was between 40 and 80 rpm. The sample volume of each blending was 49 cm^3. The measure data were the average torque from the 2 min after the on set to the end of the test (the record time was 5 min.).

RESULTS AND DISCUSSION

Melting and crystallization behaviors

The effects of the fillers on the thermal properties of LDPE have been analyzed in nonisothermal DSC experiments. The melting curves of pure LDPE and

Samples 1–6 at the heating rate of 10°C/min are shown in Figure 1. The crystallization curves of pure LDPE and Samples 1–6 at the cooling rate of 10°C/min are shown in Figure 2. Figure 2 clearly shows that the crystallization peaks of the single size filler samples (Samples 1 and 6) are sharper and higher compared with those of the efficient size distribution samples (Samples 3 and 4).

Thermal parameters such as the melting temperature (T_m), the crystallization temperature (Tc) and the supercooling ($\Delta T = T_m - T_c$) of pure LDPE and Samples 1–6 were analyzed by nonisothermal crystallization experiments. The results are listed in Table III.

It indicates that the efficient size distribution samples (Samples 3 and 4) have the lower melting temperature and the lower crystallization temperature than those filled with the single size fillers (Samples 1 and 6). The melting and crystallization temperature of Samples 2 and 5 are higher than those of the efficient size distribution filler filled PE samples, but lower than those of the single size filler filled PE samples. Because the lower melting temperature results in the lower process temperature of polymers, the efficient size distribution samples can be processed at the lower temperature and its energy consumption in the process decrease.

Isothermal crystallization kinetics

Isothermal crystallization is a process in which LDPE is heated rapidly above its melting temperature T_m (150°C in this study), and then cooled down to various temperatures, i.e., 100, 101, 102, and 103°C, respectively, which are below the melting temperature T_m but above the glass transition temperature T_g, as can be seen in Figure 3. Those temperatures are considered as the crystallization temperature T_c. Under the isothermal crystallization condition, the polymers transform from a melting liquid to a crystalline solid.

The relative degree of crystallinity, X_t, as a function of crystallization time, t, is defined as
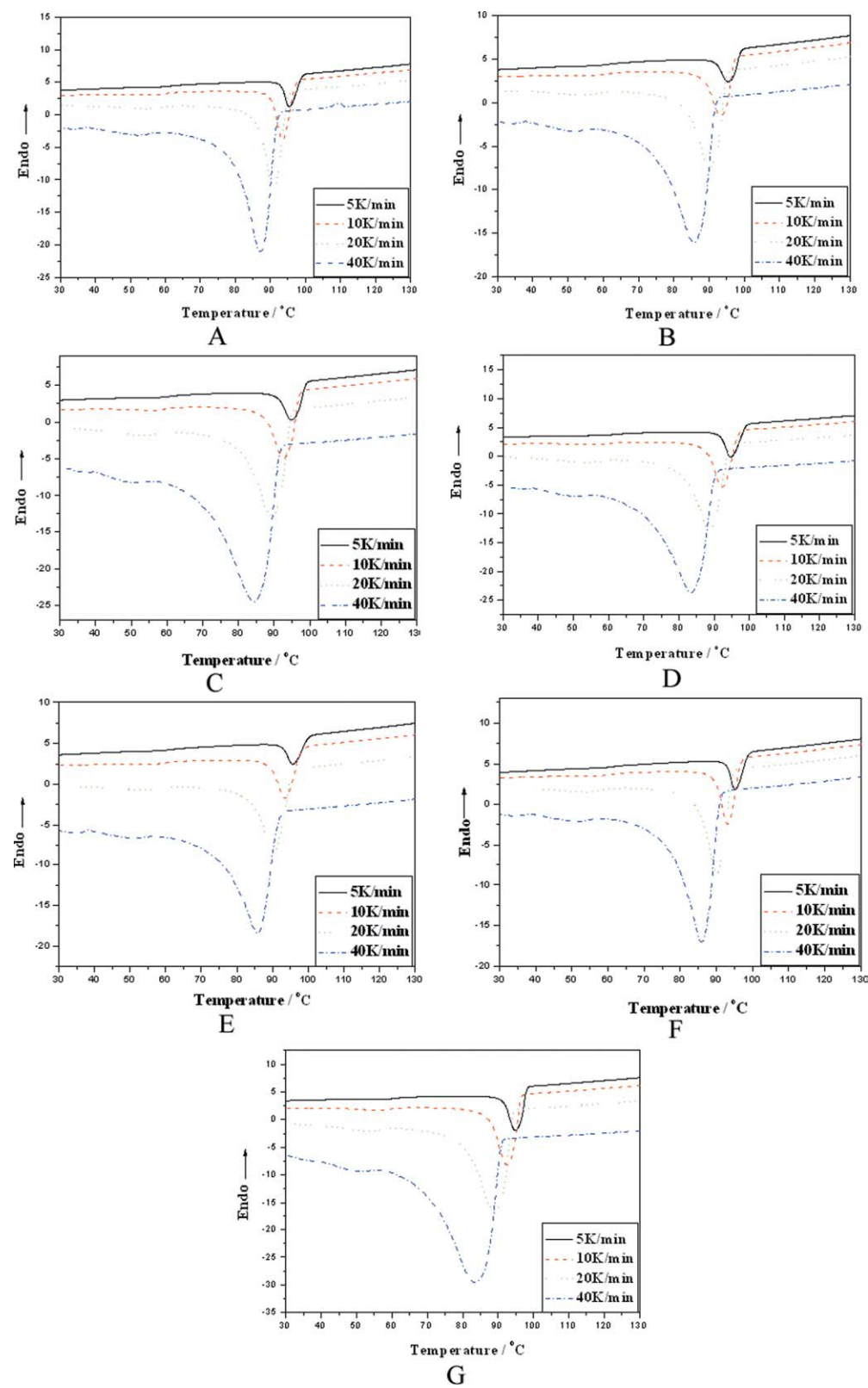
Figure 5 The nonisothermal crystallization curves of 1–6 samples and pure PE at various cooling rate (5, 10, 20, 40°C/min) (A) Sample 1; (B) Sample 2; (C) Sample 3; (D) Sample 4; (E) Sample 5; (F) Sample 6; (G) pure PE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]
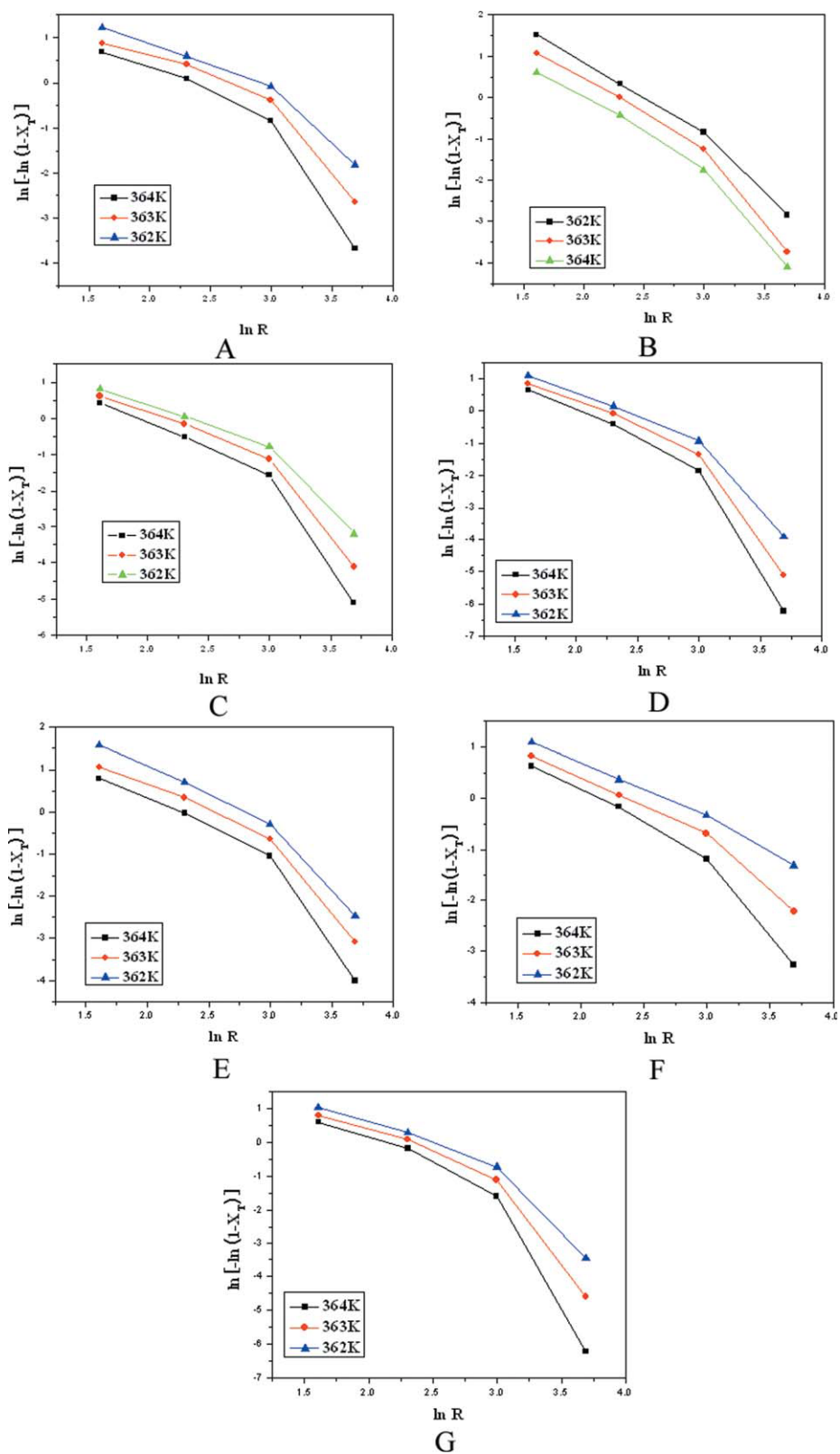
Figure 6 Plots of $\ln[-\ln(1 - X_t)]$ versus $\ln R$ by Samples 1–6 and pure PE (A) Sample 1; (B) Sample 2; (C) Sample 3; (D) Sample 4; (E) Sample 5; (F) Sample 6; (G) pure PE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE V
Nonisothermal Crystallization Kinetic Parameters of Pure PE and Samples 1–6 (Ozawa Method)

Sample		PE	1	2	3	4	5	6
362 K	$F(T)$	117.7	40.52	60.17	62.39	189.9	133.8	19.60
	m	2.06986	1.40382	2.05938	2.15085	2.31905	1.89268	1.13816
363 K	$F(T)$	226.6	49.66	81.96	100.1	363.6	94.19	26.70
	m	2.50422	1.63869	2.25769	2.38857	2.76261	1.93478	1.42914
364 K	$F(T)$	664.8	82.33	89.37	158.7	638.8	123.1	47.80
	m	3.15189	2.01791	2.23039	2.54981	3.17746	2.21954	1.83442

$$X_t = \int_{t_0}^{t} (dH/dt)dt / \int_{t_0}^{t_\infty} (dH/dt)/dt \qquad (1)$$

where dH denotes the measured enthalpy of crystallization during an infinitesimal time interval dt. The limits t and t_∞ denote the elapsed time during the course of crystallization and at the end of the crystallization process, respectively.

Most studies on the polymer crystallization rely on the Avrami equation [eq. (2)] to analysis the data,[20] which provides the information of nucleation and crystallization rate.

$$1 - X_t = \exp(-Kt^n) \qquad (2)$$

where, X_t is the volume fraction of crystalline materials at a time t and at a given temperature T; n is the Avrami exponent; and K is the crystal growth rate constant. The parameters n and $\ln K$ could be obtained from the slope and the intercept of the plots of $\ln[-\ln(1 - X_t)]$ versus $\ln t$ at the different temperatures for the isothermal crystallization (Fig. 4).

n, $t_{1/2}$, and K values of pure LDPE and LDPE composites filled with the different size distribution CaCO₃ at the different temperatures are listed in Table IV. The n value of neat LDPE is approximate to 2. This suggests that neat LDPE has a spontaneous homogeneous nucleation process. And the n value of efficient size distribution filler filled PE is higher than those of the neat PE and single size of filler filled PE. This indicates the occurrence of heterogeneous nucleation in the 3, 4 samples and seems to make the crystallization dimension of PE polymer more complex because of the increasing n values. From Table IV, we also can see that the composites filled with the different size and size distribution fillers (Samples 3 and 4) have higher n, $t_{1/2}$ and lower K than those filled with single filler (Samples 1 and 6).

Nonisothermal crystallization kinetics

Nonisothermal crystallization is a process in which LDPE is heated above its melting temperature (T_m), in this study at 150°C, to various cooling rate, i.e., 5,

10, 20, 40°C/min, respectively, as can be seen in Figure 5.

The relative degree of crystallinity, X_T, as a function of temperature, can be formulated as:

$$X_T = \int_{T_0}^{T} (dH/dT)dT / \int_{T_0}^{T_\infty} (dH/dT)/dT \qquad (3)$$

where dH denotes the measured enthalpy of crystallization during an infinitesimal temperature interval dT the limits T and T_∞ denote the elapsed ΔT temperature during the course of crystallization and at the end of the crystallization process, respectively.

Again, the crystallization temperature can be converted to the crystallization time by using the following equation:

$$t = (T_0 - T_C)/R \qquad (4)$$

where R is the cooling rate.

The Ozawa method

As the nonisothermal crystallization process, it can be analyzed using the Ozawa analysis.[21] The Ozawa equation is:

$$1 - X_T = \exp[-F(T)/R^m] \qquad (5)$$

where m is Ozawa exponent; $F(T)$ is the cooling function which is related to the crystallization rate, and $F(T)$ indicates how fast crystallization proceed; R is the cooling rate. The equation can be shown in eq. (6).

$$\ln[-\ln(1 - X_T)] = \ln F(T) - m \ln R \qquad (6)$$

By using eq. (6), plots of $\ln[-\ln(1 - X_T)]$ versus R for the nonisothermal cooling crystallization at the temperatures 362, 363, and 364 K, respectively, are shown in Figure 6. From it, the slope $-m$ and the intercept $\ln F(T)$ can be obtained.

It is well known that the Qzawa equation is valid when the plots of $\ln[-\ln(1 - X_T)]$ versus R are straight lines at the given temperature. From Figure 6, we can see that the Ozawa equation is suitable to
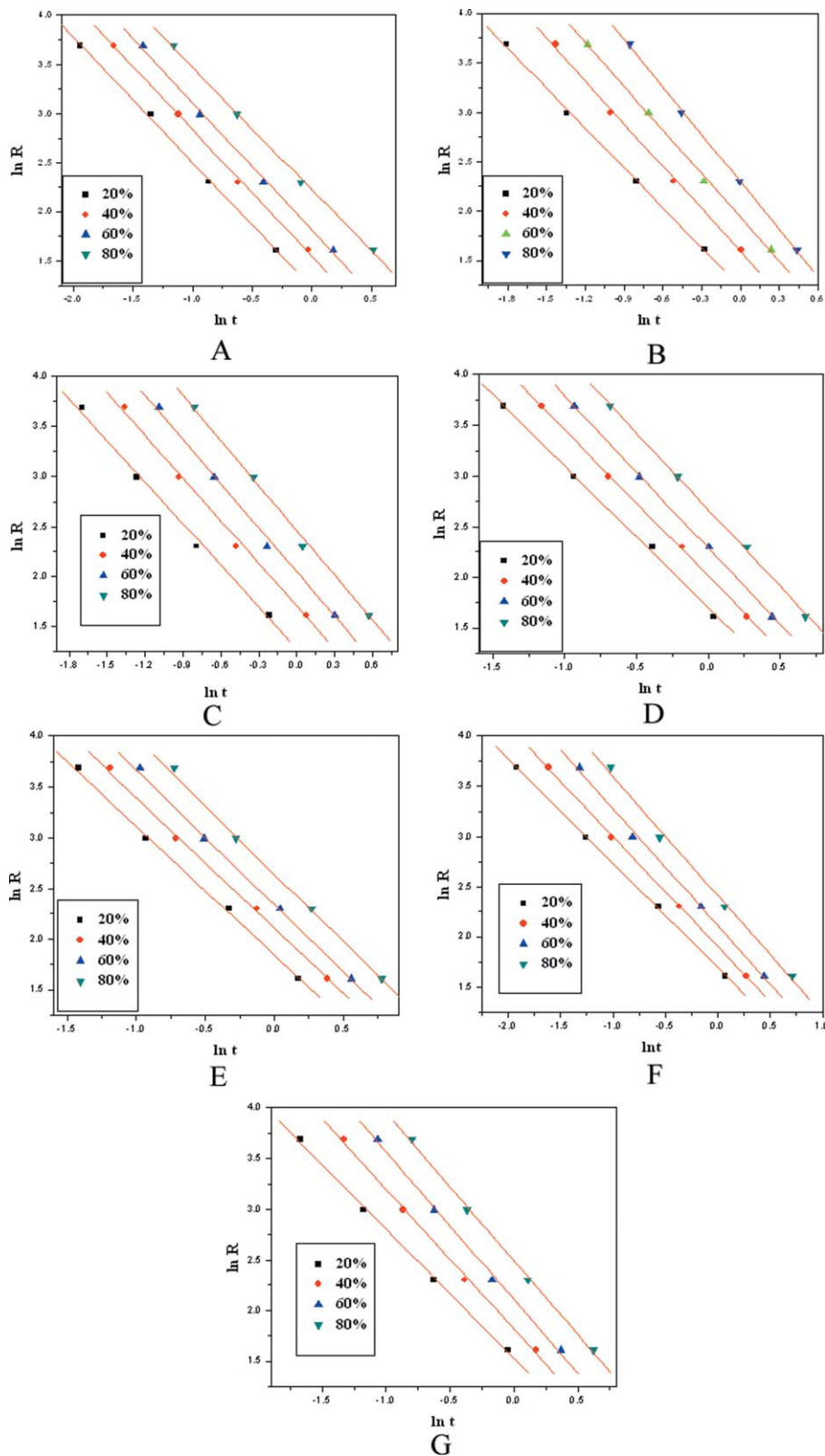
Figure 7 Plots of ln$R$ versus ln$t$ by Samples 1–6 and pure PE (A) Sample 1; (B) Sample 2; (C) Sample 3; (D) Sample 4; (E) Sample 5; (F) Sample 6; (G) pure PE. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

TABLE VI
Nonisothermal Crystallization Kinetic Parameters of Pure PE and Samples 1–6 (Mo Method)

Sample		PE	1	2	3	4	5	6
20%	$K(T)$	4.879	3.406	3.401	3.504	5.464	6.309	5.443
	α	1.27689	1.2763	1.3471	1.40445	1.4005	1.27579	1.04075
40%	$K(T)$	6.142	4.713	4.885	5.324	7.469	8.237	6.705
	α	1.38373	1.2833	1.44394	1.45184	1.44164	1.29024	1.09826
60%	$K(T)$	8.208	6.104	6.917	7.259	9.861	10.37	8.258
	α	1.45813	1.29899	1.4775	1.50549	1.50084	1.33025	1.1661
80%	$K(T)$	12.07	9.222	9.881	11.52	13.58	14.06	11.15
	α	1.46179	1.24741	1.50791	1.52607	1.51586	1.34459	1.18752

describe the kinetics results only at the slower cooling rate (from 5°C/min to 20°C/min) but at the higher cooling rate (40°C/min) in our experiments.

The results of the Ozawa method are shown in Table V. It indicates that the composites filled with the different size and size distribution fillers (Sample 3 and 4) have higher m and $F(T)$ than those filled with single filler (Sample 1 and 6).

The Mo method

Mo and his coworkers[22] improved the method of nonisothermal crystallization. The Mo equation is:

$$\ln R = \ln K(T) - \alpha \ln t \qquad (7)$$

Both Avrami equation and Ozawa equation are related to the above equation. Where $\alpha = n/m$. The parameters $-\alpha$ and $\ln K(T)$ could be obtained from the slope and the intercept of the plots of $\ln R$ versus $\ln t$ at the different temperatures for the isothermal crystallization (Fig. 7).

The results of the Mo method are shown in Table VI. It suggests that the composites filled with the

Figure 8 Torque curves of Samples 1–6. [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

different size and size distribution fillers (Sample 3 and 4) have higher α than those filled with single fillers (Sample 1 and 6).

Relationship between the crystallization behaviors and the viscosity

It is well known that crystallization of polymers is controlled by two processes, nucleation and crystal growth. The rate of nucleation and crystal growth is sensitive to the viscosity. The observable number of nuclei decreases when the viscosity decreases. The rate of crystal growth only depends on the viscosity. Polymeric crystal growth rate increases with the decrease of the viscosity. The crystal rate depends on the process of the lower rate between the nucleation and the crystal growth.

The equilibrium torque curves of Samples 1–6 at the different rotor speeds are shown in Figure 8. The torque values show the melting viscosity of the composites. From it, we can see that the melting viscosity of PE composites filled with different size and size distribution fillers (Samples 3 and 4) evidently decreased. In our former study, we think that the lower viscosity of polymer filled with efficient size distribution filler can be attributed to the efficient arrangement of the filler in the samples.[18] And the lower melting viscosity of resin can result in the lower melting temperature and the lower crystallization temperature. At the low viscosity, the rate of nucleation decreased while the rate of crystal growth increased. Therefore, Samples 3 and 4 have the lower nucleation rate, the higher crystal growth rate and the more wide crystal growth temperature area compared with those filled with the single size CaCO$_3$. These cause a more wide crystallization peak.

The difference of $F(T)$ values between the efficient size distribution filler filled samples and the single size filler filled samples can be attributed to the difference of retard mobility.
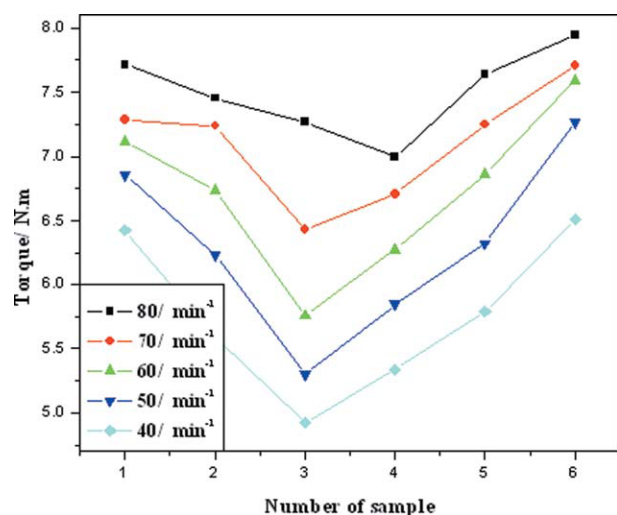
CONCLUSIONS

1. The samples filled with the different size and size distribution fillers have the lower melting

temperature and crystallization temperature than those filled with the single size fillers.

2. The crystallization rate constant (K) of samples filled with the different size and size distribution fillers decreases, and their Avrami exponents (n) and crystallization half-life ($t_{1/2}$) increase compared with those of the samples filled with the single size fillers.

3. The low viscosity of samples filled with the different size and size distribution fillers results in the wide crystallization temperature area, the different isothermal and nonisothermal crystallization kinetics parameters.

References

1. Pukánszky B.; Móczó J. Macromol Symp 2004, 214, 115.
2. János, M.; Béla, P. J Ind Eng Chem 2008, 14, 535.
3. Ray, V. V.; Banthia, A. K.; Schick, C. Polymer 2007, 48, 2404.
4. Fijiyama, M.; Wakino, J. J Appl Polym Sci 1991, 42, 2739.
5. Lincoln, D. M.; Vaia, R. A.; Wang, B. S.; Hsiao, B. S.; Krishnamoorti, R. Polymer 2001, 42, 9975.
6. Miltner, H. E.; Assche, G. V.; Pozsgay, A.; Pukánszky, B.; Mele, B. V. Polymer 2006, 47, 826.
7. Li, Y. L.; Liu, H. Z.; Zhang, Y.; Yang, G. S. J Appl Polym Sci 2005, 98, 2172.
8. Jain, S.; Goossens, H.; Duin, M.; Lemstra, P. Polymer 2005, 46, 8805.
9. Li, L. Y.; Li, C. Y.; Ni, C. Y.; Rong, L. X.; Hsiao, B. Polymer 2007, 48, 3452.
10. Mulla, A. A. M.; Mathew, J.; Yeh, S. K.; Gupta R. Compos A 2007, 39, 204.
11. Islam, M. A.; Hussein, I. A.; Atiqullah, M. Eur Polym J 2007, 43, 599.
12. Liang, G. D.; Xu, J. T.; Xu, W. B. J Appl Polym Sci 2004, 91, 3054.
13. Kang, X.; He, S. Q.; Zhu, C. S.; Lu, L. W. L.; Guo, J. G. J Appl Polym Sci 2005, 95, 756.
14. Liu, H. Z.; Yang, G. S.; He, A. H.; Wu, M. Y. J Appl Polym Sci 2004, 94, 819.
15. Chen, M.; Chang, W. C.; Lu, H. Y.; Chen, C. H.; Peng, J. S.; Tsai C. J Polym 2007, 48, 5408.
16. Li, J; Zhou, C. X.; Gang, W. Polym Testing 2003, 22, 217.
17. Dai, S.; Ao, G.; Kim, M. S. J Ind Eng Chem 2007, 13, 1162.
18. Zhang, J.; Cheng, J.; Hu, B. X.; Ren, J.; Shen, J. Polym Mater Sci Eng 2003, 19, 184.
19. Zhang, J.; Ding, Q. J.; Zhou, N. L.; Li, L.; Ma, Z. M.; Shen, J. J Appl Polym Sci 2006, 101, 2437.
20. Avrami, M. Chem Phys 1939, 7, 1103.
21. Oawa, T. Polymer 1971, 12, 150.
22. Liu, T. X.; Mo, Z. S.; Wang, S.; Zhang, H. F. Polym Eng Sci 1997, 37, 568.