Studies on Crystal Morphology and Crystallization Kinetics of Polypropylene Filled with CaCO₃ of Different Size and Size Distribution

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ABSTRACT: Changes in the crystal morphology, crystallinity, and the melting temperature of thermoplastics resulted in significant changes in the mechanical behavior of composites containing them. For this reason, the research of crystal morphology and crystallization kinetics in thermoplastic composites became an important requirement. The thermoplastic filled with the filler of different size gradation was a new method for improving processability of thermoplastic composites. We have previously reported that the melt viscosity of polypropylene (PP) composites, which were filled with 30 wt % CaCO₃ of effective size gradation, could be evidently declined. In this study, two sizes of CaCO₃, 325 meshes and 1500 meshes, were blended by different proportions and filled into PP matrix with 30 wt %. Crystal morphology and isothermal crystallization kinetics of a series of composites were characterized by differential scanning calorimeter (DSC) and polarizing microscope. The results showed that composites filled with CaCO₃ of effective size gradation leaded to a well-crystalline order and a large crystal size, while their isothermal crystallization kinetics and crystallization rate constant (k) were declined, and their Avrami exponents (n) and crystallization half-life ($t_{1/2}$) were increased compared with the composites filled with single size CaCO₃. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 2437–2444, 2006

Key words: effective size gradation; differential scanning calorimeter; isothermal crystallization kinetics; polarizing microscope

INTRODUCTION

In crystalline thermoplastics, the crystal morphology, crystallinity, and the melting temperature are the most important factors in determining mechanical and physical properties of the final products. The crystallization of these polymers is often influenced not only by processing conditions, but also by the presence of the reinforce phases. Accordingly, a comprehensive understanding of the matrix by filler is required for the development of crystalline thermoplastic composite systems.

Polypropylene (PP), particularly isotactic polypropylene (iPP), has stimulated many researches in the structural aspect. One of the most important reasons is its wide application in industry, which attracts the attention devoted to all aspects of its solid-state organization. There are also, however, more fundamental motives.[1–6] Mineral fillers can reduce the cost of PP products, increase the stiffness of material and heat deflection temperature, reduce the shrinkage and increase the tensile strength, which depends mainly on the particle morphology and surface coating.[7–10] In spite of the benefits offered by fillers, high melt viscosity and deterioration in the processing will be induced at high filler contents.[11–15]

In our former study, we have found that the melt viscosity of PP composites, which were filled with 30 wt % CaCO₃ of effective size gradation (325 meshes and 1500 meshes fillers were blended, and the proportion of 1500 meshes in the filler was between 20 and 60 wt %), could be evidently declined.[16] In this study, we investigated the crystal morphology and crystallization kinetics of PP filled with different size and size distributed CaCO₃ using differential scanning calorimeter (DSC) and polarizing microscope. Most of the work in this study was focused on the kinetics of the nucleation and crystal growth of the filled PP composites. The crystallization processes are either isothermal condition between 118 and 124°C or nonisothermal condition with a constant cooling rate of 10°C/min. Some special crystal morphologies and isothermal crystallization kinetics of efficient size gradation samples were reported.

TABLE I
Size and Purity of CaCO₃ Used as Fillers

Size of CaCO$_3$ (meshes)	CaCO$_3$ Content (%)	Top cut (98%)	Mean particle size (d 50%)	D (3, 2) (μm)
325	≥98	46	12	8.11
1500	≥98	16.5	2.8	3.37

EXPERIMENTAL

Materials

The unfilled PP used as matrix was provided by Yangtze Chemical Ind. Ltd. The CaCO$_3$ of different sizes was used as fillers, i.e., 325 meshes, 1500 meshes, which were purchased from Nanjing OMYA Fine Chemical Ind. (Nanjing, China). The size gradation of CaCO$_3$ samples of different size was measured by LS-CWM[1] laser particle sizer, which was provided by OMEC. The characteristics and size of fillers are given in Table I.

Samples preparation

Stearic acid-modified CaCO$_3$ was prepared by suspension of cyclohexane-mixed CaCO$_3$ and stearic acid (2%) in a 500-mL flask. The reaction was carried out at 50°C and completed within 2 h. The filler was then filtered, washed with cyclohexane, and dried in an oven at 50°C.

The CaCO$_3$ of different sizes was blended with different percentages and filled into PP matrix at 30 wt %. Table II lists the proportions of 325 and 1500 meshes CaCO$_3$ in the filled mixture. The PP and CaCO$_3$ were blended on a CS-194AV mini-extruder, which was provided by Custon Scientific Instruments (USA). The mixing conditions are as follows: screw speed, 50 rpm; extrusion die temperature, 230°C; and screw temperature, 220°C.

Measurement of crystallization kinetics

Crystallization kinetics was measured on Perkin–Elmer DSC-7. During the isothermal crystallization kinetic measurements, the samples were heated from room temperature to 200°C at a heating rate of 50°C/min, and held at that temperature for 10 min to elim-

TABLE II
Percentage of Different Size CaCO₃ in the Samples

Samples	1500 meshes (%)	325 meshes (%)
1	0	100
2	20	80
3	40	60
4	60	40
5	80	20
6	100	0

inate any thermal history in the material. Then, the samples were cooled rapidly to the crystallization temperatures (at a cooling rate of 500°C/min) in the range of 118 and 124°C, and held at that temperature for the entire crystallization process. During the nonisothermal crystallization kinetic measurement, the samples were heated up to 200°C at a heated rate of 10°C/min and held there for 10 min. Then, the samples were cooled at the same rate (10°C/min). All operations were carried out under the purge of nitrogen gas. Sample weights varied between 6 and 8 mg.

The crystal morphologies at different times were examined with a Leit2 polarizing microscope. The samples were heated up to 200°C and held there for 10 min followed by a rapid cooling to 130°C for 72 h.

RESULTS AND DISCUSSION

Crystallization process and crystal morphology

The effect of the fillers on the thermal properties of PP has been analyzed in nonisothermal DSC experiments. The melting curves of PP and samples 1–6 at a cooling rate of 10°C/min are shown in Figure 1. The results indicated that pure PP had a melting peak corresponding to the melting point of crystal form α, and samples 1–6 have two melting peaks, perhaps, corre-
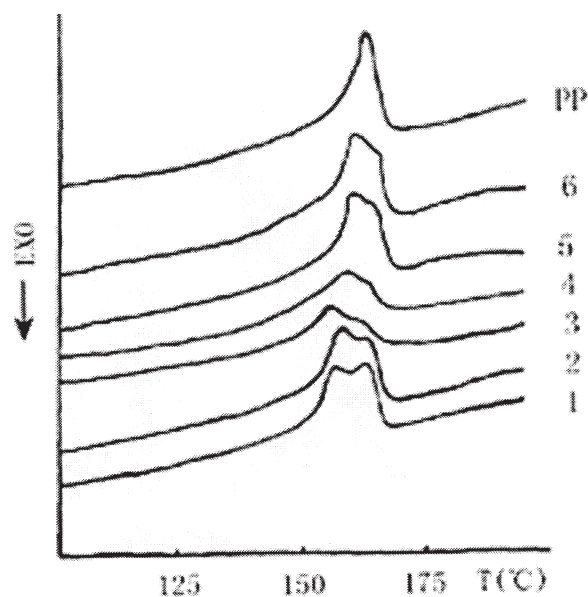

Figure 1 The melting curves of samples 1–6 and pure PP.

TABLE III
DSC Results of Pure PP and Samples 1–6

Samples	T_m (°C)	T_c (°C)	ΔT (°C)	X_c (%)
Pure PP	163.7	108.2	55.5	54.2
1	160.2	115.3	44.9	65.1
2	158.5	112.0	46.5	65.3
3	157.0	111.4	46.4	68.1
4	159.4	112.9	46.5	68.2
5	160.4	114.1	46.3	67.5
6	160.7	116.6	44.1	60.8

sponding to two crystal forms. The melting points of α and β crystal form are 155 and 165°C, respectively.

Thermal parameters such as melting temperature (T_m), crystallization temperature (T_c), supercooling ($\Delta T = T_m - T_c$) and the crystallinity (X_c) of pure PP and samples 1–6 were analyzed by nonisothermal crystallization experiments. The results are given in Table III. Crystallinity (X_c) of pure PP was calculated using the following expression

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100 \qquad (1)$$

The crystallinity (X_c) of samples 1–6 was obtained by adjusting the fraction of PP in the composites, which is 0.7, using the following equation

$$X_c = \frac{\Delta H_f}{\Delta H_f^0} \times 100/0.7 \qquad (2)$$

ΔH_f^0 was obtained by an extrapolation of the thermal enthalpy of PP crystals to 100% crystallinity, leading $\Delta H_f^0 = 137.9$ J/g.[17]
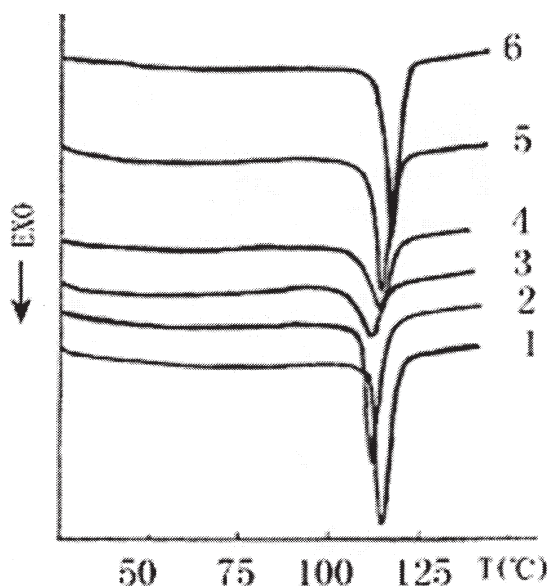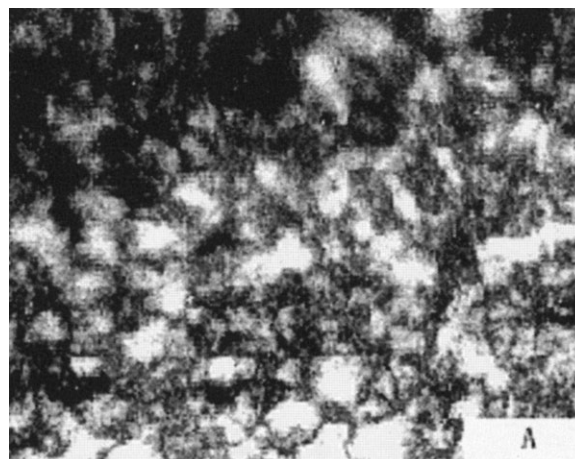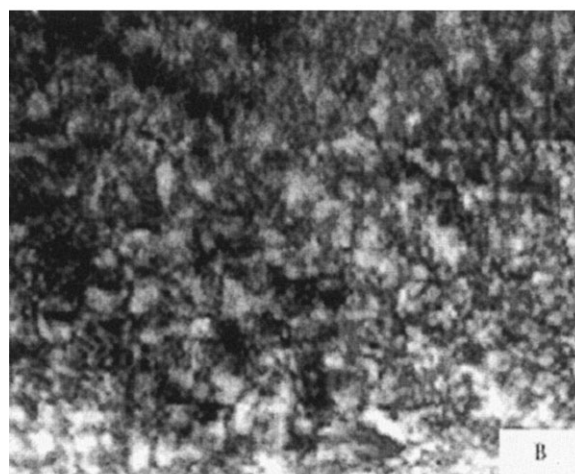

Figure 2 The crystallization curves of samples 1–6.

Figure 3 Polarizing microscopic image ($\times$250) of samples 6 and 3 at 130°C after 72 h. (A) Sample 6 and (B) Sample 3.

In Table III, the supercooling of pure PP was higher than that of samples 1–6. There were two mechanisms for polymer nucleation: spontaneous homogeneous nucleation and heterogeneous nucleation, which always occurs at lower supercooling than homogeneous nucleation. Thus, these heterogeneities were frequently referred to as nucleation sites. The β crystal form of PP was formed mostly by heterogeneous nucleation.[18,19] The shallow supercooling of the CaCO$_3$ filled PP composites could be explained by the strong heterogeneous nucleation ability of stearic acid-modified CaCO$_3$ filler during the crystallization of PP molecules.

The data in Table III also shows that composites filled with efficient size gradation filler had higher crystallinity (X_c), lower crystalline temperature compared with the composite filled with single size CaCO$_3$ filler.
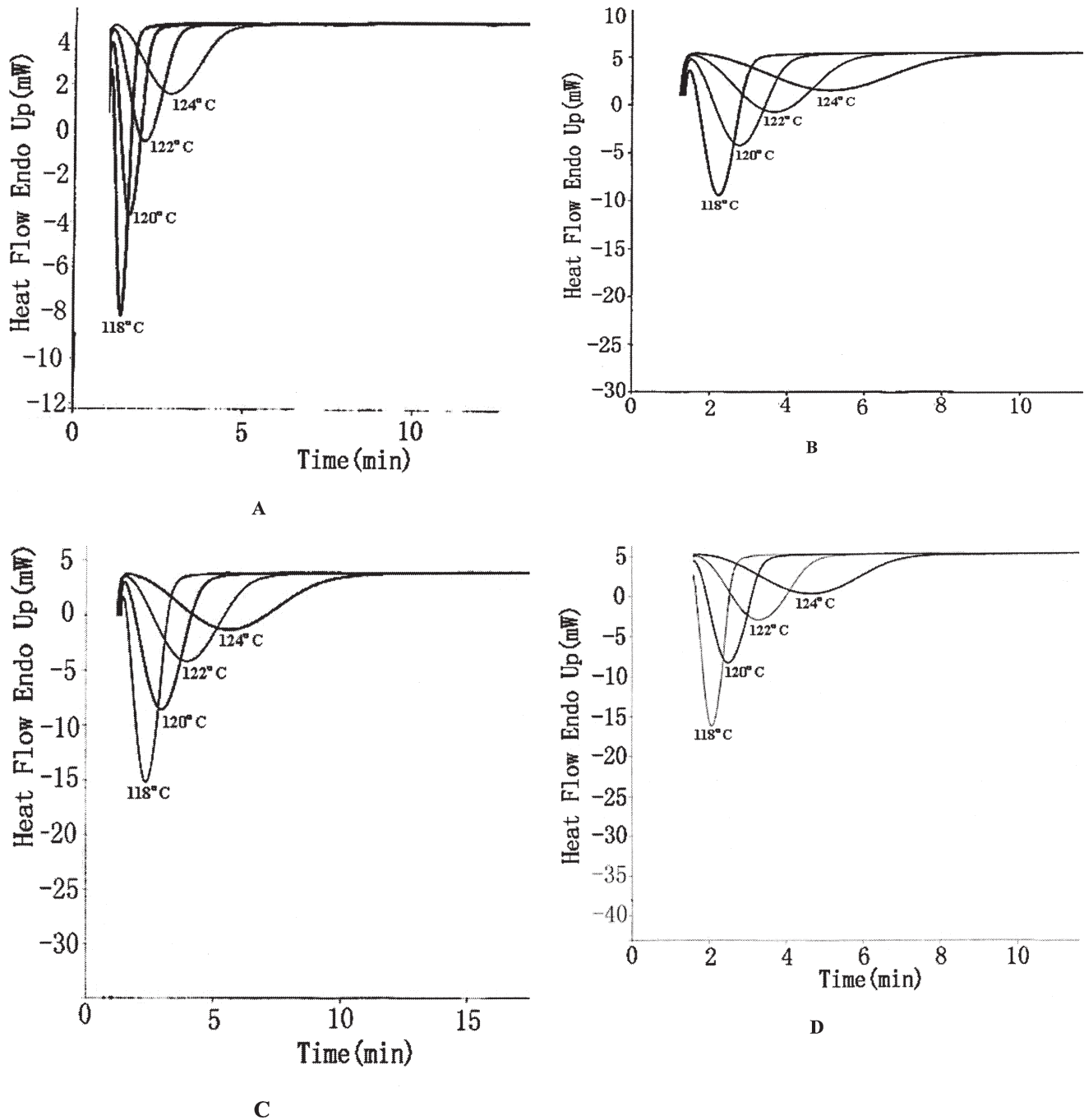
Figure 4 The isothermal crystallization curves of samples 1–6 and pure PP at various temperatures (118, 120, 122, and 124°C). (A) sample 1; (B) sample 2; (C) sample 3; (D) sample 4; (E) sample 5; (F) sample 6; and (G) pure PP.

The crystallization curves of samples 1–6 at the cooling rate of 10°C/min are shown in Figure 2. This figure clearly shows that the crystallization peak of PP composites filled with single size filler is sharper and higher compared with those filled with $CaCO_3$ of effective size gradation.

Figure 3 shows the results of polarizing microscopic images of sample 3 and sample 6 after 72 h at 130°C. Evidently, the composites filled with $CaCO_3$ of effec-

tive size gradation had well crystalline orders and large crystallite sizes.

Isothermal crystallization kinetics

Isothermal crystallization is the process in which PP is heated rapidly above its melting temperature (T_m), in this study at 200°C, to various temperatures, i.e., 118, 120, 122, and 124°C (Fig. 4), respectively, which are
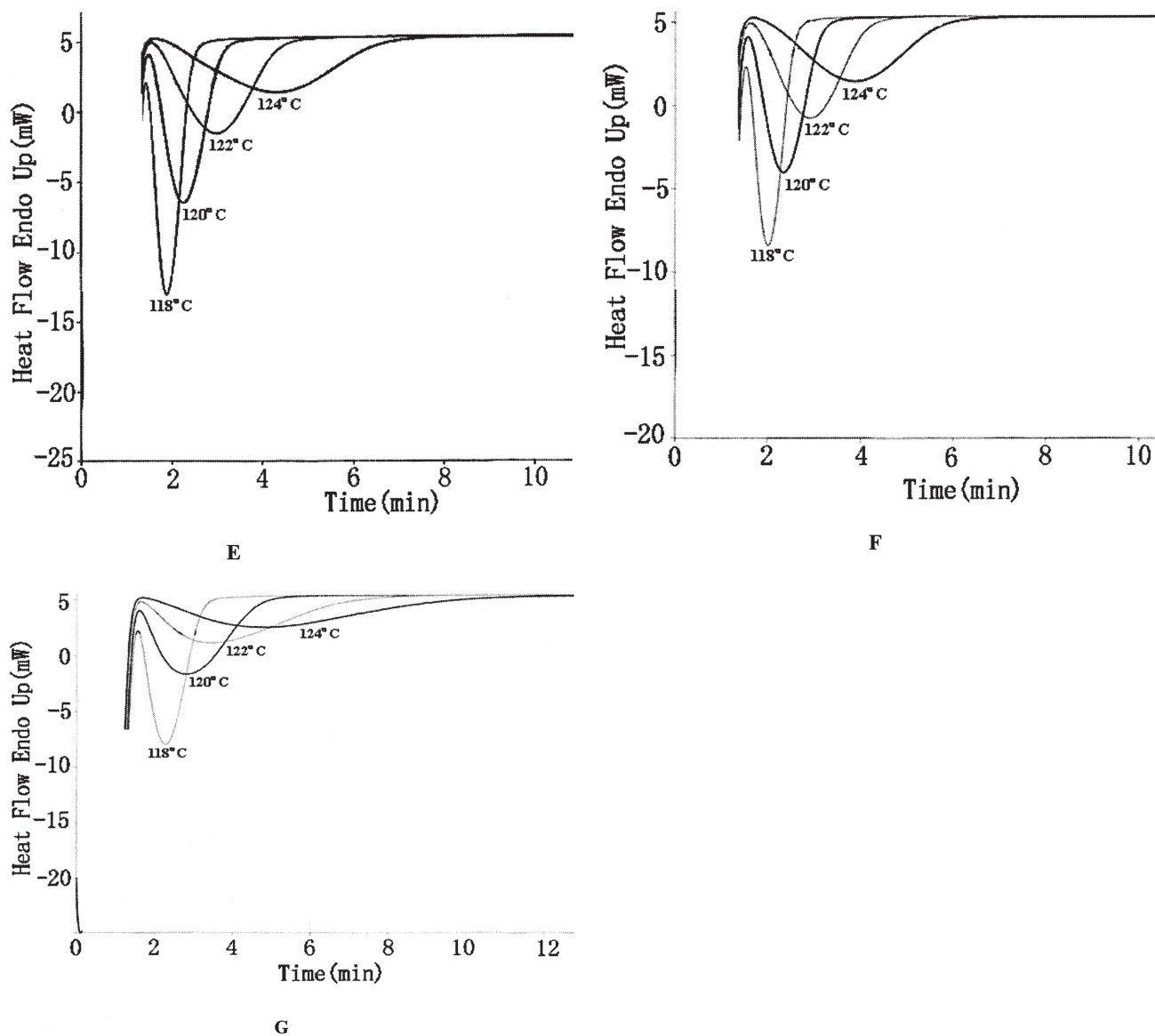
E

F

G

Figure 4 (*Continued from the previous page*)

below the melting point, but above the glass-transition temperature (T_g). Those temperatures are considered as the crystallization temperatures (T_c). During the isothermal crystallization condition, the polymers transform from a melt to a crystalline solid.

Most studies of polymer crystallization rely on the Avrami equation (eq. (3)) to analysis the data,[20] which provides the information of nucleation and crystallization rate.

$$1 - C_v = \exp(-Kt^n) \qquad (3)$$

Here, C_v 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

$\ln[-\ln(1 - C_v(T))]$ vs. $\ln t$ in different temperatures for the isothermal crystallization (Fig. 5).

The Table IV shows that n, $t_{1/2}$ and K values of pure PP and PP composites by filled different size gradation $CaCO_3$ at different temperatures. The n value of pure PP is approximate to 2, which confirmed that pure PP has a spontaneous homogeneous nucleation process. It also showed that the composites filled with effective size gradation fillers have higher n and $t_{1/2}$, but lower K than the composite filled with single filler.

Relationship between crystallization kinetics and viscosity

Figure 6 depicts the viscosity of samples under different shear velocities. The viscosity results show that
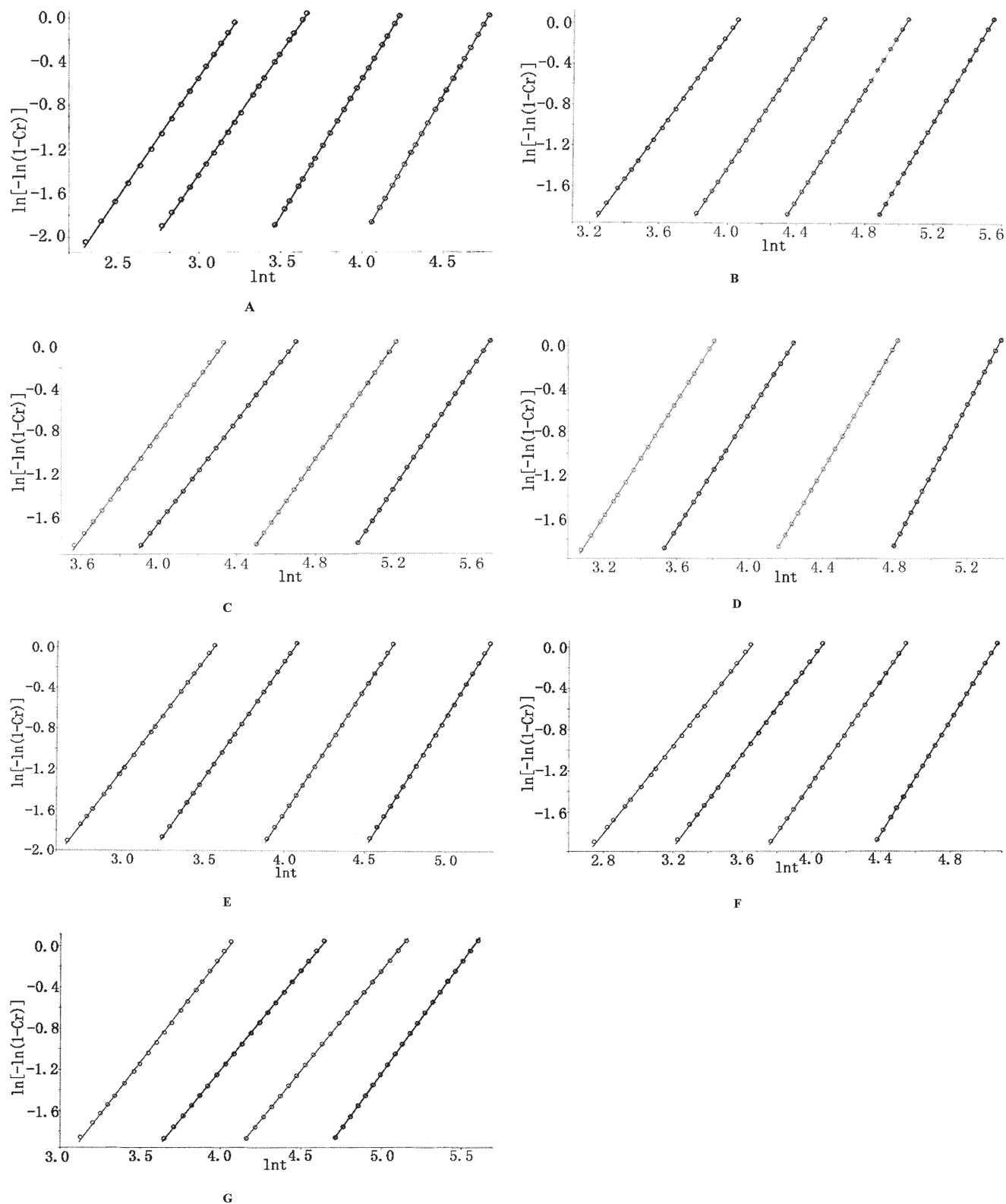
Figure 5 Plots of $\ln[-\ln(1 - C_v)]$ vs. $\ln t$ for samples 1–6 and pure PP. (A) sample 1; (B) sample 2; (C) sample 3; (D) sample 4; (E) sample 5; (F) sample 6; and (G) pure PP.

with the decrease of shear viscosity, n and $t_{1/2}$ increase while k decreases.

It is well-known that crystallization of polymers is controlled by two processes, nucleation and crystal growth. The nuclei density and the rate of nucleation are sensitive to the crystallization temperature. The observable number of nuclei decreases when the temperature increases. The rate of crystal growth only

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

Samples		Pure PP	1	2	3	4	5	6
118°C	n	2.03	2.20	2.38	2.50	2.66	2.14	2.13
	$K(s^{-n})$	2.48×10^{-4}	7.86×10^{-4}	6.71×10^{-5}	2.09×10^{-5}	3.13×10^{-5}	5.15×10^{-4}	4.40×10^{-4}
	$t_{1/2}(s)$	49.9	23.5	48.6	64.3	43.0	29.0	31.7
120°C	n	1.92	2.18	2.59	2.41	2.68	2.31	2.27
	$K(s^{-n})$	1.32×10^{-4}	3.46×10^{-4}	7.94×10^{-6}	1.24×10^{-5}	1.13×10^{-5}	8.05×10^{-5}	1.01×10^{-4}
	$t_{1/2}(s)$	86.6	32.7	80.9	93.3	61.2	50.5	49.0
122°C	n	1.92	2.46	2.73	2.66	2.92	2.47	2.46
	$K(s^{-n})$	4.85×10^{-5}	2.65×10^{-5}	1.12×10^{-6}	9.95×10^{-7}	7.93×10^{-7}	1.13×10^{-5}	1.50×10^{-5}
	$t_{1/2}(s)$	145.9	62.5	132.3	157.2	108.3	86.8	78.8
124°C	n	2.14	2.60	2.89	2.80	3.21	2.59	2.74
	$K(s^{-n})$	6.05×10^{-6}	2.49×10^{-6}	1.17×10^{-7}	1.30×10^{-7}	3.20×10^{-8}	1.16×10^{-6}	9.55×10^{-7}
	$t_{1/2}(s)$	231.2	124.2	220.5	252.6	192.9	170.0	137.7
E_a	kJ/mol	−645.80	−800.39	−772.26	−729.75	−907.22	−811.38	−648.18

depends on the temperature. With the increase of the crystallization temperature, polymeric crystal growth rate increases.

The relation between crystallization rate and activation energy could be expressed by eq. (4).

$$G(T) = G_0 \exp\left(\frac{-\Delta F_D^*}{RT}\right) \exp\left(\frac{-\Delta F^{\neq}}{RT}\right) \quad (4)$$

Here, ΔF_D^* is the activation energy of diffusion of polymer segment from random coil to crystal surface, and

ΔF^* is the activation energy of nucleation. The overall crystallization rate is reversal proportional to the ratio of ΔF_D^* to the difference between the crystallization temperature (T_c) and glass-transition temperature (T_g), and also reversal proportional to the ratio of ΔF^* to the difference between the melting temperature (T_m) and crystallization temperature (T_c). From this relation, it is obvious that the crystallization rate is controlled by the rate of nucleation at high temperature and by the rate of diffusion of polymer segment from random coil to crystal surface at low temperature. In our former
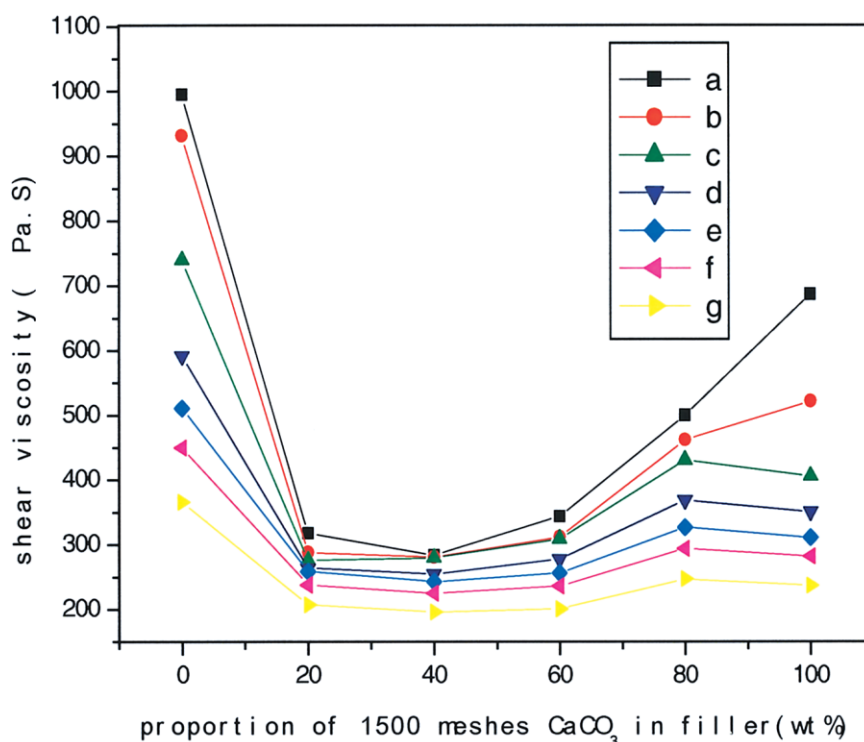

Figure 6 Viscosity curves of samples 1–6 in different shear velocities. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

study, we found that the melt viscosity of PP composites, which was filled with 30 wt % CaCO$_3$ of effective size gradation (325 meshes and 1500 meshes fillers were blended and the proportion of 1500 meshes in the filler was between 20 and 60 wt %), could be evidently declined.[16] Therefore, the efficient size gradation of the filler decreases the viscosity of PP composites and increases the diffusion of PP segment during the crystallization. At low temperature, the rate of nucleation is increased while the rate of crystal growth is decreased, and crystal growth still proceeds finally. Therefore, PP composites, which were filled with 30 wt % CaCO$_3$ of effective size gradation, have fewer crystal nuclei, faster crystal growth rate, and wider crystal growth temperature compared with that filled with CaCO$_3$ of single size. This generates a wide crystallization peak and a large crystal size. This viewpoint might be useful to explain the experimental results of nonisothermal crystallization process, polarizing microscopic images, and isothermal crystallization kinetics.

CONCLUSIONS

The crystal morphology and crystallization kinetics of the PP composites filed with two different sized CaCO$_3$ particles at 30 wt % were studied by DSC and polarizing microscope. The crystallization kinetics experiments showed that PP composites filled with effective size gradation distributed CaCO$_3$ would lead to a high crystalline order and a large crystallite size.

For the composites of effective size gradation distribution, the crystallization rate constant (K) decrease, and their Avrami exponents (n) and crystallization half-life ($t_{1/2}$) increase, compared with the samples of single filler.

Low melt viscosity of the filled PP might be useful to explain the experimental results of nonisothermal crystallization process, polarizing microscopic images, and isothermal crystallization kinetics according to the analysis of isothermal crystallization kinetics.

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