

Processing Characteristics of Low-Density Polyethylene Filled with Calcium Carbonate of Different Size Distributions

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ABSTRACT: Low-density polyethylene (LDPE) was filled with blends of different proportions of two sizes of calcium carbonate (CaCO₃; 600 and 2500 mesh). The torque of the LDPE/CaCO₃ samples was measured with a torque rheometer. The results showed that the process torque values of the LDPE/CaCO₃ samples obviously decreased when LDPE was filled with a blend of two sizes of CaCO₃ (600- and 2500-mesh CaCO₃ blend) in comparison with samples filled with CaCO₃ of a single size (600 or 2500 mesh). When the ratio of 600-mesh CaCO₃ to the total CaCO₃ was in the range of 40–60 wt %, the lowest torque value of the LDPE/CaCO₃ samples was achieved. When the content of CaCO₃ in a sample was 30 wt %, LDPE filled with CaCO₃ of different size distributions showed the largest decrease in the torque ratio in

comparison with the samples filled with CaCO₃ of a single size. The torques of LDPE samples filled with CaCO₃ of a single size and those filled with CaCO₃ of different size distributions at different temperatures were also studied. The results showed that the flow activation energy and flow activation entropy of LDPE samples filled with CaCO₃ of different size distributions increased obviously. The increase in the flow activation entropy was used to explain the phenomenon of the process torque decreasing for LDPE samples filled with CaCO₃ of different size distributions. © 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 118: 2408–2416, 2010

Key words: blending; nanocomposites; polyethylene (PE); processing; viscosity

INTRODUCTION

Low-density polyethylene (LDPE) is a typical commodity polymer and is widely used because of its high strength, cheap cost, and excellent processability.

Calcium carbonate (CaCO₃) in the form of chalk, whiting, and limestone, perhaps the most widely available and used mineral in the world, is used as an additive today. Because CaCO₃ can be processed in a wide range of particle sizes, the resulting products function as low-cost fillers that are added to extend and cheapen the applications of polymeric systems.¹

Inorganic fillers can be mixed with LDPE binders to form molding compounds and processed to form molded components by processes such as hot pressing, injection molding, and extrusion. The successful application of injection molding to inorganic powder systems depends on the powder characteristics, formulations of binders, good mixing, rheological behavior, and proper filling of the mold.^{2–7}

The purpose of adding a CaCO₃ filler to LDPE is primarily to reduce the product cost. Wang et al.⁸ investigated the mechanical properties, microstructure, and thermal degradation of LDPE filled with different contents of CaCO₃. Liang⁹ found that the melt flow rate of CaCO₃/LDPE/LLDPE composites decreased with increasing CaCO₃ content. Bomal et al.¹⁰ reported the relationship between the relative melt viscosity of LDPE composites and the volume fraction of CaCO₃. Most studies on the modification of LDPE with CaCO₃ or other inorganic fillers, especially high-content fillers, have described a significant decrease in processability in comparison with pure LDPE because the viscosity of composites

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TABLE I
 Sizes and Characteristics of the CaCO₃ Samples Used as Fillers

Size of CaCO ₃ (mesh)	CaCO ₃ content (%)	Top cut (98%; μm)	<i>d</i> _{50%} (μm)	<i>D</i> (3,2) (μm)
325	≥98.0	46	11.2	8.11
600	≥98.0	25.7	5.4	3.71
800	≥98.0	25	4.8	3.54
1500	≥98.0	16.5	3.3	3.37
2500	≥98.0	8	1.7	1.96

D(3,2) is a function of $\sum(nd^3)/\sum(nd^2)$. (*n* is the number of particles; *d* is the diameter of particles).

increases with a high-content filler. Therefore, processability is an important characteristic for filled polymers. Suitable rheology can improve the processability of filled polymers to a great extent.^{11–15} This can decrease the consumption of energy and equipment in the process when the viscosity of polymer composites is reduced to a reasonable extent. A plasticizer often is used to decrease the viscosity of filler/polymer composites. Some articles have shown that the viscosity of composites decreases with increasing plasticizer content at the same temperature. However, Young's modulus and the mechanical properties decrease with increasing plasticizer content because the plasticizer has a lower molecular weight.^{16–19}

Rheological research is also an important way of investigating the processability and structure of polymer composites. The instruments of rheological research include torque, rotational, and capillary rheometers.^{20–30} A torque rheometer often is used to simulate and fit real-world processing conditions because its use is the closest factual process in comparison with the other rheometers.^{20,31–36}

Several studies on the application of polymers with fillers of different size distributions have been reported in recent years. Most reports on polymer matrices filled with fillers of different size distributions have focused on their mechanical properties, crystalline structure, and interfacial characteristics.^{37–41} Studies on the rheological properties of polymer matrices filled with fillers of different size distributions have seldom been reported. Zhou et al.⁴² reported only the relationship between the size of fillers and the rheological properties of composites; they did not report the relationship between the size distribution of fillers and the rheological properties of composites.⁴²

In our previous study,^{43,44} we found that the melt viscosity of PP composites filled with 30 wt % CaCO₃ of a reasonable size gradation (325- and 1500-mesh fillers were blended, and the proportion of the 1500-mesh filler was between 20 and 60 wt %) might evidently decline.^{43,44} In this work, we studied the process torque of LDPE filled with CaCO₃ of different size distributions (325, 600, 800, 1500, and 2500 mesh) with a Haake torque rheometer (Thermo

Fisher Scientific Inc., Waltham, MA, U.S.). The expected experimental results with respect to the torque, flow activation energy (ΔE_{η}), and flow activation entropy of LDPE samples filled with fillers of different size distributions were attained.

EXPERIMENTAL

Materials

CaCO₃ samples of different sizes were used as fillers (i.e., 325, 600, 800, 1500, and 2500 mesh) and were kindly provided by Nanjing OMYA Fine Chemical Industry Co., Ltd. (Nanjing, China).

The unfilled LDPE used as matrices was provided by Yangtze Chemical Industry Co., Ltd. (Nanjing, China). The melt flow rate of LDPE was 2.176 g/10 min (190°C, 2.16 kg).

The size distribution of the CaCO₃ samples was measured with an LS-CWM(2) laser granulometer (provided by OMEC Co., Zhuhai, China) at room temperature. The characteristics and sizes of CaCO₃ are listed in Table I and Figure 1.

Filler preparation

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

Torque measurements of LDPE filled with CaCO₃ of different size distributions

First, CaCO₃ fillers of different sizes were blended in different proportions; then, they were blended with LDPE (10–50 wt %).

All LDPE/CaCO₃ samples were mixed at room temperature for 5 min before the blends were melted. All LDPE/CaCO₃ samples were blended in a Haake PolyLab 600 torque rheometer for 5 min before the composites were measured. The blend temperature was 180°C, and the rotor speed was 40 rpm. All LDPE/CaCO₃ samples were measured in a Haake PolyLab 600 torque rheometer. The

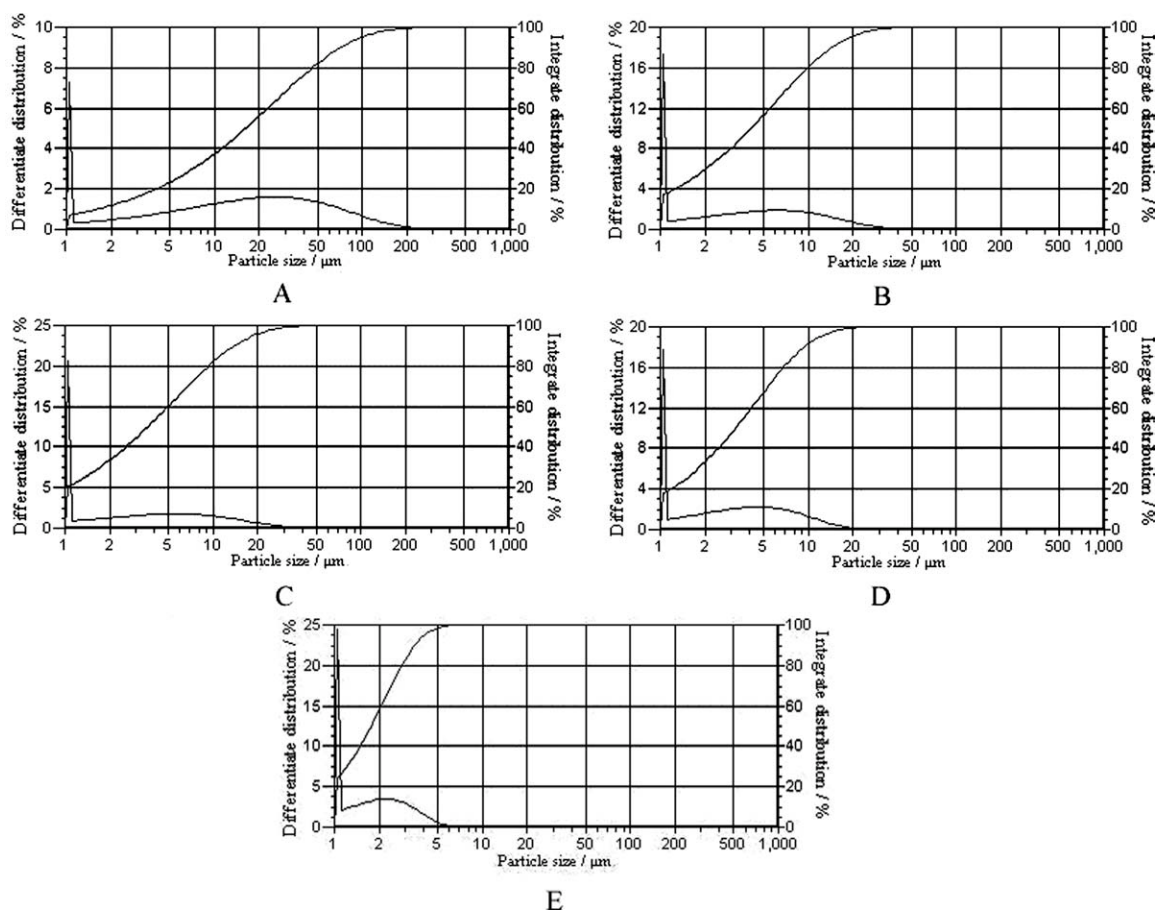


Figure 1 Size distribution curves of CaCO_3 of different sizes: (A) 325, (B) 600, (C) 800, (D) 1500, and (E) 2500 mesh.

measurement temperature was 180°C , and the rotor speed was 40–80 rpm. The sample volume of each blend was 49 cm^3 . The measurement time was 5 min.

The proportions of 600- and 2500-mesh CaCO_3 in the filled mixtures are listed in Table II.

With 325-, 600-, 800-, 1500-, and 2500-mesh CaCO_3 , CaCO_3 samples of two sizes were blended at random, and their proportions and experimental conditions were the same as those for samples 1–6.

Torque measurements at different temperatures

The torque of LDPE samples filled with CaCO_3 of different size distributions and with CaCO_3 of a single size was measured with a Haake PolyLab 600 torque rheometer. The measurement temperature was between 180 and 210°C , and the rotor speed was 40 rpm. The sample volume of each blend was 49 cm^3 .

Tensile tests

The tensile tests were performed at room temperature with an Instron 4200 tensile test machine (Instron, Inc., High Wycombe, U.K.). The test speed

was 50 mm/min. All measurements were carried out 10 times.

Differential scanning calorimetry (DSC) measurements

The melting and crystalline behaviors of pure polyethylene (PE) and samples 1–6 were measured with a PerkinElmer DSC-7 (PerkinElmer Inc., Wellesley, MA). First, samples 1–6 were heated from room temperature to 150°C and held at that temperature for 10 min to eliminate any thermal history in the materials. Then, the samples were cooled to 50°C at a cooling rate of $10^\circ\text{C}/\text{min}$ to

TABLE II
 CaCO_3 Samples of Different Size Distributions for the Blending of 600- and 2500-Mesh Fillers

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

The samples were filled with 30 wt % CaCO_3 .

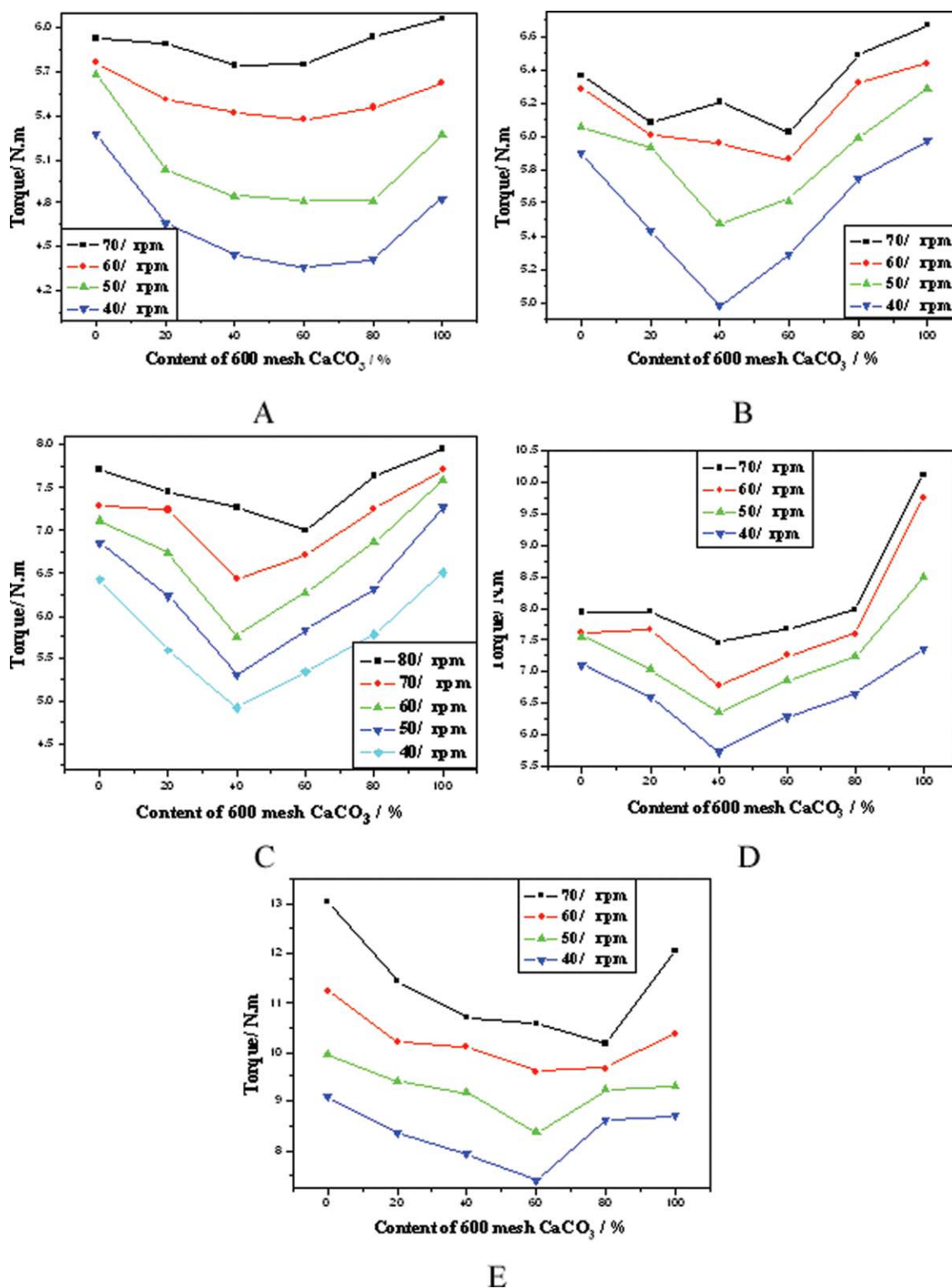


Figure 2 Torque curves of LDPE samples filled with CaCO₃ of different size distributions (600- and 2500-mesh CaCO₃ blend): (A) LDPE samples filled with 10 wt % CaCO₃, (B) LDPE samples filled with 20 wt % CaCO₃, (C) LDPE samples filled with 30 wt % CaCO₃, (D) LDPE samples filled with 40 wt % CaCO₃, and (E) LDPE samples filled with 50 wt % CaCO₃. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

obtain their crystalline characteristics. Lastly, the samples were heated to 150°C at a heating rate of 10°C/min to obtain their melting characteristics.

All operations were performed under a nitrogen flow. The sample weight was in the range of 4–5 mg.

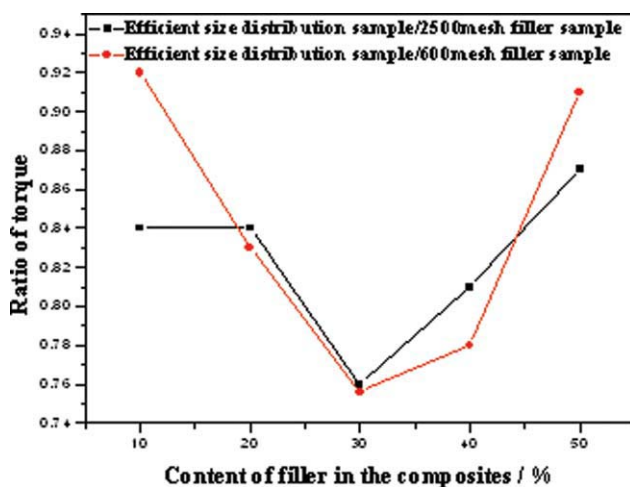


Figure 3 Torque ratio for the efficient-size-distribution samples and single-size-filler samples (180°C, 40 rpm, and 40 wt % 600-mesh filler and 60 wt % 2500-mesh CaCO₃ in the total filler). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

RESULTS AND DISCUSSION

Torque study of different samples at 180°C

Figure 2(A–E) shows for LDPE samples filled with various proportions of CaCO₃ (10, 20, 30, 40, and 50 wt %) the variation of the torque versus the 600-mesh CaCO₃ percentage in a filler including two different sizes of CaCO₃ (600 and 2500 mesh). Figure 1 shows that the torque values of LDPE samples filled with a CaCO₃ blend of two different sizes (600 and 2500 mesh) decreased obviously in comparison with samples filled with a single-size CaCO₃ (600 or 2500 mesh). When the percentage of 600-mesh CaCO₃ with respect to the total weight of CaCO₃ was in the range of 40–60%, the torque of LDPE samples filled with CaCO₃ of different size distributions was lowest. In Figure 2(A–E), we can see that the torque value followed the same change rule even when the content of CaCO₃ increased from 10 to 50 wt % in the samples. Therefore, LDPE samples filled with 600- and 2500-mesh CaCO₃ blends, when the percentage of 600-mesh CaCO₃ with respect to the total weight of CaCO₃ was in the range of 40–60%, could be named efficient-size-distribution samples. From Figure 2, we can also see that when the rotor speed increased from 40 to 80 rpm, the effect of the torque decrease for the efficient-size-distribution samples was weakened. This result showed that the efficient-size-distribution samples had higher efficiency at a lower shear velocity.

Figure 3 shows the efficiency of efficient size distribution versus the content of CaCO₃ in composites at 40 rpm and 180°C. When the content of CaCO₃ in an LDPE sample increased from 10 to 30 wt %, the

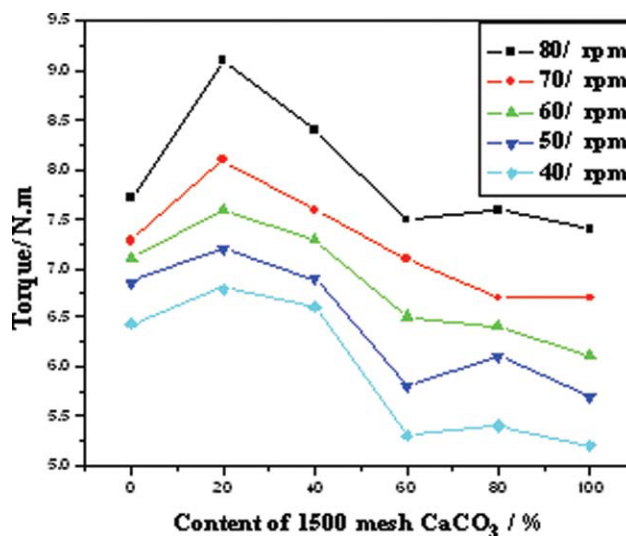


Figure 4 Torque curves of LDPE samples filled with 30 wt % CaCO₃ of different size distributions (1500- and 2500-mesh CaCO₃ blend). [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

efficiency of efficient size distribution increased, and when the content of CaCO₃ in an LDPE sample increased from 30 to 50 wt %, the efficiency of efficient size distribution decreased. Therefore, it can be suggested that, when the content of CaCO₃ in the efficient-size-distribution samples was 30 wt %, these samples had the best efficiency of efficient size distribution.

Figure 4 presents curves of the torque of LDPE filled with 30 wt % CaCO₃ fillers with different proportions of 1500- and 2500-mesh CaCO₃. The torque

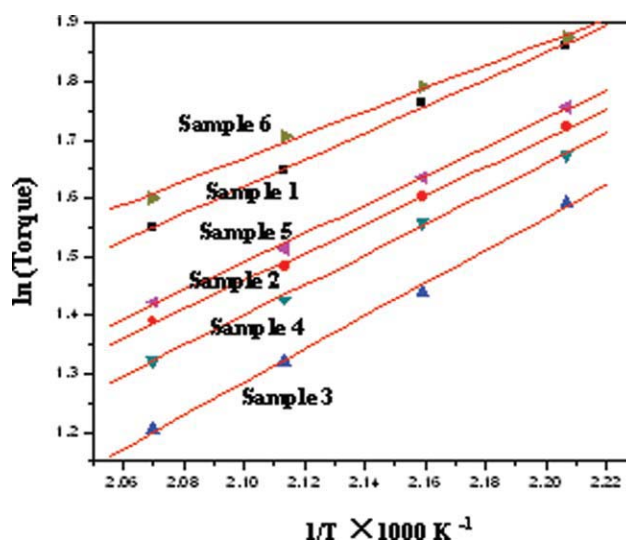


Figure 5 Plots of the natural logarithm of the torque versus the reciprocal of the temperature (1/T) for efficient-size-distribution samples and single-size-filler samples. [Color figure can be viewed in the online issue, which is available at www.interscience.wiley.com.]

TABLE III
 ΔE_η and KA Values of Samples 1–6

	Sample					
	1	2	3	4	5	6
KA	4.10×10^{-2}	2.56×10^{-2}	9.45×10^{-3}	1.70×10^{-2}	2.59×10^{-2}	8.38×10^{-2}
ΔE_η (kJ/mol)	19.0	20.3	23.5	21.8	20.4	16.4

did not decrease as it did in Figure 2. The LDPE samples filled with 1500- and 2500-mesh CaCO_3 blends were invalid size distribution samples. Therefore, it can be concluded that efficient size distribution must ensure a special size ratio between a big filler and a small filler.

Melt-viscosity study at different temperatures

The well-known Arrhenius equation is used to analyze the rheological behavior above the melting temperature;⁴⁵ it determines the relative viscosity (η) at a constant temperature (T):

$$\eta = A \exp(\Delta E_\eta/RT) \tag{1}$$

where A is a rate constant related to the flow entropy parameter and R is the universal gas constant. T is a measured temperature, and the equation is usually shown in the form of a logarithm:

$$\ln \eta = \ln A + (\Delta E_\eta/RT) \tag{2}$$

It is well known that the relative torque with the viscosity might be determined as follows:

$$\text{Torque} = K\eta \tag{3}$$

where K is a constant related to the properties of the mixer, sample volume, and rotor speed. With the same mixer, sample volume, and rotor speed, K does not change. Therefore, eq. (2) can be rewritten as follows:

$$\ln \text{torque} = \ln KA + (\Delta E_\eta/RT) \tag{4}$$

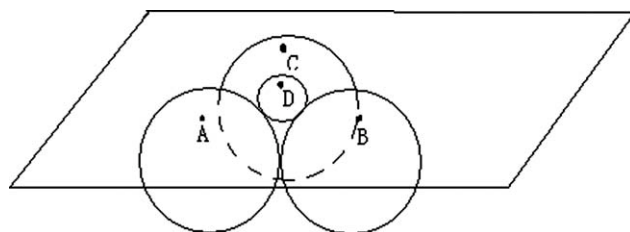


Figure 6 Small ball filled with the interspace of big balls (the peaks of A, B, C, and D lie in the same plane, and r/R is 1/3.)

The parameters ΔE_η and KA were obtained from the slopes and intercepts of plots of \ln torque versus $1/T$ at different temperatures (Fig. 5).

ΔE_η and KA values of LDPE samples 1–6 are listed in Table III. ΔE_η of samples 3 and 4 increased and A of samples 3 and 4 decreased in comparison with samples 1 and 6 because K was a constant.

It is well-known that A is a parameter related to the transformation of the flow activation entropy parameter of a fluid.⁴⁶ Therefore, the difference in the torque values of the LDPE samples filled with the efficient-size-distribution filler and the LDPE samples filled with a single-size filler was due to the increase in the flow activation entropy parameter.

Because of the molecular chain configuration of the polymer, the increase in the activation entropy resulted in the decrease in the torque of the samples filled with the efficient-size-distribution filler. On the basis of the experimental results, we concluded that the efficient size distribution decreased the baffled effect of the filler on polymer chains. It was very difficult for the filler to maintain the same velocity as the polymer chains when the LDPE samples were packed into the shear fraction. The partial orientation of the polymer chains, which resulted from the shear force, was baffled by adjacent fillers. Some conformational changes in the polymer chains resulting from the shear force disappeared because of the filler block. In the efficient-size-distribution samples, the baffled effect of the filler on the conformational

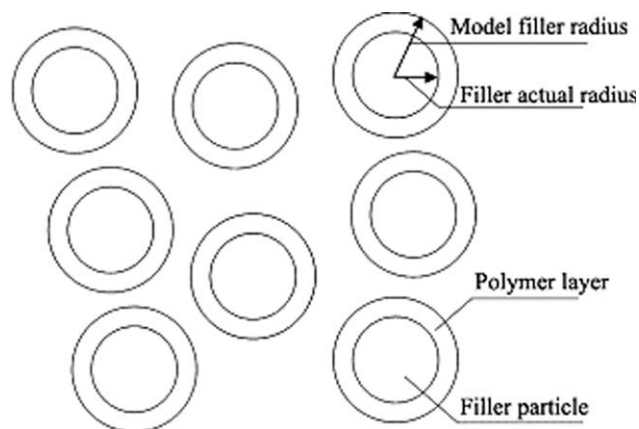


Figure 7 A slim layer of resin adheres to the filler surface.

TABLE IV
Effects of the Size Distribution of the Filler on the Torque of the Composites and the $r_{\text{small}}/r_{\text{large}}$ Ratios of the Samples of Different Size Distributions

Filler 1 (mesh)	Filler 2 (mesh)	$r_{\text{small}}/r_{\text{large}}$	Effect of the size distribution of the fillers on the torque of the composites
325	600	0.48	Inefficient
325	800	0.43	Inefficient
325	1500	0.30	Efficient
325	2500	0.15	Inefficient
600	800	0.89	Inefficient
600	1500	0.61	Inefficient
600	2500	0.32	Efficient
800	1500	0.69	Inefficient
800	2500	0.36	Inefficient
1500	2500	0.52	Inefficient

changes of the polymer chains decreased when small fillers were filled into the gap of large fillers. Therefore, the sum of the conformational transition resulting from the shear force increased in comparison with that of the single-size-distribution samples. This resulted in the increase in conformational entropy and the decrease in torque of the efficient-size-distribution samples.

When a small ball (with radius r_{small}) fills the gap of three large balls (with radius r_{large}) and the vertexes of the four balls are on the same tangent plane (Fig. 6), the $r_{\text{small}}/r_{\text{large}}$ ratio is 0.33. This value is very close to 0.32 [the ratio of the mean particle size ($d_{50\%}$) for 2500 mesh to $d_{50\%}$ for 600 mesh; Table I]. The case of spherical particles provides the simplest example. As pictorially illustrated in Figure 6, the

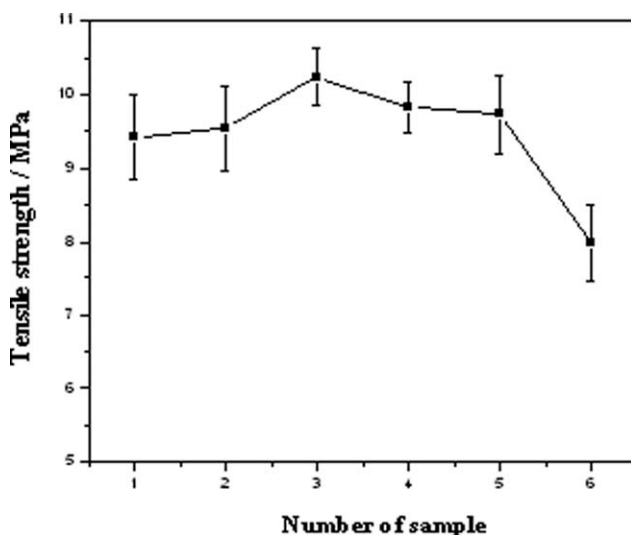


Figure 8 Tensile strength of samples 1–6.

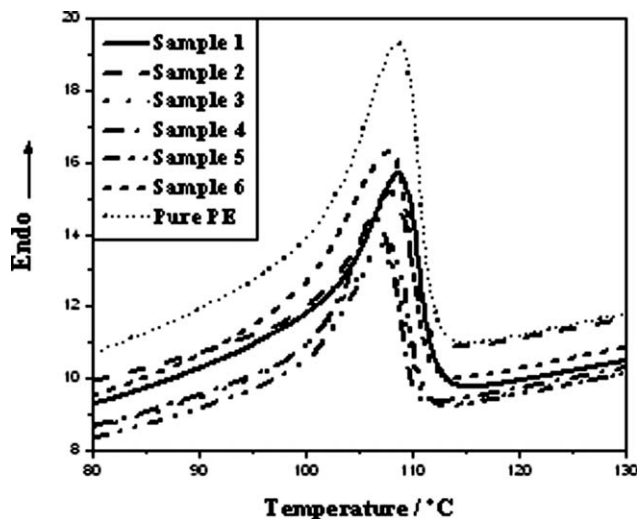


Figure 9 Melting curves of samples 1–6 and pure PE.

small particles may fill the gaps between the large particles when their sizes match. Thus, the baffled effect of the filler on the conformational changes of the polymer chains decreased when small fillers filled the interstices of large fillers, and the flow entropy parameter of the sample increased.

In the filler/polymer composites, a slim layer of a resin was formed when the resin could adhere to the filler surface because all fillers were treated with a surface modifier. The resin layer covering the filler surface was very thin. The thickness of the resin layer was the same no matter what the size was of the fillers. As a result, in the model, the filler radius was just a little bigger than the actual radius of the filler (Fig. 7).⁴⁷ Thus, the model radii of the big filler and small filler increased by the same amount. As a

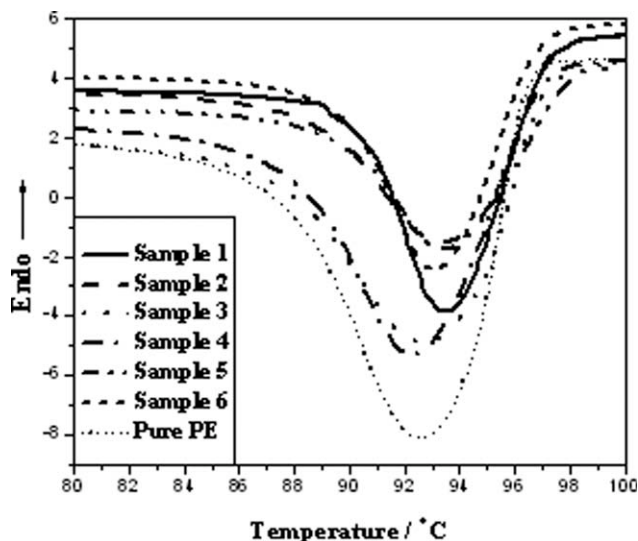


Figure 10 Crystallization curves of samples 1–6 and pure PE.

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

	Sample						PE
	1	2	3	4	5	6	
Melting temperature (°C)	108.6	107.8	106.7	106.2	107.5	107.7	108.7
Crystallization temperature (°C)	93.5	93.3	92.5	92.1	93.5	93.2	92.6
Supercooling (°C)	15.1	14.5	14.2	14.1	14	14.5	16.1

result, in the model, the values of $r_{\text{small}}/r_{\text{large}}$ for the composites were a little larger than the actual value of $r_{\text{small}}/r_{\text{large}}$. This was in agreement with our experimental results.

With 325-, 600-, 800-, 1500-, and 2500-mesh CaCO_3 , CaCO_3 samples of two sizes were blended at random, and their proportions and experimental conditions were the same as those for samples 1–6. The experimental results are listed in Table IV. The process torque for only 325/1500-mesh samples and 600/2500-mesh samples decreased, and their $r_{\text{small}}/r_{\text{large}}$ values were a little lower than 0.33. Therefore, it could be used to prove our previous supposition about the structure of the efficient-size-distribution samples.

Tensile strength

The tensile strength of samples 1–6 is summarized in Figure 8. From this figure, it can be seen that the efficient-size-distribution samples (samples 3 and 4) had the best tensile strength, but the difference for all the samples was negligible.

Melting and crystallization behaviors

The effects of the fillers on the thermal properties of LDPE were analyzed with nonisothermal DSC experiments. The melting curves of LDPE and samples 1–6 at a heating rate of 10°C/min are shown in Figure 9. The crystallization curves of samples 1–6 at the cooling rate of 10°C/min are shown in Figure 10. Figure 10 clearly shows that the crystallization peaks of the single-size-filler samples (samples 1 and 6) were sharper and higher than those of the efficient-size-distribution samples (samples 3 and 4).

Thermal parameters such as the melting temperature, crystallization temperature, and supercooling (supercooling = melting temperature – crystallization temperature) of pure LDPE and samples 1–6 were analyzed with nonisothermal crystallization experiments. The results are listed in Table V.

Table V shows that the efficient-size-distribution samples (samples 3 and 4) had lower melting and crystallization temperatures than those filled with the single-size filler (samples 1 and 6). Because the lower melting temperature could result in a lower

processing temperature of the polymer, the efficient-size-distribution samples could be processed at the lower temperature, and the energy consumption in the process could decrease.

CONCLUSIONS

When LDPE samples were filled with 600- and 2500-mesh CaCO_3 blends and the percentage of 600-mesh CaCO_3 with respect to the total weight of CaCO_3 was in the range of 40–60% (effective size distribution), the torque of LDPE samples could decrease evidently. When LDPE samples were filled with 30 wt % CaCO_3 with an effective size distribution, the lowest process torque was achieved.

The LDPE samples filled with efficient-size-distribution CaCO_3 at a lower shear velocity had higher efficiency than those samples at a higher shear velocity.

ΔE_{η} and the flow activation entropy of LDPE samples filled with efficient-size-distribution CaCO_3 increased obviously in comparison with LDPE samples filled with CaCO_3 of a single size.

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