

# Preparation and Characterization of High-Density Polyethylene/Expanded Graphite Conducting Masterbatch

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**ABSTRACT:** High level of expanded graphite (EG) was melt-blended with high-density polyethylene to prepare electrical conducting masterbatch. Some factors such as processing temperature, EG contents, treating time were discussed for the effect on electrical and mechanical properties of composites. Results showed that EG tends to reunite while the content of EG is higher than 60% because of the large aspect ratio and surface area of EG nanosheets. In addition, increasing processing temperature and mixing

time appropriately could enhance the dispersion of EG, leading to improvement in electrical and mechanical properties. Scanning electron microscopy (SEM) measurements were used as an assistant analysis to study the microstructure of composites. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 106: 3119–3124, 2007

**Key words:** conducting; masterbatch; expanded graphite; high-density polyethylene

## INTRODUCTION

Masterbatch is produced since the beginning of 1950s,<sup>1</sup> in which additives are filled remarkably into carriers to make congeries. In the past several decades, masterbatch (so called plastic concentrate) has been used vastly and broadly in plastic industry because of its excellent characters such as easy preparation, simple techniques, convenient uses, low-cost, and least air pollution.<sup>2</sup>

There are different kinds of masterbatches sorted by their different uses or additives, for example, color masterbatch,<sup>3</sup> flame-retardant masterbatch,<sup>4</sup> filler masterbatch,<sup>5</sup> conducting masterbatch,<sup>6</sup> and so forth. Conducting masterbatch is one of an important masterbatch in the preparation of conducting materials. Commonly, the fillers used in preparing a conducting masterbatch are some kind of inorganic conducting particles, such as metals,<sup>7</sup> carbon black,<sup>8</sup> carbon fiber,<sup>9</sup> graphite,<sup>10</sup> and carbon nanotubes.<sup>11</sup> Among them, graphite has an excellent electrical conductivity of  $10^4$  S/cm at ambient temperature.<sup>12,13</sup> Naturally abundant and light weight properties make it to be an ideal substitute in preparing electrically conductive composites. However, natural graphite particles always

bring to a great decrease in electrical and mechanical properties. Nanoscale graphite is gradually taken into consideration.

Expanded graphite (EG) is a kind of graphite with the same crystal structure and similar electrical conductivity to natural graphite. It is obtained by thermal treatment of graphite intercalation compound (GIC) at high temperature about  $1000^\circ\text{C}$ .<sup>13,14</sup> EG was always used as conductive filler in polymer composites recently owing to its much smaller particle size and lower percolation threshold than that of natural graphite. Zheng et al.<sup>15</sup> reported PMMA/EG composite prepared by direct solution blending with a percolation threshold of only 1 wt %. Xiao et al.<sup>16</sup> has reported PS/EG composite prepared by the polymerization-filling technique with a conductive percolation threshold lower than 2.5 wt %. However, EG has an apparent density of only  $0.004\text{ g/cm}^3$ , which leads to a large bulk volume of nearly  $250\text{ mL/g}$ .<sup>17</sup> The large volume of EG in addition to the big pores in it makes it hard to blend with polymers.

According to the literature,<sup>18</sup> increase in mixing energy is expected to enhance the dispersion of inorganic particles. Nevertheless, it is not feasible in real industrial production. Thus, masterbatch process has gained a broad application. However, EG-based masterbatch has not been reported. In this paper, we studied a conductive masterbatch based on HDPE and EG, where EG was premixed and dispersed in HDPE matrix under intensive rolling on a two-roll mill. The effect of processing temperature, EG contents, treating time on the electrical and mechanical properties were investigated and discussed.

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## EXPERIMENTAL

### Materials

EG with a worm-like or accordion-like structure, supplied by Shandong Qingdao Company (China). Commercial grade of high-density polyethylene (HDPE, BK160-4604) with a melt-index (MI) of 8 g/10 min was chosen as the carrier. Another HDPE (HD-BB105-001, Japan) with higher MI (2 g/10 min) was used as the matrix to prepare composites. Polyethylene wax (PEW) was chosen as the dispersant.

### Preparation of HDPE/EG masterbatch

EG was dried under a thermostat at 100°C for 2 h before use. HDPE carrier was melted and masticated on a two-roll mill, respectively, at 160 and 190°C. Then, a high level of EG was loaded and blended for different mixing time. As a comparison, PEW was added as a dispersant to enhance the dispersion of EG. The masticated composites were extruded and then palletized to grains using a single-screw extruder ( $L/D = 11$ ). A conductive masterbatch was prepared.

### Preparation of HDPE/EG composites

HDPE/EG composites were obtained by diluting HDPE/EG masterbatch with HDPE matrix on the same single-screw extruder at 150°C. After extruding, the samples were chopped into pellets for the next extrusion. As a comparison, direct melt-blending of HDPE matrix and EG composites were prepared and all samples were extruded thrice.

### Characterization and measurements

Short sticks of 16–17 mm in length were cut from the extruded samples at different places. The volume resistance of composites were tested on DT 9205A multimeter ( $R < 10^8 \Omega$ ) and ZC-36 high resistance tester ( $R > 10^8 \Omega$ ) at room temperature. The surfaces of the sample were coated with thin conductive adhesive to reduce the contact resistance before test. The volume conductivity was calculated by using the following equation:

$$\sigma = \frac{1}{\rho} = \frac{l}{RS} = \frac{l}{R\pi(D/2)^2}$$

where  $l$  is the length and  $D$  is the diameter of stick samples,  $R$  is the resistance of composites.

Scanning electron microscopy (SEM) photos were obtained on a LEO-1530 field-emitting scanning electron microscope.

The tensile and bend properties were measured on a universal tester (CMT6000, Shenzhen, China) and the impact strength was obtained on an impact testing

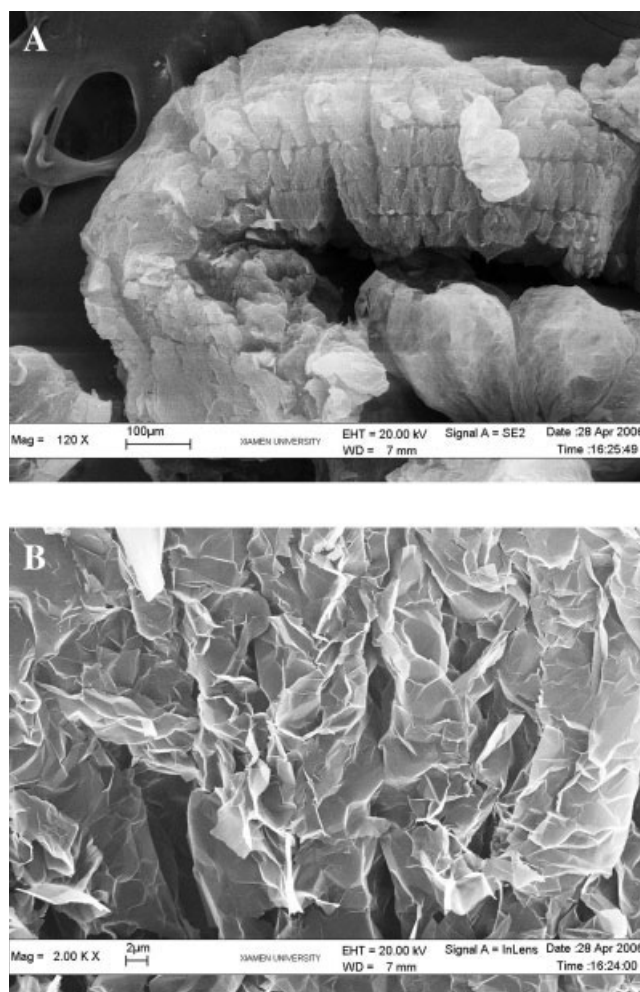


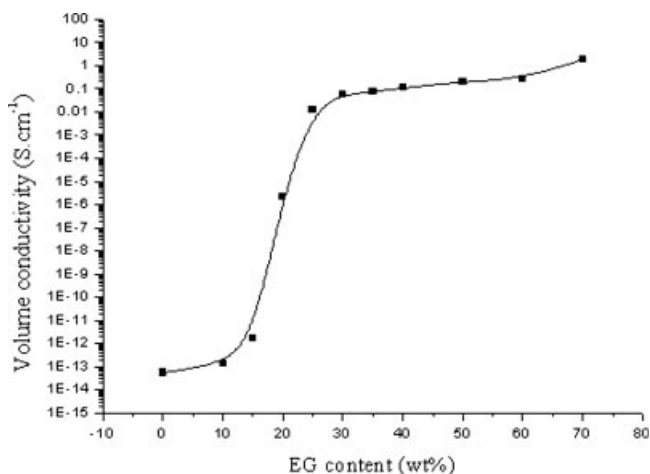
Figure 1 SEM photos of EG.

machine (ZBC-4, Shenzhen, China), and both using the Chinese testing standard GB1040-92. The double-shovel shaped samples had a gauge length of 40 mm, width of 5 mm, and thickness of 2 mm. The indentation samples had a length of 39 mm, width of 3 mm, thickness of 1.6 mm, and span of 20 mm. The flexural samples had a length of 39 mm, thickness of 1.7 mm, width of 3 mm, and span of 17 mm. The testing rate for tensile strength and bend strength are 30 and 3 mm/min, respectively. All samples were prepared by a plastic injection molding machine.

## RESULTS AND DISCUSSION

### Structure of EG

Vermicular- or accordion-like shapes of EG are shown in Figure 1(A). Another typical character of EG seen from Figure 1(B) is that the graphite flakes are tangled with each other and most of them are not exfoliated to single sheets, which leads to big closed and open poles in it. The EG possesses a large amount of open pores



**Figure 2** Electrical conductivity of HDPE carrier/EG as a function of EG contents. (140°C, extruder, 4 times).

ranging from 2 nm to 10  $\mu\text{m}^{13}$  (average size of the pores is about 2  $\mu\text{m}$ ), which results in its much smaller apparent density of 0.004  $\text{g}/\text{cm}^3$  than that of original flake graphite 2.25  $\text{g}/\text{cm}^3$ . The expansion ratio of EG, which can be generally calculated according to the apparent density, is about 550 ( $r = 2.25/0.004$ ). The thickness of EG sheets on the surface is in the range of 100–400 nm, as revealed by SEM photos. Thus, the resultant EG-filled polymer composites can be viewed as nanocomposites.

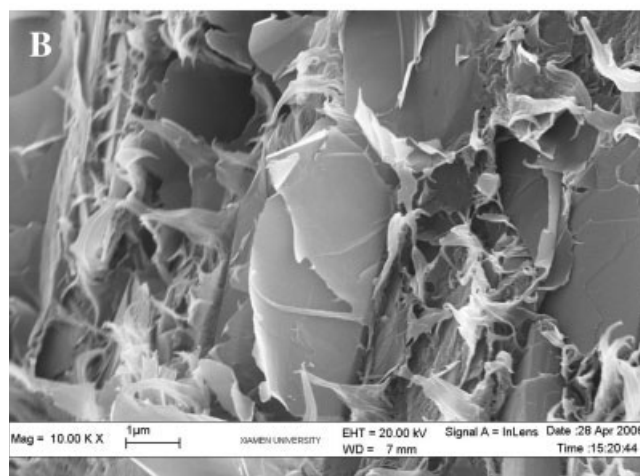
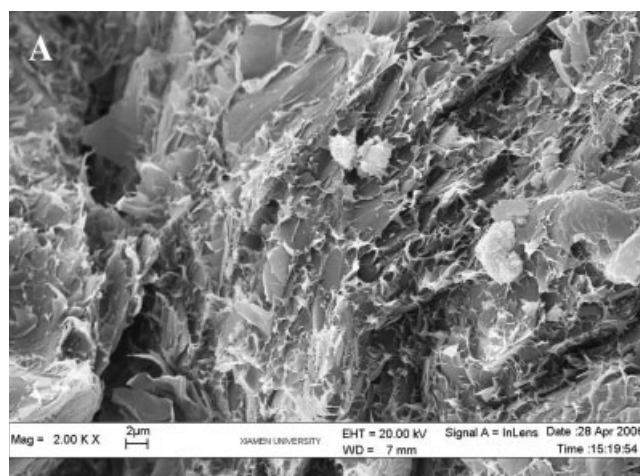
### Electrical properties for masterbatch and composites

First, conducting masterbatch should have a better or higher electrical conductivity. Figure 2 gives the electrical property of EG blended with HDPE carrier composites. As can be seen from this figure, a sharp increase in conductivity occurs when the filler content reaches 15 wt %, which is recognized to be the percolation threshold of a conductive composite from an insulator to a conductor. In addition, electrical conductivity levels off when the filler content higher than 30 wt %. The volume conductivity reaches 0.5  $\text{S cm}^{-1}$  at 50 wt % of EG content.

The morphology of HDPE/EG masterbatch was presented in Figure 3(A, B). EG flakes can be seen clearly in the blending, and most of them are less tangled after intensive rolling. Big pores that existed in EG are mostly taken up by HDPE carrier, which forms obstacles that can effectively separate EG flakes from each other. It is believed that increase in mixing energy achieved by increased mixing time and temperature is expected to enhance the dispersion of nanoparticles.

To determine the effect of preparing temperature, mixing time, and EG content on the conductivity of the masterbatch, samples of HDPE/EG masterbatch under different processing conditions have been prepared. Volume conductivity data collected from the

samples are listed in Table I. The conductivity of a masterbatch increases with the increasing filler content and increasing preparation temperature, while it does not drastically compared with the elongation of mixing time. It is believed that increasing mixing energy achieved by increasing preparation temperature and mixing time is expect to enhance the dispersion of EG, which increases the conductivity of masterbatch. However, the tangled structure of EG tends to break into pieces with the elongation of mixing time, which promotes the conductivity of the masterbatch because of EG dispersion on the one hand and decreases the conductivity of the masterbatch owing to the broken structure of EG on the other hand. Thus, the conductivity varies indistinctly with the mixing time. The effect of mixing temperature can be explained as the energy that is adequate for polymer chains to penetrate into the pores and the layered structure of EG. HDPE chains have better fluidity at high temperature and can easily penetrate into the gaps of EG forming obstacles among EG particles. This phenomenon can be deemed as the equal effect



**Figure 3** Scanning electron micrographs of 50 wt % masterbatch.

**TABLE I**  
**Electrical Conductivities of Masterbatches Prepared Under Different Preparing Conditions**

Preparing temperature (°C)	EG contents (wt %)	Electrical conductivity (S cm <sup>-1</sup> )		
		30 min	45 min	60 min
160	50	0.1337	0.1208	0.1311
	60	0.1582	0.1531	0.1397
	70	0.1779	0.1678	0.1818
190	50	0.1745	0.1645	0.1408
	60	0.3802		
	70	0.5988		

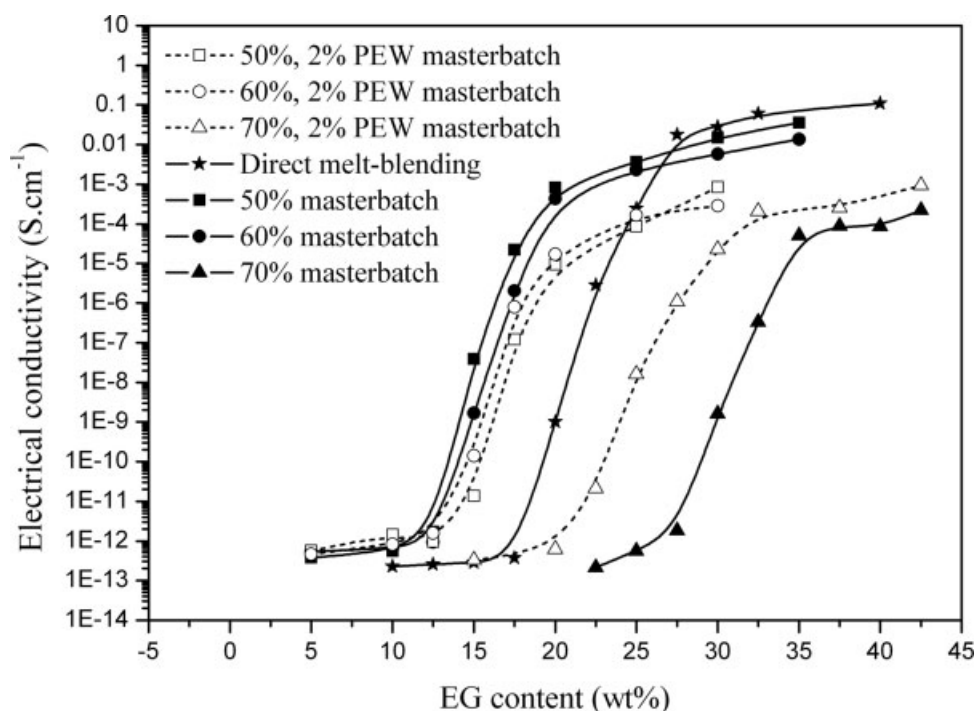
between time and temperature. That is, increasing the mixing temperature appropriately can save much processing time for the masterbatch to reach the same state.

Second, a good conductive masterbatch should have a well-dispersed inorganic phase. The composite can easily be prepared with excellent electrical properties by diluting this masterbatch. Although higher processing temperature and EG content can improve the conductivity of a masterbatch, we cannot say that a well-dispersed masterbatch was prepared. A straight way to judge which preparing condition is perfect is by diluting the masterbatch into other matrices as conductive filler. Figure 4 presents the electrical property of HDPE/EG composites prepared by masterbatch filling process as written above. Obviously, electrical properties of masterbatches containing 50 and 60 wt % EG are much better than those of 70 wt % masterbatch and direct melt-blending composites. In

addition, the percolation thresholds of 50 and 60 wt % masterbatch filling composites in the presence of 2 wt % PEW are a little higher than those of nonexistent ones, while 70 wt % masterbatch filling composite is just contrary to that. We believe these phenomena are mainly attributed to the dispersion of EG in HDPE matrix. When the masterbatch contains a higher EG content, take 70 wt % for example, there are too much agglomerates existing in the masterbatch and HDPE carrier cannot wet all EG flakes well. However, the addition of PEW can promote the dispersion of EG under the same preparing conditions. The changes of percolation threshold are not obvious for 50 and 60 wt % masterbatches filling composites. They are ascribed to the fact that there are enough HDPE carriers to wrap each piece of EG sheets effectively where the effect of PEW is not distinctly. Another feature of interest in this figure is that the final conductivity of HDPE/EG composites prepared by masterbatch filling technique is 1–3 orders of magnitude lower than that of direct melt blending process. This also can be explained by the extent of EG dispersion in the polymer carrier. Well-wrapped EG sheets prevent the effective transmission of electrons, and tunneling conduction<sup>19</sup> plays an important role in the conducting mechanism.

#### Mechanical properties of HDPE/EG composites via a masterbatch process

The mechanical property of organic–inorganic composite is greatly related to the dispersion of inorganic



**Figure 4** Electrical properties of HDPE/EG composites via a masterbatch process.

**TABLE II**  
**Mechanical Properties of HDPE/EG Composites Prepared by Diluting Different Masterbatches**

Preparing temperature (°C)	EG contents (wt %)	Mixing time (min)	Tensile strength (MPa)	Impact strength (kJ/m <sup>2</sup> )	Flexural strength (MPa)	
160	50	30	22.90	16.52	20.78	
		45	25.09	16.41	23.33	
		60	25.64	15.80	22.21	
	60	60	30	25.31	19.08	19.61
			45	26.06	18.21	19.51
			60	25.65	18.99	18.79
	70	70	30	25.71	22.51	17.36
			45	24.93	22.10	16.74
			60	23.51	22.64	15.35
190	50	30	26.90	16.53	22.00	
		45	26.39	15.68	22.06	
		60	26.50	16.94	22.11	

component. We can identify the dispersion degree of a masterbatch and its composites indirectly. HDPE/EG samples containing an exact EG content of 10 wt % are prepared by diluting different EG-content masterbatch. The tensile strength, impact strength, and flexural strength data are given in Table II. The differences indicate different dispersion states of masterbatches. Under 160°C, EG content of 60 wt % masterbatch has highest tensile strength, better impact strength, and flexural strength. Increasing preparation temperature as the 50 wt % masterbatch showed has evidently improved in the tensile strength without any major changes in impact strength and flexural strength, which indicates that increasing temperature can facilitate masterbatch processing and obtain a well-dispersed masterbatch.

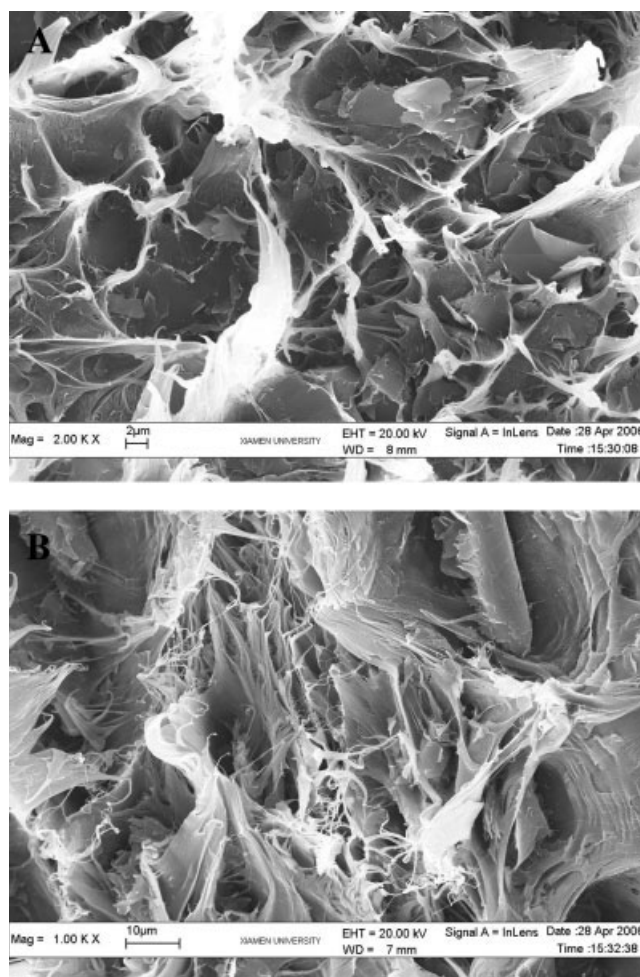
Figure 5(A, B) displays SEM images of the cross section of HDPE/EG composites via different masterbatch dilution (each composite has EG content of 10 wt %). It is clearly seen that EG has better dispersion state in 50 wt % masterbatch diluting composite [Fig. 5(A)] than that in 70 wt % masterbatch diluting composite [Fig. 5(B)] under the same preparing conditions, which indicates that EG tends to agglomerate in the masterbatch when its content reaches 70 wt % and it is difficult to obtain a well-dispersed composites by diluting this masterbatch to HDPE matrix.

To sum up, taking the effect of processing temperature and time on electrical and mechanical properties into consideration, appropriate rolling time of 30 min and processing temperature of 190°C were optimum conditions in preparing HDPE/EG masterbatch.

## CONCLUSIONS

HDPE/EG conductive masterbatches were prepared by melt blending on a two-roll mill at different processing temperature and mixing time. Electrical and

mechanical properties of different EG content masterbatches were studied. Results showed that electrical and mechanical properties of masterbatches



**Figure 5** SEM images of HDPE/EG composites via different masterbatches dilution (a, 50 wt % masterbatch; b, 70 wt % masterbatch).

depended greatly on EG dispersion, and EG flakes tended to agglomerate in polymer carrier when EG content is higher than 60 wt %. Higher processing temperature and the existence of PEW can enhance the dispersion of EG and increase the conductivity of a masterbatch. The final conductivity of HDPE/EG composites prepared by masterbatch diluting process is 1–3 magnitude lower than that of direct melt-blending process. It is believed that EG sheets are well wrapped by HDPE carrier, which forms obstacles between EG flakes that prevents the effective transmission of electrons.

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