

# Synthesis and Characteristics of Poly(methyl methacrylate)/Expanded Graphite Nanocomposites

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**ABSTRACT:** In this work, we synthesized poly(methyl methacrylate) (PMMA)/expanded graphite (EG) nanocomposites by a new polymerization method. The volume electrical conductivity of the nanocomposite prepared by this way is very high (when the content of EG is about 8 wt %, the conductivity could reach 60 S/cm). The structure of the nanocomposite was investigated by SEM, TEM, IR, and

XRD. And we found temperature and voltage were important parameters of governing the electrical conductivity of PMMA/EG nanocomposites. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 1427–1431, 2006

**Key words:** graphite; PMMA; nanocomposite; polymer

## INTRODUCTION

In the recent decades, people have been devoting themselves to design and prepare the conductive polymer nanocomposite.<sup>1–3</sup> Graphite, which is naturally abundant, has been widely used as electronical conductive filler for preparing conductive polymer composites for this few years.<sup>4,5</sup> Because there are no reactive groups on the natural graphite layers, it is difficult for a monomer to load on its surface. In addition, natural graphite particles are difficult to be dispersed because they have large volume and their shapes are regular. To be distributed well in polymer, natural graphite was often oxidized, and then expanded at very high temperature for making expanded graphite (EG) before use.<sup>2,6,7</sup> EG has a higher volume expansion ratio than that of natural graphite, and is dispersed in polymer easily. Furthermore, many factors, such as the multi-pores in EG, functional carboxyl and hydroxyl groups on the surface of EG, will facilitate physical and chemical adsorption between the graphite and the polymer molecules.<sup>7–10</sup>

Therefore, material scientists have paid more attention to the preparations and properties of polymer/EG composites. Recently, several groups<sup>11–14</sup> reported their work on situ polymerization or solution compounding to achieve nanocomposites of polymer with EG. Some new conductive polymer/EG composites with low percolation threshold of conductivity were produced, such as PMMA/EG,<sup>11</sup> Nylon 6/EG,<sup>12</sup> PS/EG,<sup>13</sup> PS-PMMA/EG.<sup>14</sup>

In this work, we used a new way to synthesize PMMA/EG nanocomposites with better conductivity. The structure and conducting properties of the composite were investigated.

## EXPERIMENTAL

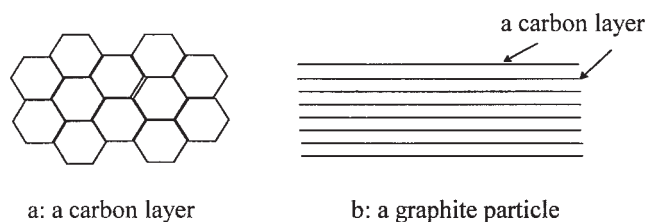
### METHODS

Natural graphite purchased from Shanghai Colloid Chemical Factory was oxidized with  $\text{KMnO}_4$  in a solution of acetic anhydride and nitric acid at 30°C for 40 min. The graphite oxide (GO) obtained was extracted with benzene for removing the impurities. The EG was prepared by heating GO at 500°C for 15 min under  $\text{N}_2$  atmosphere. The inflation rate of EG is about 250 times. The methyl methacrylate (MMA) monomer (The Shanghai First Chemical Reagent Plant, Chemical Pure) was washed by 5% NaOH aqueous solution and distilled water, respectively, then purified by vacuum distillation before use. AIBN (The Shanghai First Chemical Reagent Plant, AR) was recrystallized from ethanol before use.

### Preparation of PMMA/EG nanocomposites

MMA (60 mL) and AIBN (0.164 g) were mixed thoroughly and added into a 250 mL two-necked flask containing EG (5.02 g). To ensure that the monomers were completely absorbed into the pores of EG, the closed flask was shaken occasionally, and kept at room temperature for 12 h until no monomer was present on the surface of the graphite particles. If the surface seemed wet, a piece of filter paper was used to absorb the monomers for ensuring there was no

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Scheme 1

monomer on the surface of the particles. The in-situ polymerization of MMA in the pores of EG particles was first carried out at 60°C for 12 h, followed by polymerization at 80°C for another 12 h. The resultant PMMA/EG composite (57.71 g) was produced after removal of the un-reacted monomers at 90°C in a vacuum oven.

The composite particles were transferred to a pre-heated compression mold and hot-pressed into rectangular sheets of  $100 \times 100 \times 2 \text{ mm}^3$  at 180°C under 10–15 MPa. The composite sheets were lately cut into different sizes and geometries for the measurements of different properties.

### Characterization of PMMA/EG nanocomposites

The FTIR spectra were recorded on a VECTOR-22 (Germany) Fourier Transform Infrared Spectrometer in increment of  $0.5 \text{ cm}^{-1}$ . The scanning was 16 times. The XRD spectra were obtained on a Y-4Q (China) X-ray diffractometer (XRD). Data were collected at room temperature over the range  $5^\circ \leq 2\theta \leq 50^\circ$  in increment of  $0.2^\circ$ . Scanning electron micrograph (SEM) was carried out on a JSM-6700F scanning electron microscope. Transmission electron micrograph (TEM) was carried out on a JEM-100SX transmission electron microscope.

The testing sheets for resistance of less than  $10^6 \Omega$  were prepared as follows: A sample with  $3 \times 10 \times 2 \text{ mm}^3$  was cut from the composite sheet, and its electrical resistances of the samples were measured by a four-probe method with digital multimeters DT9208. The four electrodes were fixed on the sample by hot pressing.

When the resistance of a sample was higher than  $10^6 \Omega$ , the measurement of the resistance was carried out by a four-probe method with a Super-High Resistance Instrument ZC-36 ( $10^{17}$ ).

## RESULTS AND DISCUSSION

### Structure of expanded graphite

Graphite has a high conductivity. The structure of graphite is shown in Scheme 1. It is a form of carbon with carbon atoms  $sp^2$  bonded in flat planes, with the

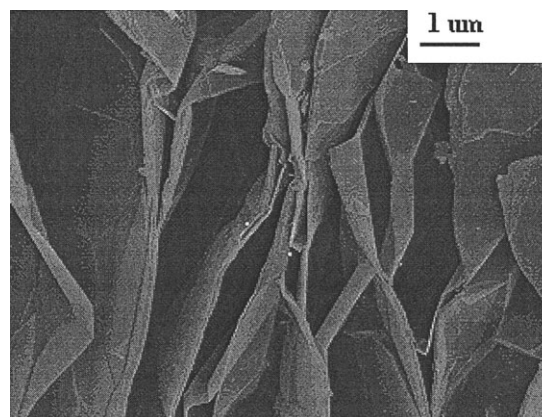


Figure 1 The SEM photos of EG.

planes held together by Vander Waals forces.<sup>15</sup> Graphite can be intercalated by exposing it to the appropriate material, known as the intercalating agent, which stayed between the carbon layers of the graphite.<sup>4</sup> But the natural graphite is difficult to disperse, and so the EG often is used for preparing nanocomposite.<sup>16,17</sup> The SEM photo of EG is shown in Figure 1. It was clear that EG maintains the layered structures similar to that of natural flake graphite, except that there were tremendous different size of pores and nanosheets sticking to each other. The EG was completely changed to sheets with thickness 100–400 nm and with diameter of 0.5–20  $\mu\text{m}$ , named graphite nanosheets.<sup>18</sup>

### Structure of PMMA/EG nanocomposite

For clarifying whether PMMA is intercalated into interlayers of EG, the XRD patterns of PMMA/EG composite were measured, and shown in Figure 2. A peak at  $2\theta = 26.44^\circ$  is observed, indicating that the crystal structure of graphite remains. So we can conclude that polymerization does not destroy the crystal structure

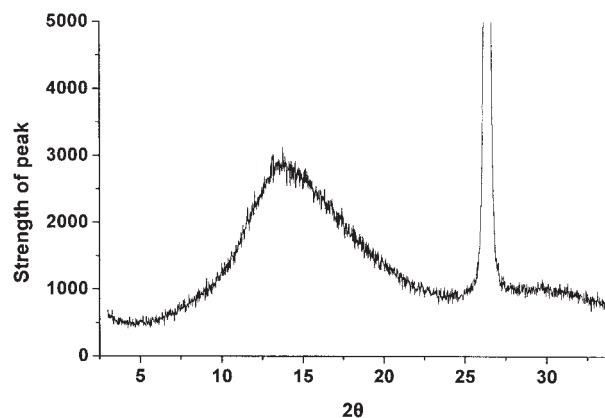
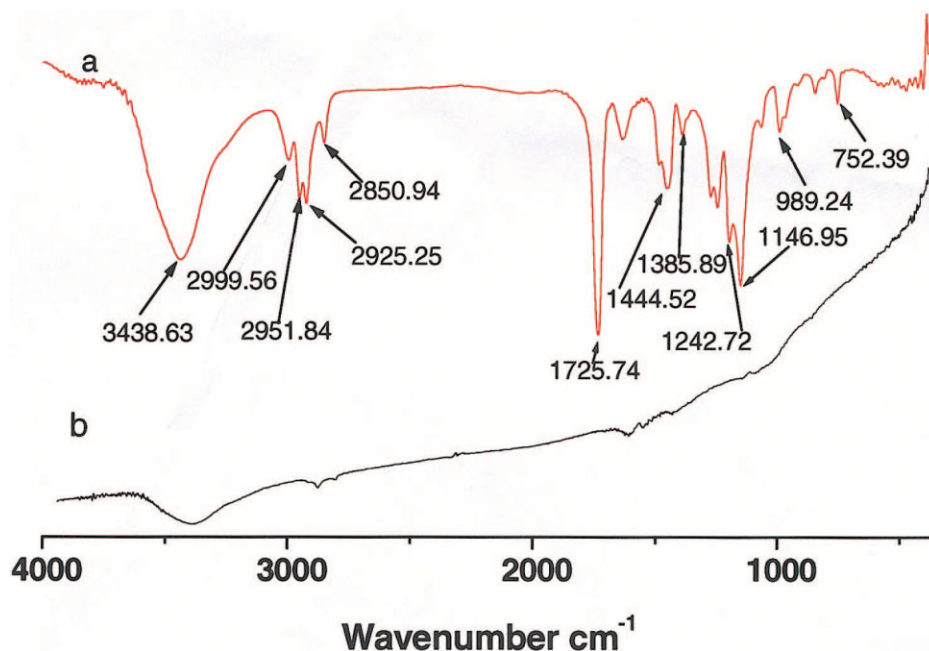


Figure 2 XRD patterns of PMMA/EG.



**Figure 3** IR spectra of PMMA/EG (a) and EG (b). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

of EG completely. A wide peak from  $2\theta = 10\text{--}20^\circ$  shows that most MMA monomer intercalated into the pores inside EG and was polymerized in situ. It can be confirmed further by their FTIR spectra. A typical spectrum of PMMA/EG composite is shown in Figure 3(a). For comparison, the FTIR spectrum of EG is also shown in Figure 3(b). The characteristic absorption bands of PMMA can be clearly seen from Figure 3(a), such as the peaks at  $\nu = 2951.84, 2925.25, 1385.89$  ( $-\text{CH}_3$ );  $1725.74$  ( $\text{C}=\text{O}$ )  $\text{cm}^{-1}$ . These peaks can not be found in Figure 3(b), which indicates the existence of PMMA and the forming of PMMA/EG composite. And there was no monomer remaining in the composite because there is no peak at  $\nu = 3000\text{--}3100$  in Figure 3(a).

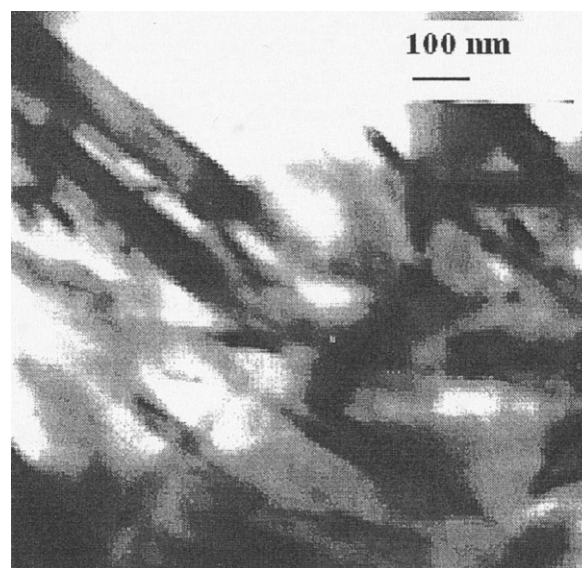
For understanding the microstructure of PMMA/EG composite, its TEM images were taken and are shown in Figure 4. In the figure, the solid lines represent the graphite nanosheets, forming network for electrical current. It is clear that the thickness of nanosheets ranged from 30 to 80 nm in thickness.

#### Electrical conductivity of PMMA/EG composites

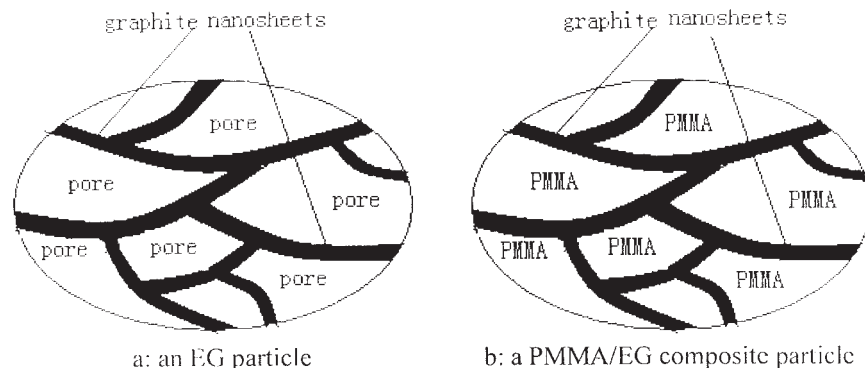
##### Conductivity of PMMA/EG composites at different EG content

Since the EG possesses abundant pores and the highest aspect ratio, polymer chains were easily intercalated in the pores of the EG by adsorption mechanisms. It makes the composite with good conductivity. The intercalation process of polymers into EG is sug-

gested as shown in Figure 5. It displayed the section diagrams of an EG particle [Fig. 5(a)] and a PMMA/EG composite particle [Fig. 5(b)]. Since the flake structures of EG have not been destroyed during the polymerization,<sup>7</sup> a PMMA/EG composite particle also has good conductivity, and the composite achieves nice conductivity because of good connection between every two composite particles.<sup>8</sup> Even though few network structures have been destroyed, the nanosheets are still very close to each other. Electrons in EG nanosheets can also generate electrical current by tunneling effect.



**Figure 4** The TEM photos of PMMA/EG composite.



**Figure 5** Formation process diagram of PMMA/EG composite. (A) the section diagram of an EG particle; (B): the section diagram of a PMMA/EG composite particle.

Table 1 shows the variation of volume electrical conductivity of PMMA/EG with different EG content. PMMA is insulator, and its volume electrical conductivity is about  $10^{-16}$  S/cm at room temperature. However, if we added EG in it, we can see the volume electrical conductivity rising very sharply. When the EG content arrived at about 8 wt %, the volume electrical conductivity of PMMA/EG could reach about 60 S/cm.

#### Effects of applied voltage on electrical conductivity

As reported by Wang,<sup>8</sup> there is graphite interpenetrating network structure in the composite. The graphite interpenetrating network structure consists of graphite nanosheets, which connect each other and form a network throughout the entire composite. Inevitably, these graphite nanosheets that connect well have some gaps between them, but they are very close to each other, just be blocked off by very thin polymer. If the bosom electric field engendered within electric graphite particles is strong, electron has great odds to get across the potential rampart of polymer interface to the nearby electric graphite particle and form auto electronic current. Figure 6 shows the conductivity of PMMA/EG composite affected by different applied voltage (EG: 9.32 wt %, 25°C). At the beginning, the electrical conductivity of composites is greatly influenced by the applied voltage, then the increase of conductivity become mild. This is because as the ap-

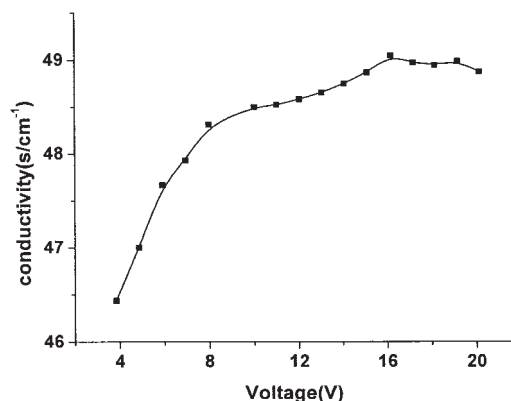
plied voltage is increasing, the electron transitions tend to reach saturation.

#### Effects of temperature on electrical conductivity

Caloric vibration can activate electron to get across the potential rampart of polymer interface to the nearby electric particle, forming higher tunnel electrical current. Figure 7 revealed the increase in the electrical conductivity of the composites (EG: 9.32 wt %, applied voltage: 10 V) due to temperature. This phenomenon is known as tunnel effect in quantum mechanics. As temperature increasing reinforce the tunnel effect, so the conductivity of composites become higher.

### CONCLUSIONS

The PMMA/EG nanocomposite prepared by this procedure possessed much higher conductivities than those of composites made by conventional methods when the contents of graphite in the two kinds of composites were the same. The electrical conductivity of PMMA/EG reached 60 S/cm (Temperature: 25°C,



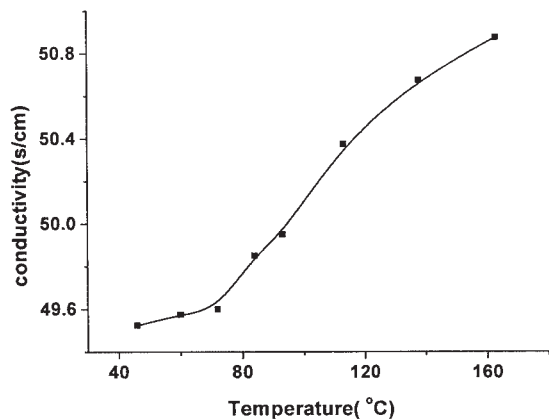
**Figure 6** The conductivity of PMMA/EG composite affected by different applied voltage (EG = 9.32 wt %, 25°C).

**TABLE I**  
The Conductivity of Different EG Content

Content of EG (wt %)	Conductivity (S/cm)
10.05	77.65
9.32	65.175
8.08	60.7
6.94	4.1575

Experimental condition: 10 V, 25°C.





**Figure 7** The conductivity of PMMA/EG composite affected by different temperature (EG = 9.32 wt %, applied voltage: 10 V).

Applied voltage: 10 V) at EG content of about 8 wt %. With the increase of filler content, the electrical conductivity of the PMMA/EG composites is also increased.

The temperature and the applied voltage appeared to be among the important parameters governing the electrical conductivity of PMMA/EG composites.

## References

- Alexandre, M.; Dubois, P. *Mater Sci Eng* 2000, R28, 1.
- Usuki, A.; Kojima, Y.; Kawasumi, M.; Okada, A.; Fukushima, Y.; Kurauchi, T.; Kamigaito, O. *J. Mater Res* 1993, 8, 1179.
- Pinto, G.; Jimenez-Martin, A. *Polym Compos* 2001, 22, 65.
- Celzard, A.; Mareche, J. F.; Furdin, G.; Puricelli, S. *J Phys D: Appl Phys* 2000, 33, 3094.
- Matsuo, Y.; Tahara, K.; Sugie, Y. *Carbon* 1997, 35, 113.
- Ezquerria, Y. A.; Kulescza, M.; alta-Calleja, F. J. *Synth Met* 1991, 41, 915.
- Chen, G.-H.; Wu, C.-L.; Wang, W.-G.; Wu, D.-J.; Yan, W.-L. *Polymer* 2003, 44, 1781.
- Wang, W.-P.; Pan, C.-Y. *J Polym Sci Part A: Polym Chem* 2003, 41, 2715.
- Daoulas, K. C.; Terzis, A. F.; Mavrantzas, V. G. *J Chem Phys* 2002, 116, 11028.
- Cao, N.; Shen, W.; Wen, S.; Liu, Y. *Chem Bull* 1996, 4, 37.
- Zheng, W.; Wong, S.-C. *Compos Sci Technol* 2003, 63, 225.
- Pan, Y.-X.; Yu, Z.-Z.; Ou, Y.-C.; Hu, G.-H. *J Polym Sci Part B: Polym Phys* 2000, 38, 1626.
- Xiao, P.; Xiao, M.; Gong, K. *Polymer* 2001, 42, 4813.
- Chen, G.-H.; Wu, D.-J.; Weng, W.-G.; Yan, W.-L. *J Appl Polym Sci* 2001, 82, 2506.
- Chung, D. L. *J Mater Sci* 1987, 22, 4190.
- Zheng, W.; Wong, S.-C.; Sue, H.-J. *Polymer* 2002, 73, 6767.
- Celzard, A.; McRae, E.; Mareche, J. F.; Furdin, G.; Dufort, M.; Deleuze, C. *J Phys Chem Solids* 1996, 57, 715.
- Chen, G.-H.; Wu, D.-J.; Weng, W.-G.; Wu, C.-L. *Carbon* 2003, 41, 579.