

# Temperature Dependence of the Conductivity Behavior of Graphite Nanoplatelet-Filled Epoxy Resin Composites

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**ABSTRACT:** In this article, epoxy/graphite nanoplatelet (GNP) conductive composites with the low percolation threshold of  $\sim 0.5$  vol % were prepared. The effect of microstructure, particularly the spatial distribution of fillers in the matrix on the resistivity and its dependence on temperature, also was investigated. It is suggested that the high aspect ratio and good distribution of GNPs in the matrix contribute to the low threshold of the composite. The thermal–electrical behavior of the composite is also significantly influenced by the GNP content and micro-

structure of the composite. When the GNP content is greater than percolation threshold, a noticeable positive temperature coefficient of resistivity disappears. It is explained by the unique conductive network formed by plane contact between GNPs, which is hardly affected by the expansion of matrix during heating. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 113: 1515–1519, 2009

**Key words:** epoxy resin; graphite nanoplatelets; electrical properties; nanocomposites

## INTRODUCTION

Conductive polymer composites (CPCs) are becoming increasingly useful as the result of their unique combination of metallic conductivity and polymer properties. These materials are widely used as microwave absorbing materials, electromagnetic shielding materials, and antistatic materials, to name a few applications.<sup>1–3</sup> In addition, CPCs, with the properties of temperature dependence of the conductivity, are regarded as promising materials for applications in self-regulating heaters, self-resetting, overcurrent protectors, and sensors.<sup>4–6</sup> A significant part of investigations in this field concern carbon black-filled polymer composites,<sup>7–10</sup> which exhibit positive temperature coefficient (PTC) and negative temperature coefficient (NTC) effects in a wide range at or greater than the percolation threshold. It is believed that the strong intensity of temperature dependence of the conductivity for CPCs always occurs near the percolation threshold. Both percolation effect and the

thermal–electrical behavior of conductive polymer composites are significantly affected by the type of filler and its spatial distribution.<sup>11–14</sup>

Graphite nanoplatelet (GNPs), which are two-dimensional and layered conductive materials, are promising conductive fillers for CPCs with a low percolation threshold because of their high aspect ratio, large surface area, their abundance as natural resources, and inexpensiveness. Most works on GNP-filled polymers have only been concerned with how to decrease the percolation threshold of the composites,<sup>15,16</sup> and few investigation have been reported on thermal–electric behavior, particularly the effect of microstructures of conductive fillers on the temperature dependence of the conductivity.

In this work, epoxy/GNP composites were prepared by use of a liquid mixing method to ensure the homogeneous dispersion of GNPs in the matrix. The electrical resistivity and its dependence on temperature as a function of GNP content were investigated. The effects of spatial distribution of conductive fillers in the matrix on percolation threshold and PTC effect also were investigated. On basis of the experiment results, a general model and mechanism for PTC effect of GNP-filled polymers are proposed.

## EXPERIMENTAL

### Materials

All the chemical reagents were analytical grade and used without further purification. Graphite flakes

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(270  $\mu\text{m}$ ) were supplied by Qingdao Graphite Company (Qingdao, China). Epoxy resin (Bisphenol-A epoxy resin E 44) was supplied by Wuxi Resin Factory (Wuxi, China). Curing agent (dicyandiamide) was supplied by Tianjin Chemical Reagent No. 6 Factory (Tianjin, China).

### Preparation of epoxy resin/GNP composites

Graphite flakes, concentrated nitric acid (65 wt %), oxalic acid, and potassium permanganate were mixed in a weight ratio of 1 : 2 : 0.3 : 0.4 and stirred continuously for 30 min at 30°C to prepare graphite intercalation compounds (GICs). Then, the mixture was washed thoroughly with water until the solution became neutral and dried at 60°C to remove the remaining moisture. The dried particles were heat treated at 900°C for 20 s to obtain expanded graphite (EG). The as-produced EG was dispersed in acetone by mechanical stirring for 30 min followed by sonication for 20 h to obtain GNP suspension. Epoxy resin was dissolved into acetone, the curing agent was dissolved into the mixture of acetone and ethanol, and then the two solutions were added into the GNP suspension under continuous stirring in a ratio of epoxy to curing agent of 100 : 6.5 by weight. Then, the mixture was subjected to high-shear mixing at 60°C in water bath for 1 h. The residual solvent was removed at 80°C in a vacuum oven. After that, the mixture was loaded into a designed mold and cured at 120°C for 1 h and at 185°C for additional 3 h to complete the curing process. A series of composites with 0–2.5 vol % GNPs were prepared. The surfaces of specimens were polished with sandpaper (1500 mesh) to remove the polymer-rich surface layer and eliminate surface irregularities.

### Testing

Morphologies of samples were examined by scanning electron microscopy (SEM; HITACHI S4800). The glass transition temperatures ( $T_g$ ) of samples were determined using a thermal analyzer (NETZSCH STA 409PC) over the temperature range 25–500°C at 15°C/min by heat-cool-heat cycle. The volume resistivity ( $\rho$ ) was measured by a two-probe method by the use of digital multimeter FLUCK 17B ( $<10^8 \Omega \text{ cm}$ ) and FLUCK 1508 ( $>10^8 \Omega \text{ cm}$ ). These samples were cut into dimensions of  $1 \times 1 \times 0.5 \text{ cm}^3$ . Opposing sides of samples were coated with conductive adhesive to control the contact resistance during measurement. The values of  $\rho$  were calculated using the following equation:

$$\rho = (R \cdot S)/L \quad (1)$$

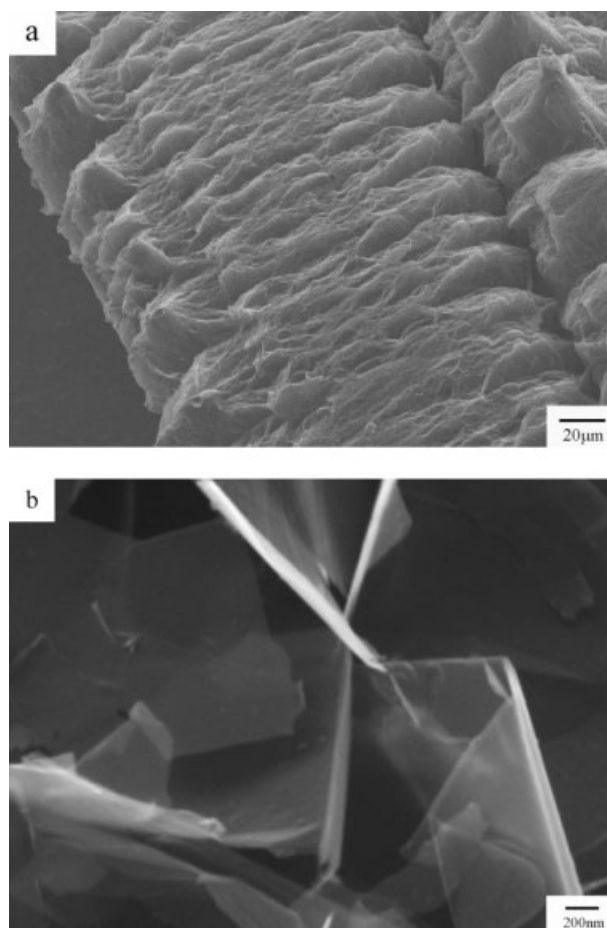
where  $R$  ( $\Omega$ ) is electrical resistance,  $L$  (cm) is the thickness of the sample, and the  $S$  ( $\text{cm}^2$ ) is the sam-

ple cross-sectional area. Three specimens were tested for samples prepared under same condition. The temperature dependence of electrical resistivity of epoxy/GNP composites was measured from 25 to 150°C at the heating rate of 3°C/min.

## RESULTS AND DISCUSSION

Figure 1 shows the morphologies of EG and GNPs. It can be observed that EG shows a loose and porous worm-like shape consisting of numerous parallel graphite platelets [Fig. 1(a)]. The loosely connected graphite nanosheets could be separated into GNPs with thickness of 30–50 nm and diameter of 3–10  $\mu\text{m}$  [Fig. 1(b)] by ultrasonication process.

Figure 2 shows the variation of conductivity as a function of GNP volume fraction. The introduction of GNPs significantly improves the conductivity of epoxy resin, and the percolation threshold of epoxy/GNP is  $\sim 0.5 \text{ vol } \%$  (1 wt %). This value is close to the percolation threshold of unsaturated polyester resin/graphite nanosheet (0.64 vol %)<sup>16</sup> but lower



**Figure 1** SEM micrographs of EG (a) and GNPs (b).

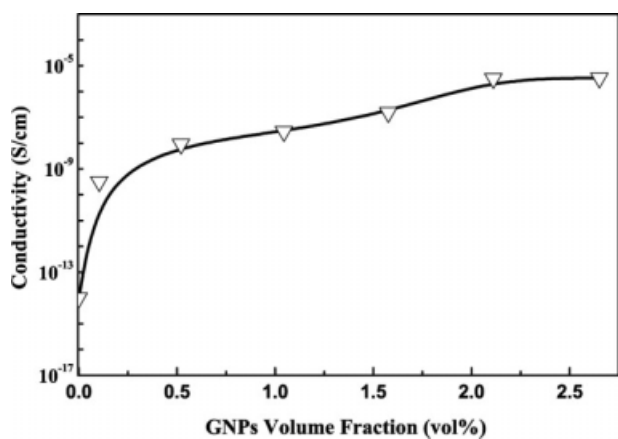


Figure 2 The electrical conductivity of epoxy/GNP composites as a function of GNP volume fraction.

than that of epoxy/expanded graphite nanosheet (3 wt %).<sup>17</sup>

Figure 3 shows SEM images of the fracture morphology of epoxy/GNP composites with different GNP content. It can be observed that GNPs are well distributed in the epoxy matrix and rarely touch, with a GNP content of 0.1 vol % [Fig. 3(a)]. With the increase of GNP content, the distance between GNPs decreases, and some GNPs even touch each other to form conductive networks in the matrix [Fig. 3(b,c)]. When GNP content is 2.5 vol %, GNPs are homogeneously impregnated and touch each others to form a perfect conductive network in the epoxy matrix [Fig. 3(d)].

Figure 4 shows the temperature dependence of electrical resistivities of epoxy/GNP composites

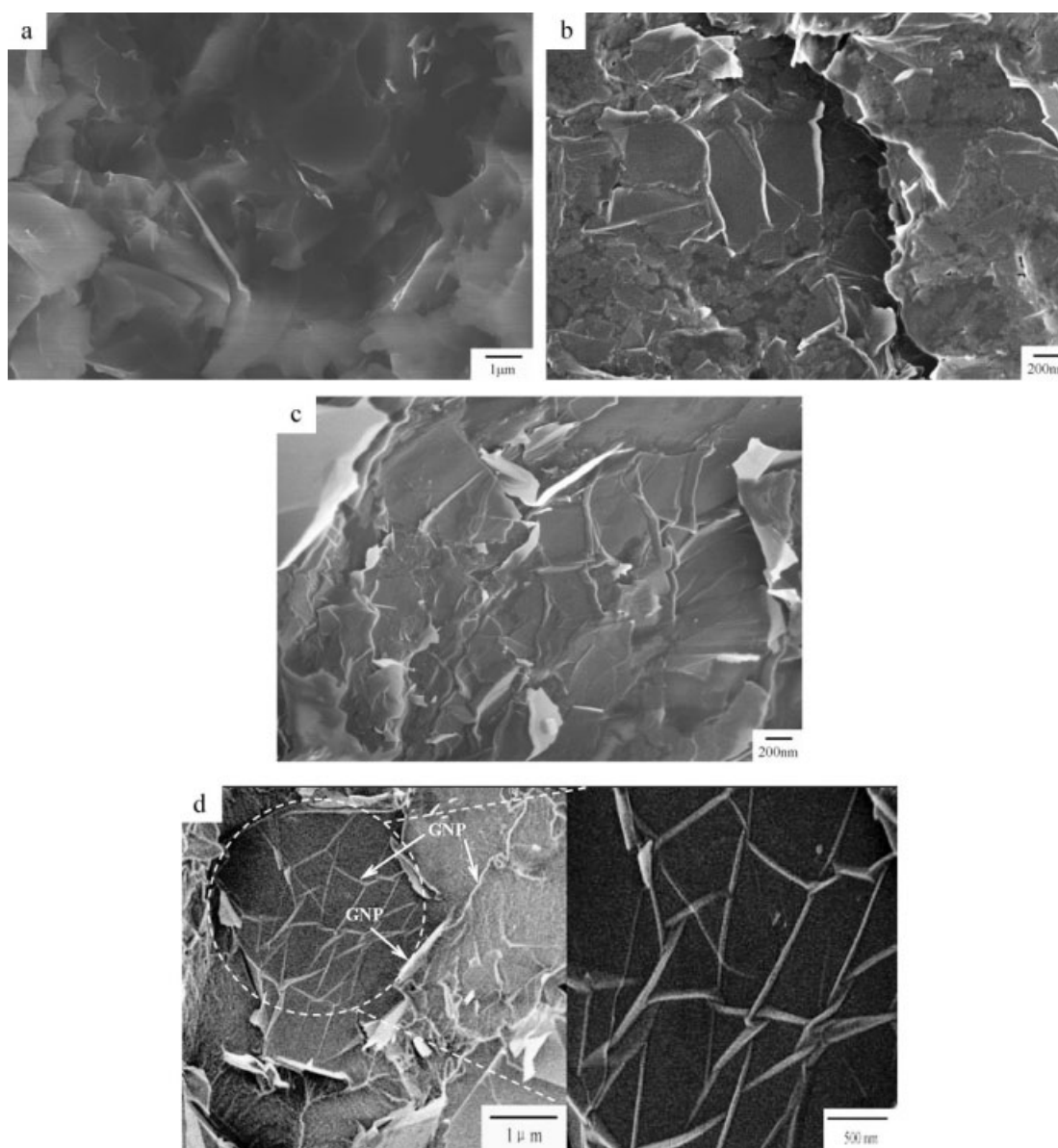
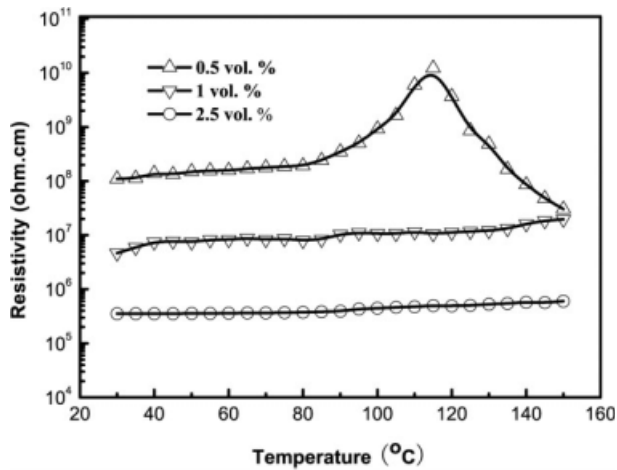


Figure 3 SEM micrographs of fracture surfaces of (a) 0.1, (b) 0.5, (c) 1, and (d) 2.5 vol % GNP/epoxy resin.

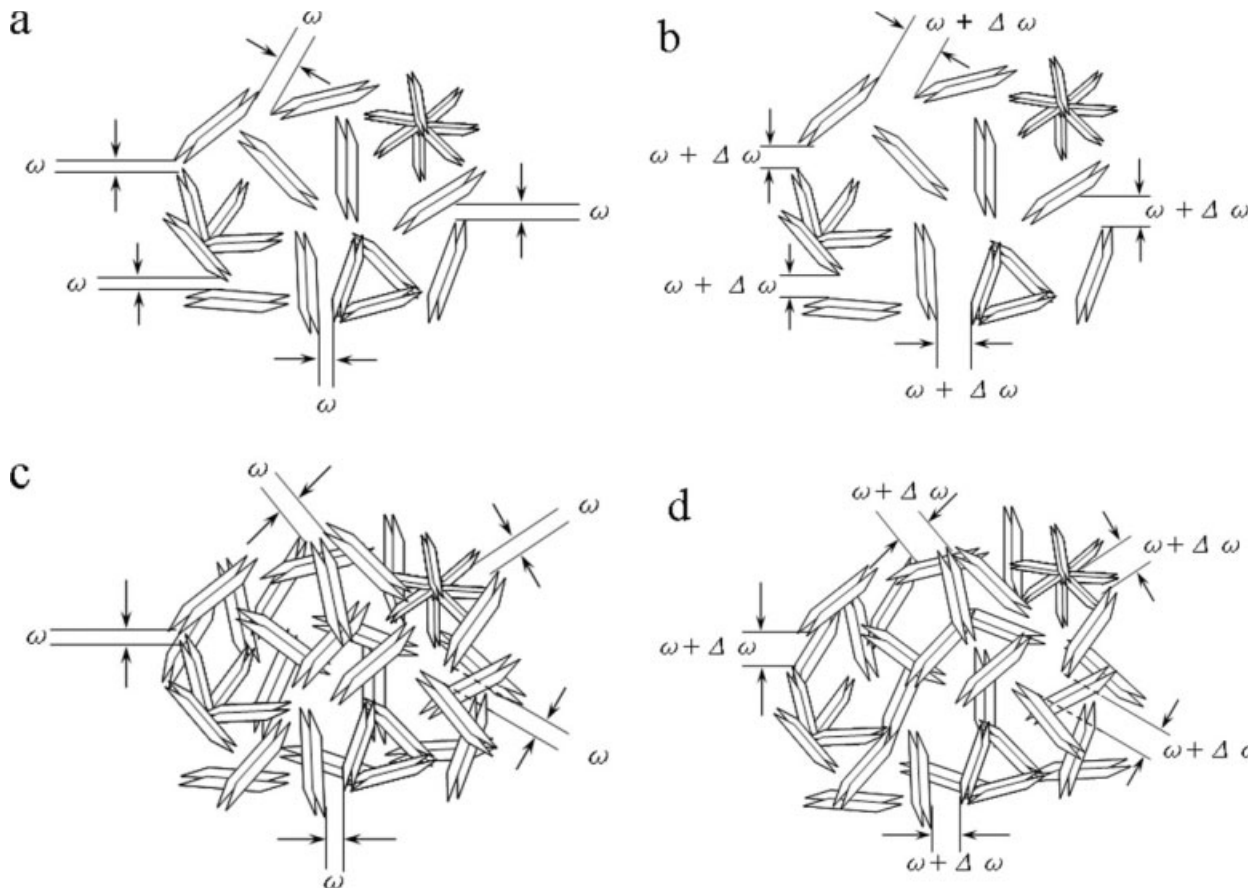


**Figure 4** The temperature dependence of epoxy/GNP composites on the electrical resistivity as a function of GNP content.

with different GNP contents. The PTC effect is well explained by the increase of interparticle distance and the decrease of the number of conductive paths. The NTC effect is mainly induced by the reagglomeration of the conductive particles (floculation),

leading to the formation of more conductive networks during heating. For the composite with 0.5 vol % GNP, the resistivity of composite increased slowly at the beginning of heating process, and then increased remarkably when temperature was greater than 80°C, displaying maximum  $\rho$  value at 117°C (i.e., PTC effect). Above that, further increase of temperature induces the decrease of resistivity (NTC effect). The reasons for this may be that the low adhesion and elastic modules of the matrix result from the migration of the GNP particles previously compressed in the original amorphous area into newly developed amorphous areas, which causes reagglomeration of the GNP particles to form further conductive networks with an increase in temperature. However, for composites with 1 and 2.5 vol % GNP, the resistivities of both composites hardly changed with an increase in temperature. It can be observed that the variation of resistivity with temperature is strongly dependent on the GNP content.

The reasons can be explained as follows: for most carbon black-filled polymer composite, both PTC and NTC effects can be observed in a wide range at and above the percolation.<sup>18–20</sup> Because carbon black



**Figure 5** Schematic illustrations for intersheet separation change for a low loading of GNPs in the matrix before (a) and after applied heat (b), and high loading of GNPs in the matrix before (c) and after applied heat (d).

particles are of spherical structure and point contact in the polymer matrix, the conductive network formed by carbon blacks is easy to break up as the result of the different volume expansion between conductive fillers and the matrix during heating. Therefore, PTC and NTC effect still occur for carbon black-filled polymer composites when carbon black loading is much greater than percolation threshold. Unlike carbon black, GNPs have unique lamellar structure with a high aspect ratio. Hence not only the GNP filled polymer has low percolation, but also the fillers plane contact with each other in the matrix [Fig. 3(d)]. When the GNP loading is at or lower than the percolation, the GNPs are not fully contact with each other [Fig. 5(a)], the conductivity of the composite is determined by hopping or tunneling mechanism of charged particles (i.e. electrons) present in the system. With increasing temperature, the intersheet average distance ( $\omega$ ) increases as the result of the difference in the thermal expansion of epoxy resin and conductive fillers [Fig. 5(b)], and at  $T_g$  of the composite (82°C for 0.5 vol % epoxy/GNP composite determined by DSC), intersheet distance considerably increases due to the sharp expansion of the matrix. Hence, the probability of tunneling decreases due to the scattering of carriers in the composite between the fillers, resulting in a sharp increase of resistivity in GNP filled composites (PTC effect). Besides, the formation of some new conductive network from the rearrangement of GNPs simultaneously occurs at elevated temperatures.<sup>21,22</sup> At high temperature (>120°C), this phenomena is predominant and results in the NTC effect.

At high loading of GNPs (above the percolation threshold), more GNPs touch each other, and the conductive network tends to be formed by plane contact between GNPs [Fig. 5(c)]. Thus, the conductivity of the composite is mainly determined by the constriction of electron flow due to sheet-sheet contact resistance. Unlike the point contact of carbon blacks, the conductive network formed by plane contact between GNPs will be hardly affected by displacement ( $\Delta\omega$ ) of the composite with the increase of temperature [Fig. 5(d)] and, consequently, the resistivity of the composite hardly changes with the increase of the temperature.

## CONCLUSIONS

In this study, epoxy/GNP conductive composites were successfully prepared via liquid mixing

method, which showed a homogeneous dispersion of the fillers in the matrix. The conductive composites have a percolation threshold of  $\sim 0.5$  vol %. The composite loading of 0.5 vol % GNPs exhibits strong PTC effect and NTC effect. When GNP loading is higher than percolation threshold, GNPs could form overlapping conductive networks in the matrix, and volume expansion of the matrix with increase of temperature has little effect on the conductivity of composite due to its two-dimensional structure and high aspect ratio.

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