

# Positive Temperature Coefficient Effect and Interaction Based on Low-Density Polyethylene/Graphite Powder Composites

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**ABSTRACT:** In this article, the positive temperature coefficient (PTC) and interaction based on low-density polyethylene (LDPE) filled with the loading of graphite (G) powder have been investigated. The dependence of the room temperature resistivity on filler content showed the significant decrease. The PTC behavior enhanced with increasing graphite content but this was not always the case. The maximum PTC effect was observed in LDPE/G composites (G, 45 wt %) with the relatively low room temperature resistivity. The thermal behavior was measured by differential

scanning calorimetry (DSC). The structure characteristic for LDPE/G composites was examined by X-ray diffraction (XRD), field-emission scanning electron microscopy (SEM), and stress-strain test. The fact was revealed that the slight interaction between LDPE matrix and graphite may lead to change the thermal-electric properties of the PTC materials. © 2011 Wiley Periodicals, Inc. *J Appl Polym Sci* 123: 2338–2343, 2012

**Key words:** polyethylene (PE); graphite; composites; X-ray; PTC

## INTRODUCTION

Since Frydman reported the phenomenon of positive temperature coefficient (PTC) effect of resistance in low density polyethylene (LDPE)-carbon black (CB) composites,<sup>1</sup> the doped conductive composites which consisted of insulating semicrystalline polymer matrix and conductive filler have attracted considerable attention. Now, they have been widely applied in thermal-electric devices such as temperature sensors, thermistors, self-regulating heaters, over temperature protection devices, etc.,<sup>2,3</sup> owing to their unique conductive properties. These composites exhibited a specific electric feature and a sharp transition from the conductive to insulating state near the melting temperature of polymer matrix due to the influence of the loading of conductive filler and the change of the structure of the composites. At present, the explanation for PTC effect of the composites mainly existed three electric conductive theories, concluding thermal volume expansion,<sup>4</sup> the electron tunnelling,<sup>5</sup> and the crystalline phase change.<sup>6</sup> However, these mechanisms remained controversial.

The use of metal, carbon black, carbon fibers, and graphite (G), etc., as the conductive filler in the composites was largely reported in the literatures.<sup>7–13</sup> Among them, polymer/G composites prepared by the traditional or other new methods were investigated extensively in recent years because they possessed good electric conductivity, high thermal conductivity, abundant nature resources, and inexpensive cost.<sup>13–18</sup> For example, Panwar et al.<sup>16</sup> reported that abnormal percolation behavior in LDPE/G occurred and sharp PTC effect near the melting temperature of LDPE was well explained by the random resistor network of Miller and Abrahams model. Wu et al.<sup>19</sup> presented that the newly composites poly(acrylic acid)/graphite oxide (PAA/GO)*n* film was prepared by layer-by-layer self-assembly and a typical PTC effect above the PAA melting temperature was investigated.

In summary, although great achievements on the improvement of various performances of polymer/G composites have been received, the exact relationship between the PTC effect and microstructure of the composites was still essential to well understand. So the conductive composites with LDPE as the matrix material and graphite powder as the conductive filler were prepared by conventional melt blending. The dependence of electric resistivity on the temperature and filler content for LDPE/G composites was investigated. The thermal properties of the composites were performed by differential scan calorimetry (DSC). Microstructure characteristic of the composites

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was measured by field-emission scan electron microscope (SEM), X-ray diffraction (XRD), and stress-strain test.

## EXPERIMENTAL SECTIONS

### Materials and preparation

#### Materials

LDPE as the matrix material (melt index of 1.9 g/10 min and a density of 0.9227 g/cm<sup>3</sup>) was obtained from Lanzhou Petrochemical Company of Chinese petrochemical, China. The graphite powder as the conductive filler (its grain degree ( $\leq 30 \mu\text{m}$ )  $\geq 95\%$ , pure degree  $\geq 99.85\%$ ) was purchased from Shanghai Huayi (group) Company, China.

#### Preparation of the sample

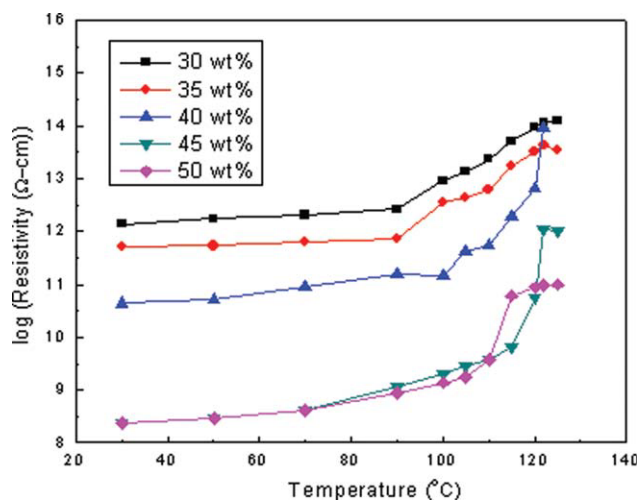
The LDPE/G composites were prepared by conventional melt blending in a rheometer (RM-200A, Ha Erbin Kesite Technology Company, China) at 130°C with a rotating speed of 30 rpm for 30 min, respectively. Subsequently, the samples were removed and compression molded at about 120°C under a pressure of 50 kg/cm<sup>2</sup>, then holding at 120°C for 30 min and cooled down to the room temperature, respectively. Whereafter, the samples were compression molded sheets with a diameter of 30 mm and a thickness of about 1.5 mm (the thickness of sheet mold) for later electric testing. The samples were rested over-night to release residual thermal stress based on previous reports in the literature<sup>17,18</sup> before the subsequent measurement.

#### Measurements of the sample

The electrical properties of LDPE/G composites were measured at various temperatures in the chamber. The volume electrical resistivity was tested using a digital multimeter when the resistance was lower than  $2 \times 10^6 \Omega$  and high-resistance meter (Model ZC-36) was used when the resistance exceeded  $2 \times 10^6 \Omega$ , respectively. To check the reproducibility of the PTC profiles, the electric resistivity of LDPE/G containing 45 wt % filler as an example was measured for three heating and cooling cycles. All numerical values of resistivity ( $\rho$ ) mentioned in this work were calculated according to the following equation:

$$\rho_v = R_v \frac{A}{t}$$

where  $R_v$  was resistance,  $A$  was the area (21.24 cm<sup>2</sup>), and  $t$  was the thickness of sample.



**Figure 1** Resistivity-temperature behaviors of the composites LDPE with various contents of the graphite. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

The drawing strength of the samples was tested by using a microcomputer numerical control electronic universal testing machines (CMT6503) at a speed of 50 mm/min.

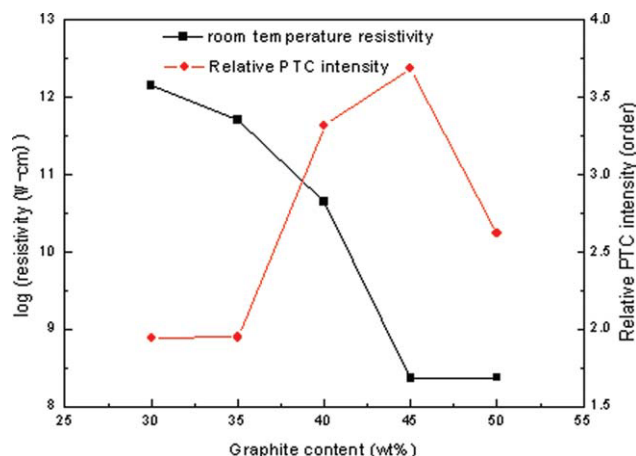
The thermal behavior of the composites was performed by differential scan calorimetry (DSC, Model 200F3-Maia made in Germany). The samples (about 10 mg) were heated and cooled between ambient temperature and 140°C for two cycles at a rate of 10°C/min under a nitrogen atmosphere.

X-ray diffraction was carried out using XD-3 powder diffractometer manufactured by Beijing Purkinje General Instrument Co., (China). By this step, the samples prepared at the same condition were scanned in 2-theta ranging from 10 to 50° at a scan speed of 1°/min.

Investigation of the morphology was carried out by using field-emission scan electron microscope (SEM, Hitachi S-4800). The samples were fractured in liquid nitrogen, and then, the freeze fractured surfaces were vacuum-coated with a thin gold layer before the electron microscope scan.

## RESULTS AND DISCUSSION

Figure 1 showed resistivity-temperature behaviors of the LDPE/G composites with various contents of the graphite loading level of 30, 35, 40, 45, and 50 wt %. It was observed that the PTC intensity had a strong dependence on the graphite content. Relative peak resistivity gradually increased with the conducting filler content comparing with room temperature resistivity, until the doped content of 45%. They were detected at about 100°C for LDPE/G composites, which was slightly lower than their melting temperature by DSC measurement.



**Figure 2** The relationship between room temperature resistivity and relative PTC intensity for composites with different contents of the graphite. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

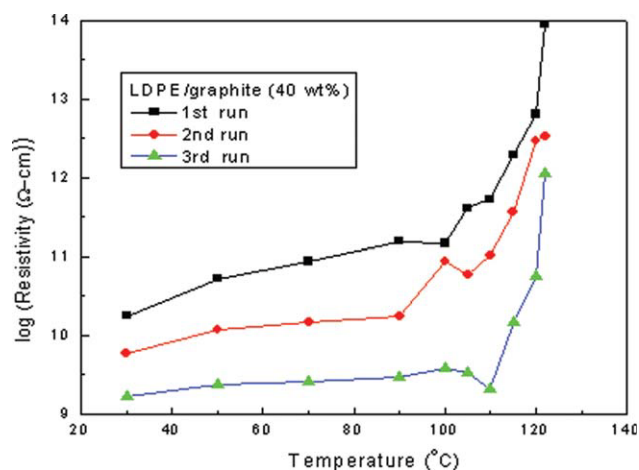
Figure 2 showed the relationship between the room temperature resistivity and relative PTC intensity for LDPE/G as a function of graphite content. As shown in Figure 2, a sharp drop in the room temperature resistivity of LDPE/G was observed with increasing graphite content, which was attributed to the difference in numbers of formation of a conducting network. Furthermore, the room temperature resistivity no longer remarkably dropped with the further increase of graphite content, until it exceeded 45 wt %. This suggested that the numbers of the conducting network hardly increased remarkably when the filler content was over 45 wt %. Simultaneously, the relative peak resistivity for LDPE/G increased rapidly with increasing the graphite content. Moreover, among the five different levels of graphite content, the composites with 45 wt % graphite showed the highest PTC intensity (over 3.5 orders of magnitude comparing with the room temperature resistivity), indicating that the optimal graphite content for the doped composites was present and an excess of graphite did not interfere with the network structure of conducting materials. Therefore, a balance between the PTC intensity and the room temperature resistivity could be achieved by improving the optimum content of the conductive filler in LDPE/G composites, which would affect the practical application of the PTC materials.

To investigate the reproducibility of the PTC properties of LDPE/G composites, the thermal-electric tests of LDPE/G composites containing the 40 wt % filler as a representative example were carried out. Figure 3 showed the resistivity as a function of temperature in LDPE/G composites containing the 40 wt % filler for three heating and cooling cycles. Unfortunately, the PTC of LDPE/G composites exhibited very poor reproducibility. The first PTC

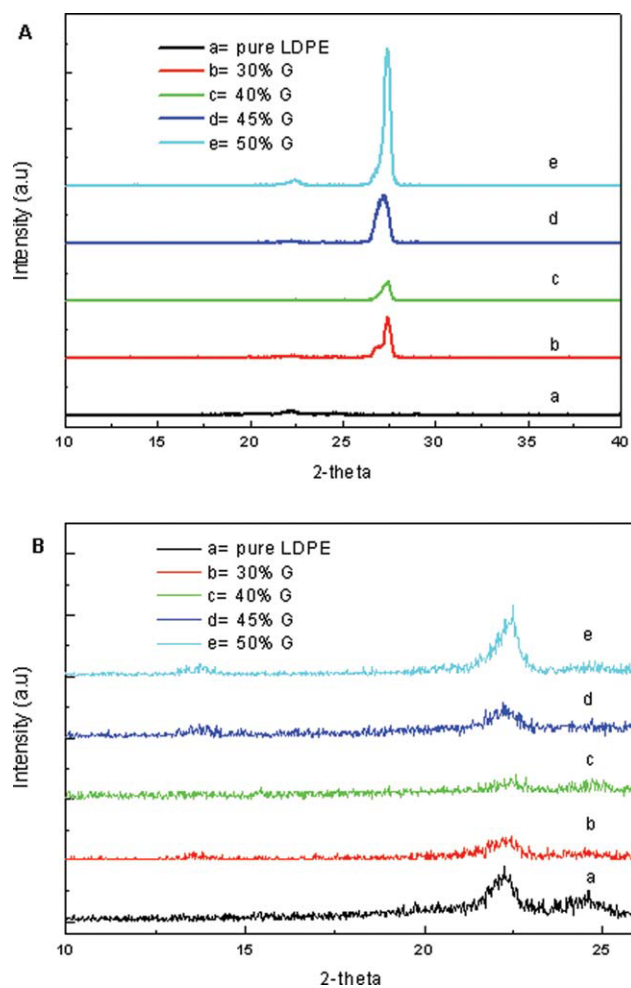
curve was obviously different from the subsequent curves, and the room temperature resistivity and the PTC intensity decreased in turn in the additional cycles. This result was generally believed that when the composites were hot-mixed and pressed, the nonuniform distribution and the congregation of the conducting filler came into being, and the further intermixing enhanced the contact surface area between the graphite and LDPE matrix during the repeatable heat cycles, resulting in the increase of the conducting network.

The disadvantages of poor repeatability can be improved by many methods (such as crosslinking or other additives) in later study.

To detect the relationship of electric conducting properties and microstructures of LDPE/G, the microstructures of LDPE/G were investigated. First, XRD measurements were carried out using XD-3 powder diffractometer. Figure 4(A,B) presented the XRD pattern of the LDPE/G composites containing various contents of the filler. All composites except for pure LDPE showed three characteristic peaks for the crystalline phase of LDPE/G composite, which scattering angles  $2\theta$  were at about  $22.25^\circ$ ,  $24.6^\circ$ , and  $27.4^\circ$ , respectively. According to XRD peaks of pure LDPE, a widely diffused peak at  $22.25^\circ$  and another less intense peak at  $24.6^\circ$  in Figure 4(B) were attributed to the crystalline phase of LDPE matrix in the composites. The intense peak at  $27.4^\circ$  in Figure 4(A) was confirmed to be the crystalline phase of graphite based on the reports in the literature.<sup>19,20</sup> Meanwhile, a surprising phenomenon was found from XRD curves in Figure 4(B). The curve peak intensities decreased progressively with increasing the graphite content, until the weakest peak was observed when the content of graphite in the composites was 40 wt %. Subsequently, the curve peaks



**Figure 3** The resistivity-temperature curves of 40 wt % Graphite filled LDPE for heating cycles. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



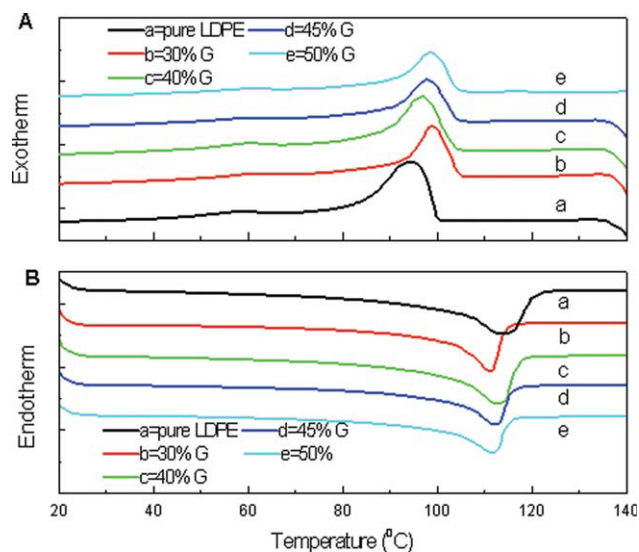
**Figure 4** XRD diffraction spectra of the LDPE/G composites: (a) pure LDPE, (b) 30%, (c) 40%, (d) 45%, and (e) 50%. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

became higher gradually with further increasing the graphite concentrations. Those results indicated that the degree of crystallinity in LDPE matrix for LDPE/G composites gradually became smaller with the addition of the graphite until the filler content reached 40 wt %, and then the crystallization degree increased gradually again. Because the low doped content of graphite affected on the construction of the conducting network and the crystallinity of LDPE matrix, and high doped content may mainly affect on the crystalline degree of LDPE matrix. On the other hand, the XRD pattern of the graphite filler also displayed the similar results [Fig. 4(A)]. Hence, this slight interaction between LDPE matrix and graphite may lead to a significant change of thermo-electric properties of the composites.

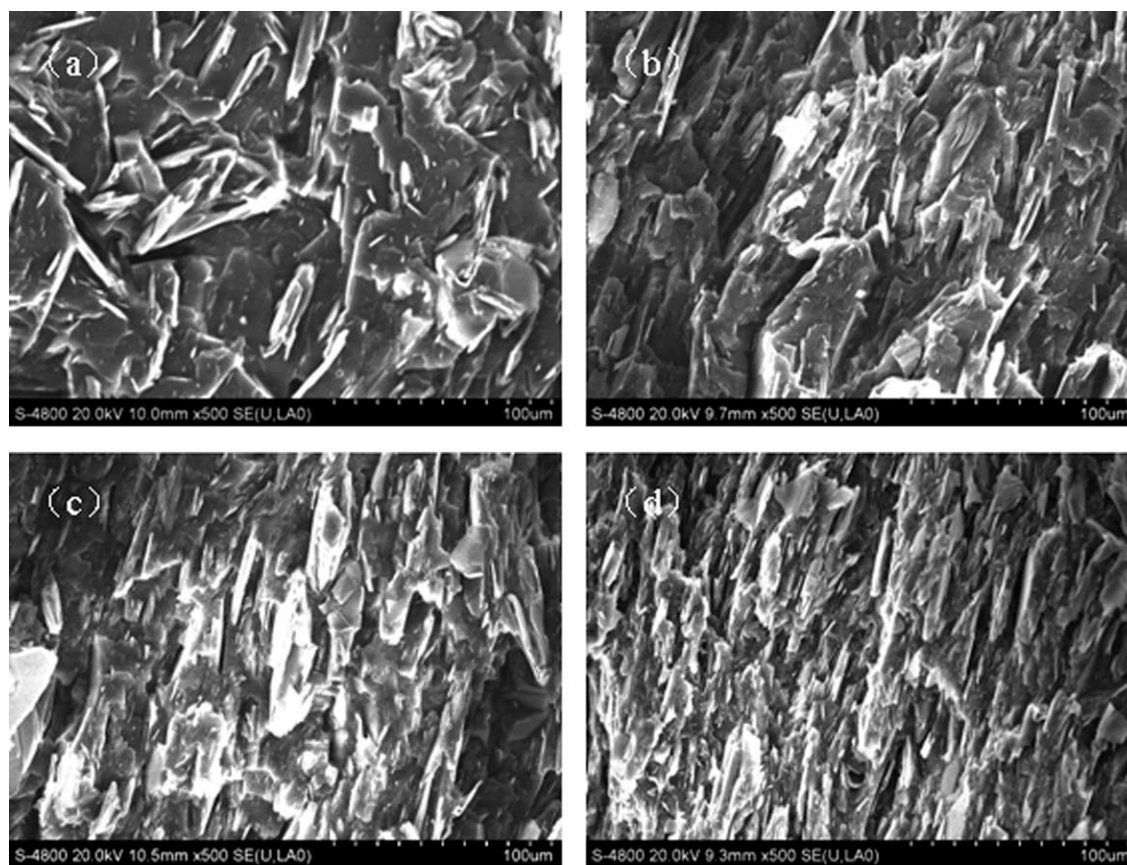
To make the further understanding for the influence of the filler content on the PTC effect of the composites, the melting behavior and crystallization properties of pure LDPE and LDPE/G composites were characterized by DSC measurement. The DSC

curves of pure LDPE and all composites for heating and cooling cycles were shown in Figure 5 (A,B), respectively. It was found that the DSC endothermic curves of the composites were not identical with the corresponding exothermic curves, which suggested that the composites suffered different thermal behavior during the rapid heating and cooling processes. Meanwhile, it was noticed that the DSC curves of the composites were slightly different from those of pure LDPE. That is, the intrinsic thermal and crystalline properties of LDPE matrix were slightly affected by the introduction of graphite. The melting peak of the pure LDPE was observed at about 114.5°C. And then, the obvious endothermic peak of the composites estimated from DSC curves was between 111°C and 113.5°C. Especially, the highest melting temperature and the lowest crystal temperature for the composites containing 40 wt % graphites were measured at about 113.2°C and 96.8°C, respectively. This result was in agreement with that of the XRD measurement. It further suggested that a sudden change of thermal-electric properties occurred when graphite content in the composites reached 40 wt %.

Figure 6 displayed SEM images of the freeze fracture cross section of a series of LDPE/G composites with different contents of graphite, respectively. As shown in Figure 6, the effect of conductive filler on the structures of the composites was well observed in the fracture section. Figure 6(a) showed the distinct interface of LDPE/G composite with the content of graphite equal to 30 wt%, in which the conductive fillers were dispersed randomly and LDPE matrix displayed the layer or egg-rolled structures. Both the interface of the composites and distribution



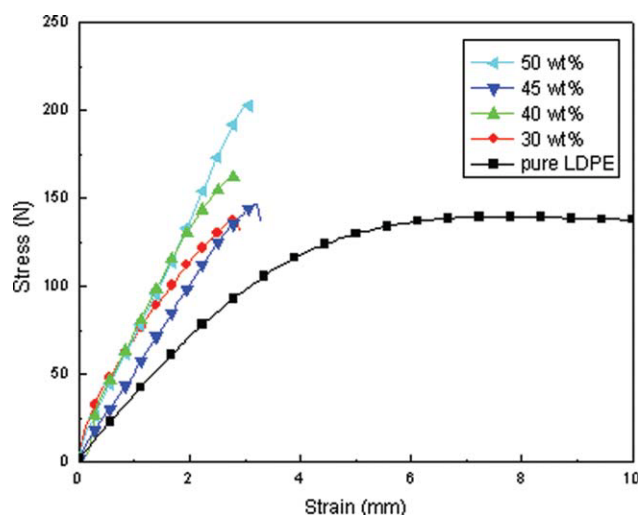
**Figure 5** Endothermic and exothermic DSC curves of the LDPE/G composites: (a) pure LDPE, (b) 30%, (c) 40%, (d) 45%, and (e) 50%. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 6** SEM images of a series of the LDPE/G composites: (a) 30%, (b) 40%, (c) 45%, and (d) 50%.

of graphite in LDPE matrix began to become indistinct when the filler content reached 40 wt %. Further, increasing the content of filler, this phenomenon became worse and interface became more illegible. It may be ascribed to the reason that the influence of filler may lead to a slight increase in the

crystalline phase of LDPE matrix. Namely, the composites showed the better brittleness with the increase of the filler. It was proved by the mechanics experiment below. As shown in Figure 7, stress-strain curves of pure LDPE and LDPE/G composites were measured using the numerical-control electronic universal testing machines. All curves except that of pure LDPE revealed the brittle fracture, and this extent was more with increasing the content of graphite. It was suggested again that the graphite as the conductive filler can influence on the crystalline phase of the polymer matrix. Finally, these results further proved that the subtle change in the microstructure of polymer matrix may lead to the significant effect on the thermal-electric properties of PTC material.



**Figure 7** Stress-strain curves of the composites filled with different graphite contents. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## CONCLUSIONS

The LDPE/G composites were prepared by the conventional melt-blending. The thermal-electric properties and micromorphology of the composites were investigated by resistivity measurement, DSC, XRD, SEM, and stress-strain test, respectively. The typical PTC effect occurred near the melting temperature of LDPE, and the dependence of electric resistivity on the temperature and filler content for LDPE/G

composites was detected. As a result, the balance between lower room temperature resistivity and relatively high PTC resistivity were achieved in the composites with 45 wt % graphite powders. The thermal properties were studied by DSC measurement, and the evidence for the influence of graphite on PTC effect and the microstructure characteristic of LDPE/G composites was offered by XRD curves, SEM images, and stress-strain test. In conclusion, the results indicated that the slight interaction between LDPE matrix and graphite, or the subtle change in the microstructure of polymer matrix may lead to a significant change of thermo-electric properties of the composites.

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