

PTC effect of polyethylene/foliated graphite nanocomposites

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It is well known that PTC materials have various technological applications, such as current or temperature sensors, as well as detection and control of parameters related to temperature. The PTC effect, which is characterized by a sharp increase in electrical resistivity at a transition temperature, has been widely investigated in conducting polymer composite materials [1–5] and ceramic thermistors [6–8]. Several models have been proposed to explore the mechanisms of the PTC effect [9–13] and there is a general agreement that the expansion of the matrix at the transition temperature is the origin of the PTC effect [14].

Although several investigations about the PTC effect in conductive composites have been carried out, almost no study on the PTC effect in polymer/graphite nanocomposite has been reported. Exploration of the PTC effect in HDPE/graphite nanocomposite is favorable to understand the mechanisms of the PTC effect and to exploit the new-style PTC nano-materials. Generally, for conventional conductive fillers such as metallic powders and conventional graphite, low conductive filler concentration (near the percolation thresholds) composites show a high room resistivity and a high PTC intensity, while high conductive filler concentration composites exhibit a low room resistivity and a low PTC intensity [4]. It is still difficult to fabricate a PTC material that exhibits not only low filler loading but also high PTC intensity. Recently, we have successfully fabricated HDPE/foiled graphite (FG) nanocomposites and found such nanocomposites have low FG loading [15] and high PTC intensity. FG is prepared by the exfoliation of expanded graphite [15]. The resulting foiled graphite nanosheets possess high aspect ratio with diameter ranging from 5 to 20 μm and average thickness of 40 nm (see Fig. 1). Owing to this special structure FG is very favorable to form conducting paths in the polymer matrix. As a result, low graphite concentration is required to satisfy the critical percolation transition [15–17]. Due to the reduction of the filler loading, the conductive networks in the polymer matrix are much easier to disconnect, thus leading to a strong PTC effect. In addition, lower loading will result in less materials redundancy and detrimental mechanical properties [18].

High-density polyethylene (HDPE, Polyolefins Company, Japan) with a melting point of 138 °C was used as the polymer matrix. Foiled graphite nanosheets with an aspect ratio of about 240 were prepared by an ultrasonication powdering technique

as reported in our previous papers [15, 19]. Commercially available natural graphite powders (7500 mesh and 2000 mesh) were used for comparison. The conductive fillers were mixed with HDPE using a twin-roll mill at 140 °C for 15 min.

The resistivity as a function of temperature was measured using a system, comprising a digital multimeter (UT70A) and a programmable oven. The heating rate was 1 °C/min. Prior to the electrical measurement, conductive paints were coated on the samples surfaces to eliminate contact resistance.

The morphology of FG observed by a scanning electron microscope (SEM, Hitachi S-520) is shown in Fig. 1.

The resistivities for HDPE/FG nanocomposites and HDPE/conventional graphite composites as a function of filler content are shown in Fig. 2. From Fig. 2 it is obvious that the percolation threshold value of HDPE/FG nanocomposites (15 wt%) is much lower than HDPE/7500 mesh graphite composites (35 wt%) and HDPE/2000 mesh graphite composites (40 wt%). This result is related to the structure and aspect ratios of conductive fillers. Foiled graphite nanosheets possess high aspect ratios and thus gain great advantages over spherical or elliptical fillers in forming conducting networks in polymer matrices [20].

As a result, less amounts of FG are required to achieve the percolative transition.

The ratio of the peak resistivity (ρ_{max}) to the room temperature resistivity (ρ_{RT}) is defined as the PTC intensity ($I_{\text{PTC}} = \rho_{\text{max}}/\rho_{\text{RT}}$). Fig. 3 shows that the HDPE/FG nanocomposites exhibit higher PTC intensity than the HDPE/2000 mesh graphite composites in the vicinity of the respective percolation thresholds.

The temperature-dependent expansion of the polymer matrix plays a key role in the PTC phenomenon. The disturbance in the continuity of the conducting paths is the intrinsic mechanism behind the changes in the resistivity of the composites. Due to the low FG loading, the conducting networks are easy to be disconnected and thus the HDPE/FG nanocomposites show sharp electrical response as a function of temperature. However, as depicted in the Fig. 3, after the PTC transition, resistivity decreases with increasing temperature, which is generally defined as the negative temperature coefficient (NTC) effect. The appearance of the NTC effect is mainly due to the formation of additional conducting pathways induced by the relaxation of polymer matrix and the rearrangement of filler particles [21].

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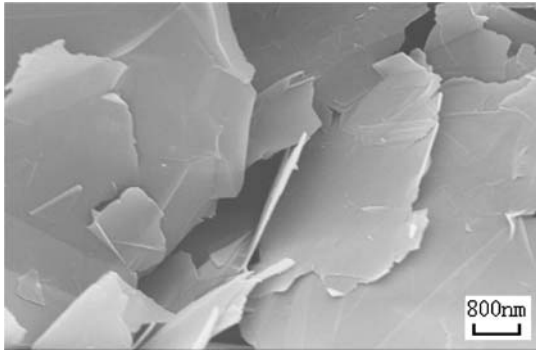


Figure 1 SEM micrograph of graphite nanosheets obtained by ultrasonic powdering technique.

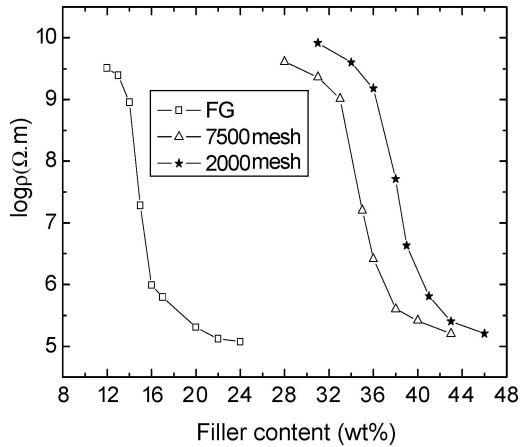


Figure 2 Different percolative behaviors of HDPE/FG and HDPE/conventional graphite as a function of the graphite weight fraction.

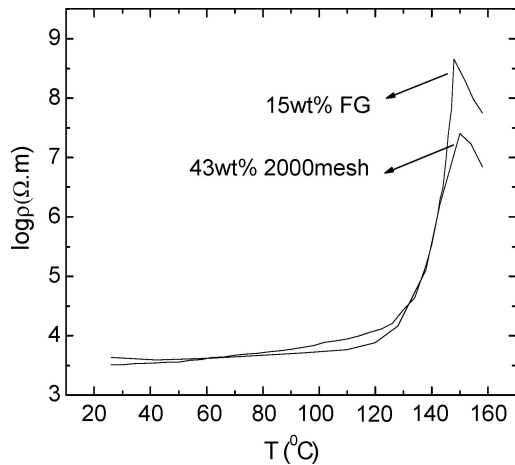


Figure 3 The resistivities of HDPE/FG nanocomposites and HDPE/2000 mesh composites as a function of temperature.

The repeat ability of the PTC/NTC effect of the HDPE/FG composite is depicted in the Fig. 4. Variations are observed for the PTC effect under succeeding temperature treatment. The phenomenon might be attributed to the change of crystallization of HDPE during treatment.

Fig. 5 presents the PTC effect of the HDPE/FG nanocomposites of various filler concentration. It is obvious that filler content in nanocomposites plays an important role in the PTC effect. From room temperature resistivity to the peak resistivity, the resistivity transi-

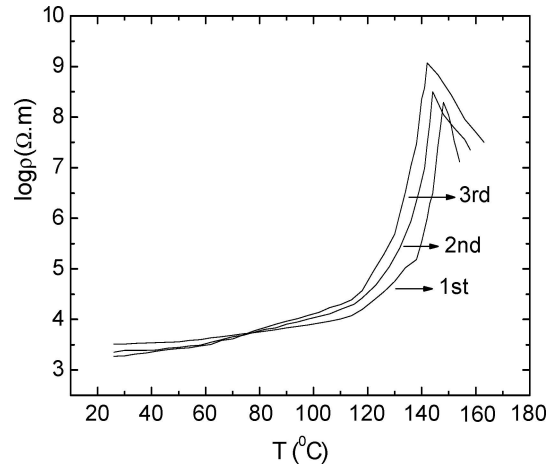


Figure 4 The repeated properties of the PTC/NTC effect of HDPE/FG nanocomposite.

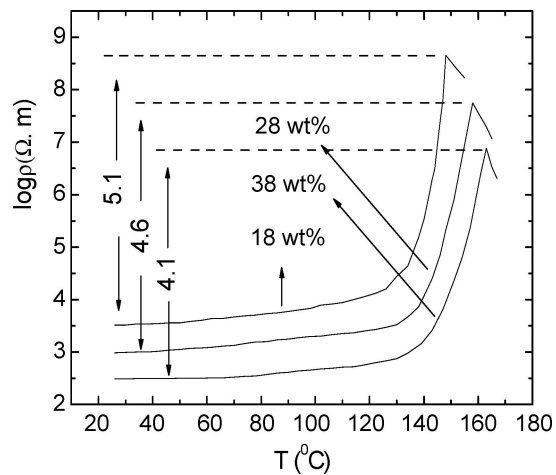


Figure 5 The PTC effects of the HDPE/FG nanocomposites at various filler contents.

tions of 18, 28 and 38 wt% HDPE/FG nanocomposites are 5.6, 4.6 and 4.1 orders of magnitude, respectively. It is noted that the transitions are sharper for the composites with lower filler contents and the PTC intensity decreases with the increasing FG concentration. The main reason is that the numbers of conducting paths decrease with the decreasing FG concentration. Therefore, the change of resistivity is more obvious with low filler contents as a function of temperature.

In summary, the PTC effect of HDPE/FG nanocomposites was investigated. The foliated graphite nanosheets possess a special structure and are favorable to form conducting networks in the polymer matrix, thus resulting in low graphite loading in the nanocomposites.

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