Modification of electrical properties for carbon black-filled high-density polyethylene through grafting polymer matrix with malefic anhydride

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Polymeric composites filled with carbon black (CB) exhibits a sharp resistivity increase with a rise in temperature in the polymer melting region (PTC, positive temperature coefficient), followed by a rapid resistivity decrease when temperature is up to the polymer matrix melt point (NTC, negative temperature coefficient). Recently, the materials that have PTC effect of resistivity have been widely used as self-controlled heaters, sensors, and micro-switches [1–4]. However, owing to the influence of the structural relaxation of the matrix and the dispersion of filler particles in the composites, the PTC materials have lots of drawbacks in application, especially the poor electrical reproducibility and NTC of resistivity. Generally, modifications of the polymer matrix, such as grafting or crosslinking, have been thought to be beneficial to improve the electrical reproducibility and eliminate the NTC phenomenon [5, 6]. It is well-known that the modification of polyethylene usually can be conducted by melt blending with other polymers or fillers, crosslinking, or grafting [4–8]. Among them, grafting, especially the melt grafting, has been extensively applied and studied [9, 10]. In this article, we introduce melt grafting modification into the investigation of electrical properties of CB filled high-density polyethylene (HDPE) system, and focused on the effect of grafting of HDPE with Malefic Anhydride (MAH) on the temperature-dependent resistivity of the PTC materials in order to improve the electrical reproducibility and to partially eliminate the NTC phenomenon of PTC materials.

HDPE was from Yangtze Petrochemistry Industry Company (China), the melt index = 9 g/10 min and density = 954 kg/m^3. CB (N550) purchased from Qingdao Degusa Chemistry Ltd. Co. (China) was used as conductive filler (average diameter = 77 nm, cetyltrimethylammonium bromide (CTAB) adsorption surface area = 50×10^3 m^2/g, dibutyl phthalate (DBP) absorption value = 121×10^{-5} m^3/kg). Dicumyl peroxide (DCP) and MAH were used as initiator and chemistry graft monomer, respectively. HDPE, CB, MAH in weight proportion of 60/39/1 were mixed in a two-roller mill at 165 for 15 min, in which MAH grafted HDPE composite (MAH-*g*-HDPE) could be generated according to reference [9, 10]. Hot pressing at the same temperature under 15 MPa was followed to prepare a plate with a thickness of 1.5 mm. Copper nets were mounted onto the two opposite sides of the plate during the hot pressing. The samples were then isothermally treated at 160 for 3 h to diminish heat history and stress history. All the temperature-dependent resistivity of the composites was measured in the thickness direction of the samples by heating the sample at 2 °C/min and cooling with air.

Resistivity-temperature curves of CB/HDPE composites after 1, 4, and 7 heating cycles are shown in Fig. 1. It can be found that the composites exhibit a sharp PTC effect and an obvious NTC effect, and the room temperature resistivity is increased after several heating cycles. Moreover, after several heating cycles the PTC transition temperatures change in order of $T_7 > T_4 > T_1$, indicating the poor PTC reproducibility of the materials.

Resistivity-temperature curves of CB filled MAH-*g*-HDPE samples after 1, 4, and 7 heating cycles are shown in Fig. 2. It can be seen that the ρ increases abruptly at temperatures approaching the melting point, and for the grafted samples the PTC intensity I_{PTC}, defined as $\log(\rho_{\max}/\rho_0)$, increases about one order of magnitude, as compared with those of the ungrafted one. It is noted that with increase of temperature from room temperature to the PTC transition temperature, the values of ρ exceed $10^{8.7}$ Ω·cm and remain until the temperature reaches to 160. It is noted that we plotted a line in the case of $\rho \geq 10^{8.7}$ Ω·cm, because the ρ up to $10^{8.7}$ Ω·cm is beyond the measurement range of devices used here. The typical NTC effect following PTC behavior is practically eliminated for MAH-g-HDPE samples. Compared with Fig. 1, it is found that the room temperature resistivity almost unchanged and the shift of the curves is very small for different heating cycles, and the PTC transition temperature appears at almost the same after several cycles. All of these imply that the electrical reproducibility is greatly improved through grafting. MAH-g-HDPE has strong radical MAH groups or unpaired radicals. They may react with the "CB radicals" [11, 12] (functional groups, such as carboxylic, quinoic, phenolic, lactonic groups, on the surface of CB) or with each other, thus some of the polymer matrix becomes crosslinked. CB particles are strongly attached to the crosslinked HDPE networks during the proceeding. This strong attachment to the crosslinked networks is expected to reduce

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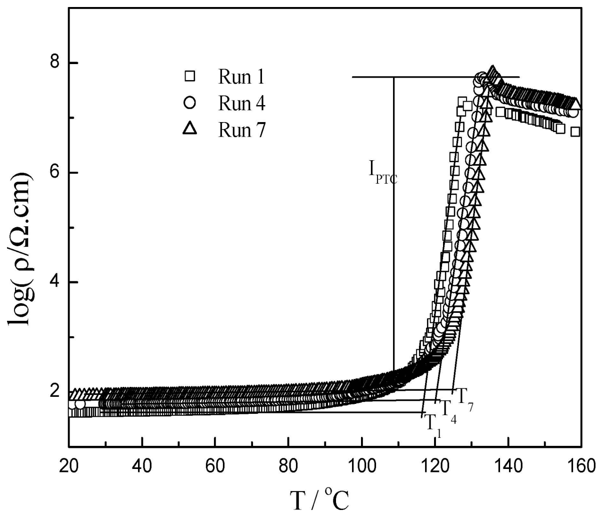

Figure 1 Resistivity ρ-temperature T curves of CB filled HDPE composites after different heating cycles.

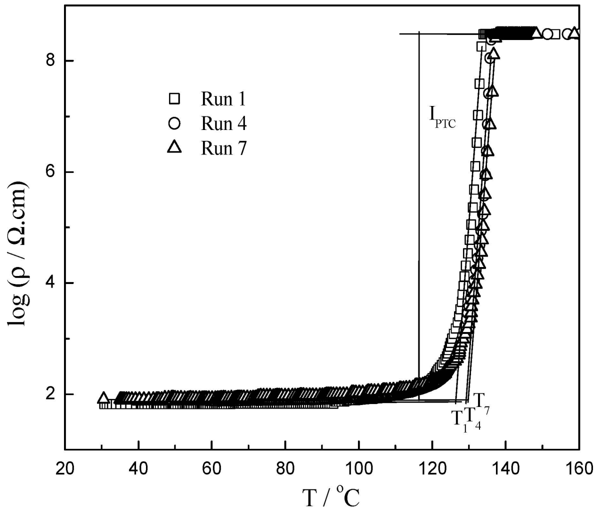

Figure 2 Resistivity-temperature characteristic curves of CB/MAH-*g*-HDPE composites after different heating cycles.

the freedom of movement of CB particles at high temperatures and weakens the CB redistribution during the movement and expansion of the polymer matrix at high temperature, and takes the particles back to the original positions while the sample is cooled. This improves the reproducibility and decreases or even eliminates the NTC effect.

Table I shows the influence of grafting on the resistivity-temperature coefficient $(\log \rho)/T$ and PTC intensity I_{PTC}. Combining Figs 1 and 2, it can be seen that I_{PTC} is remarkably increased for grafted composites. Compared with ungrafted composites, the $(\log \rho)/T$ increases more than 2 orders of magnitude for CB/MAH-*g*-HDPE composites, and almost keeps unchanged after several heating cycles.

TABLE I The effect of grafting on the resistivity-temperature coefficient and PTC intensity for grafted and ungrafted CB/HDPE composites

	Ungrafted			Grafted		
CB/HDPE samples	Run 1	Run 4	Run 7	Run 1	Run 4	Run 7
$(\log \rho)/T$	0.66	0.62	0.62	1.13	1.18	1.11
I_{PTC}	6.08	5.98	5.89	>7.0	>7.0	>7.0

In conclusion, MAH melt grafting on HDPE matrix is an efficient method for elimination of NTC effect and producing electrical reproducibility for HDPE filled with conductive particles, CB. Besides, good switching capability, together with good electrical properties (with sharp PTC effect and a reduced or eliminated NTC effect) can be obtained. It is believed that the reason for the above results is mainly due to the enhanced interaction between CB particles and the polymer matrix.

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