

Conductive behavior of composites composed of carbon black-filled ethylene-tetrafluoroethylene copolymer

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Over the past two decades, conductive polymer composites have been widely applied in the areas of electromagnetic/radio-frequency interference shielding, electrostatic discharge, conductive adhesives for die attachment in electronic packaging applications, and electroactive polymeric sensors in hand prostheses [1, 2], because of their unique electrical and mechanical properties, such as light weight, low cost, ease of processing, and corrosion resistance, in comparison with metals [3].

Conductive polymer composites exhibit some interesting features involving variations of resistivity with temperature [4, 5], mechanical stress [6, 7] or chemical environments [8–11]. Conductive composites based on semicrystalline polymer show positive temperature coefficient (PTC) effect of resistivity around its melting point, which is quite attractive for the thermo-sensitive sensor applications. The PTC effect greatly depends on the properties of the matrix and the filler as well as on the processing conditions. A greater PTC intensity (the ratio of maximum resistivity at a certain temperature to resistivity at room temperature) can be obtained when several kinds of semicrystalline polymers are employed as matrices, and further examinations reveal that the degree of crystallinity and the melting point of the matrix are closely related to the PTC intensity [12–14]. Meanwhile, a main mechanism has been suggested that the PTC effect is caused by an increase in the average interparticle distance of conducting particles, which is induced by the large thermal expansion during melting of the semicrystalline matrix [14, 15]. The

conductive composites based on semicrystalline matrix usually have poor stability during thermal cycles due to aggregation of conducting particles resulted from repeated melting and recrystallization, which limits the practical application of PTC materials.

Ethylene-tetrafluoroethylene (ETFE) alternating copolymers with a high melting point show excellent mechanical and dielectric properties, good resistance to chemical agents, and good processability [16]. Feng, et al. [15] studied the conduction behavior of CB-filled ETFE composites in relation to mechanical and heating treatments. The ETFE/CB composites have high potential value for applications of self-regulation heaters in high temperature. To our knowledge, few works concerning PTC stability of ETFE/CB composites have been reported up to date. In the present work, we focus our attention on the PTC effect of ETFE/CB composites prepared by incorporation of CB into ETFE, and attempt to examine the percolation behavior and the effect of CB concentration on the PTC intensity. Especially, we evaluate the electrical reproducibility of ETFE/CB composites during heating-cooling cycles in order to adapt for PTC products.

The composites were prepared by mixing of ETFE (ETFE-750 from DuPont, density 0.942 g cm^{-3} , melting point $250 \text{ }^\circ\text{C}$, and melt flow index 700 g/10 min) and CB (VX_c-605 from Shanghai Cabot Chemical Co., Ltd., particle size 25 nm , density 1.85 g cm^{-3} , nitrogen absorption special surface area $63 \text{ m}^2 \text{ g}^{-1}$, and dibutyl phthalate (DBP) absorption $1,480 \text{ mm}^3 \text{ g}^{-1}$) on a two-roll mill at $280 \text{ }^\circ\text{C}$ and 60 rpm for 10 min , and then by compression-molding at $280 \text{ }^\circ\text{C}$ under 14.7 MPa for 10 min to form sheet specimens. For specimens used in the resistivity measurements, two pieces of copper nets were mounted onto the opposite wide surfaces of the sheet to ensure good

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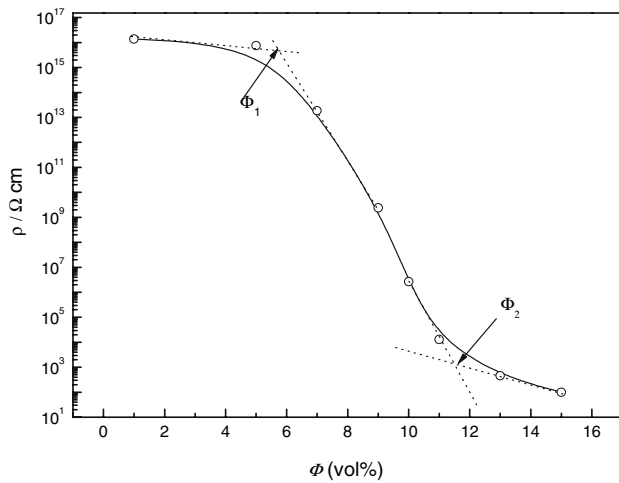


Fig. 1 Dependence of volume resistivity (ρ) on CB volume fraction (Φ) for ETFE/CB composites

electric contact with the copper electrodes. After naturally cooled to room temperature, the sheet was cut into samples with a size of $12 \times 12 \times 1.5 \text{ mm}^3$.

A two-probe resistance measurement was carried out for determining the resistivity (ρ) at room temperature with a M890 B digital multimeter when the resistance of the samples was lower than $1.2 \times 10^8 \Omega$. A high-resistance meter (ZC36; 10^{-14} A and $10^{17} \Omega$) was used to measure resistance higher than $1.2 \times 10^8 \Omega$.

The temperature-dependent ρ for the composites with various CB volume fractions (Φ) was measured with an automatic measurement system in which a 7150 Plus Digital Mutimeter (Schlumberger) was installed for the ρ test. The temperature was controlled in accordance with a desirable program. The heating and cooling rates during

ρ measurement were $2 \text{ }^\circ\text{C min}^{-1}$ and $1.5 \text{ }^\circ\text{C min}^{-1}$, respectively.

Figure 1 shows ρ as a function of Φ for the ETFE/CB composites. It can be found that ρ drops dramatically more than 10 orders of magnitude over the percolation region from 0.05 (Φ_1) to 0.11 (Φ_2) corresponding to the insulator-to-conductor transition. We believe that this percolation transition is resulted from the formation of interconnected CB pathways with increasing Φ . According to the opinion of Nakamura, et al. [17], Φ_2 is at the upper limit of percolation transition, where a tunneling conduction changes into an ohmic one.

Figure 2 illustrates the resistivity–temperature (ρ – T) relationship for ETFE/CB composites with Φ near Φ_{2C} . The resistance plateau on the upper part of the curve is due to the limited measurement range of the multimeter. A typical PTC behavior could be observed with temperature increasing toward the melting point of ETFE. The ρ reaches a maximum in the vicinity of $250 \text{ }^\circ\text{C}$. The PTC intensity decreases with increasing Φ , which is the same as in the other semicrystalline composites [18, 19]. After the PTC transition, ρ decreases with increasing temperature, which is generally denoted as negative temperature coefficient (NTC) effect of resistance. The NTC effect could be explained on the basis of the formation of additional conducting pathways induced by the relaxation of ETFE macromolecular and the rearrangement of CB aggregates in the molten matrix [20, 21]. The PTC behavior is mainly ascribed to the breakage of CB network induced by the large volume expansion during the polymer melting.

Figure 3 presents the ρ –(ρ) relationship for ETFE/CB ($\Phi = 11 \text{ vol}\%$) composites upon four heating–cooling thermal cycles. There is an obvious hysteretic change in ρ during the first cycle, which is usually associated with the

Fig. 2 Volume resistivity (ρ) as a function of temperature for ETFE/CB composites containing different CB volume fraction (Φ)

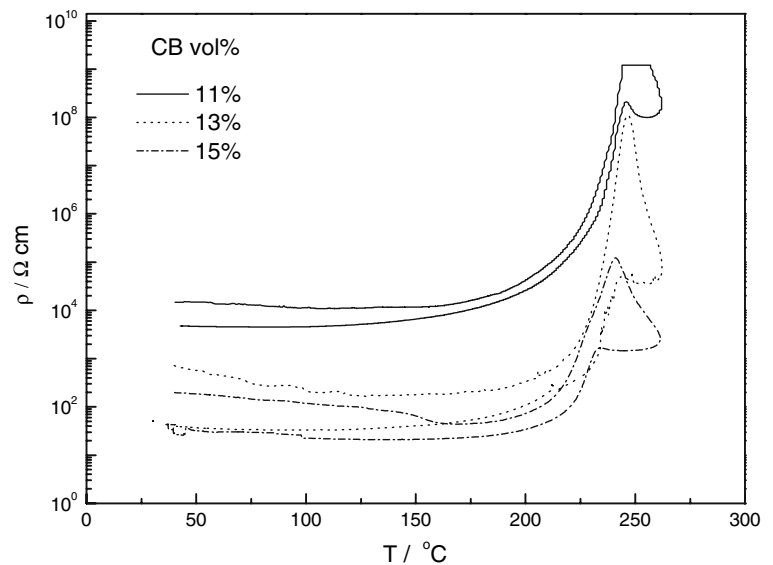
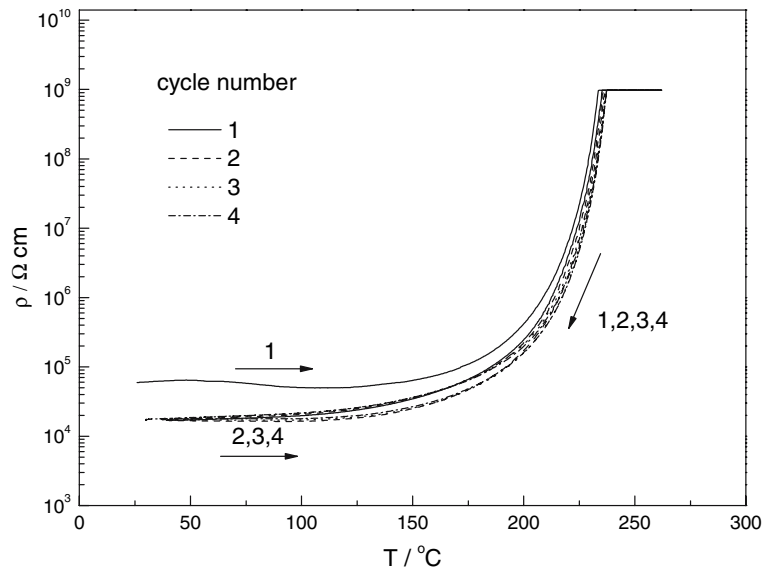


Fig. 3 Temperature dependence of volume resistivity (ρ) for ETFE/CB ($\Phi = 11$ vol%) composites upon four thermal cycles



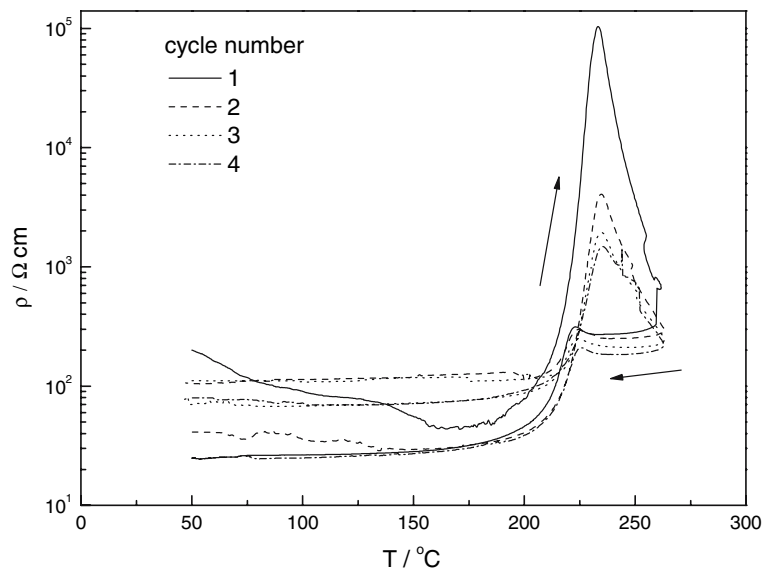
relaxation of the accumulated thermo-mechanical stress left in the heating cycle [22]. However, the ρ - T relationship during the following three cycles are considerably stable and the resistance hysteretic change is reduced obviously in comparison with the first one. In general, most of PTC materials show poor reproducibility of ρ [23–26], over a long period of time or when undergoing thermal cycles, due to the varying dispersion of CB filler in the composite. The instability of electrical conductivity has an adverse influence on the application of PTC materials. Therefore, many methods have been developed to stabilize the conducting network structure formed in the composite, such as mixing of two types of carbon black [23], adding rubber as a mechanical stabilizer [27] or using a very-high-viscosity polymer as one component of the composite [28], as well as crosslinking the matrix [29]. On the other hand,

the ETFE/CB composites containing CB with Φ in the close vicinity of Φ_2 have good reproducibility without any complicated treatment.

Figure 4 shows the ρ - T relationship for the composite containing 15 vol% of CB with a lower PTC intensity. In this composite, the CB network is labile and the melting-crystallization of the matrix leads to irreversible change in the network. The PTC intensity becomes weaker with increasing thermal cycle.

Conductive behavior of ETFE/CB composites was investigated. It is found that the percolation region is from 0.05 (Φ_1) to 0.11 (Φ_2). A strong PTC effect could be observed at the upper limit of the percolation transition, Φ_2 . In case of Φ higher than Φ_2 , the PTC intensity decreases with increasing CB concentration. The switching characteristic and PTC intensity of ETFE/CB composites show a

Fig. 4 Temperature dependence of volume resistivity (ρ) for ETFE/CB ($\Phi = 15$ vol%) composites upon four thermal cycles



reproducible stability at Φ_2 . However, the ρ – T relationship becomes unstable at high Φ . It is suggested that irreversible CB network has formed in the composite with high CB concentrations.

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