

NONLINEAR J - E CHARACTERISTICS IN THE ELECTRIC-THERMAL EQUILIBRIUM STATE FOR HIGH DENSITY POLYETHYLENE CONDUCTIVE COMPOSITES*

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Abstract The nonlinear J - E characteristics under self-heating equilibrium for conductive composites based on high density polyethylene were studied. The results show that there are identical conduction mechanisms under self-heating equilibrium for the composites with various initial resistivities determined by filler content or ambient temperature. The nonlinear conduction behavior was involved in the limited microstructure transformations of the conducting network induced by electrical field applied and the corresponding self-heating effect. A reversible thermal fuse (RTF) model was suggested to interpret the physical origin of the nonlinear J - E characteristics.

Keywords J - E characteristics, Nonlinear conduction, Self-heating equilibrium, Reversible thermal fuse model

INTRODUCTION

Conductive composites based on crystalline polymers are of industrial importance because they possess a positive temperature coefficient (PTC) of resistivity effect^[1, 2]. Important applications of the polymer PTC composites include current overload protectors and self-regulating heaters, etc^[3, 4]. Characterization of polymer PTC composites has usually been focused on measurements of temperature dependence of resistivity. The measuring conditions are usually set up in such a way that the electric current passing through the specimen is small, and the electric heating effect is thus negligible. The PTC behavior obtained by this method reflects the intrinsic resistivity-temperature characteristics of a composite. Such conditions of PTC measurement is believed to be far away from the real application conditions. In the case of self-regulating heating, electric current is appreciable and Joule heat is generated. The PTC behavior endows the composites with self-heating and self-temperature control functions. Characterization of the conduction characteristics of polymer PTC composites under conditions rather close to the application is believed to be valuable for application purposes. However, the current density-electrical field strength (J - E) relationship and the conduction mechanism in the state of self-heating equilibrium have not yet been studied adequately.

In this paper, the nonlinear J - E relationships of conductive composites based on high density polyethylene (HDPE) were measured under the self-heating equilibrium state. The physical origination of the nonlinear J - E characteristics was interpreted on the basis of the data collapses and a suggested phenomenological model.

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EXPERIMENTAL

Materials

HDPE used in this research was commercially produced by Qilu Petrochemicals, having density of 0.942 g cm^{-3} , melting point of 127°C and melt flow index of 0.14 g/10 min (2.16 kg , 170°C). Graphite powder (GP) with a particle size of $\sim 1 \mu\text{m}$ and acetylene carbon black (CB) with a particle size of 42 nm , BET special surface area of $63 \text{ m}^2/\text{g}$ and DBP absorption of $1.70 \text{ cm}^3/\text{g}$, were obtained from Shanghai Colloid Chemical and Chun'an Chemical factories, respectively.

Composite Preparation

The composites of HDPE and conductive fillers were prepared by simple mixing of HDPE and GP or CB on a two-roll mill at 160°C for 20 min, and then by compression molding at $160 \pm 5^\circ\text{C}$ under 14.7 MPa for 10 min to form sheet-shaped specimens. Two pieces of copper net were mounted on both sides of the sheet surface to ensure good electrical contact with attached copper electrodes.

Resistance Measurement

Two-probe resistance measurement was carried out by using a M890B⁺ digital multimeter, and the resistivity was thereby calculated. Before the resistance measurement of HDPE/GP composites at room temperature, at least 24 h was required to allow the as-prepared specimens to release their internal stress adequately. The resistance of the composites showed time-dependence at elevated temperatures even below the melting point (T_m) of HDPE. Before the measurement was performed at elevated temperatures, at least 24 h were also required to permit the resistance of HDPE/CB composite to attain a relatively steady value. Then the current density-electrical field (J - E) testing was carried out.

J - E Characteristics Measurement

All specimens used in J - E testing contain filler contents above the percolation threshold. J - E characteristics in an electrical-thermal equilibrium state were investigated in an alternating electric field (50 Hz) in the range of $10^2 \sim 10^3 \text{ V cm}^{-1}$. The electrical field was controlled by a stepwise transformer. Both the electric field and the current were higher than those required to generate self-heating of the specimen. Technically, the electrical field and current were recorded simultaneously with digital multimeters (SEG DT890A) only when the self-heating temperature was steady. Under this condition, the self-heating and heat dissipation were in balance.

RESULTS AND DISCUSSION

Nonlinear J - E Characteristics

The J - E characteristics of the HDPE/GP composites with various filler contents and the HDPE/CB composites at various ambient temperatures are shown in Fig. 1 and Fig. 2, respectively. Typical nonlinear conduction behavior is observed for specimens with various initial resistivities. There exists a critical point in a given J - E curve, below which J increases with E and above which J decreases with E . The critical current density and electric field strength, J_c and E_c , are the onset variables of the self-heating behavior of the specimen. It is observed experimentally that the self-heating behavior becomes more and more marked with increase in E when $E > E_c$. The remarkable self-heating effect may result in a local volume expansion of the matrix surrounding the conductive particles. As a result, some of the conducting pathways formed by physical contact of particles are disrupted, resulting in a local PTC effect. The downward deflections of J versus E are believed to be caused by the local PTC effect.

Scaled J - E Characteristics

The changes in both the filler volume fraction and the ambient temperature lead to changes in the initial resistivity of the composites. However, as shown in Fig. 1 and Fig. 2, the elevation of ambient temperature and the decrease of filler content have almost the same effect on the nonlinear J - E characteristics in the self-heating equilibrium state. The increase of initial resistivity causes an elevation in the location of the J - E characteristic curve. It seems that the microstructures of the conducting network resemble each other in nature for the

composite with various initial resistivities.

It is also found in Fig. 1 and Fig. 2 that J_c and E_c are different when the initial resistivity determined by GP content or ambient temperature is different. The decrease of initial resistivity leads to an increase in J_c and a corresponding decrease in E_c . Those curves are almost parallel to each other in the whole range of field strength. Collapse of the J - E curves is obtained when J and E are scaled with the critical variables of J_c and E_c respectively, as shown in Fig. 3 and Fig. 4. The collapse of the curves suggests that the nonlinear conduction behavior at electric-thermal equilibrium may be controlled by the same physical mechanisms, independently of both the filler content and the ambient temperature.

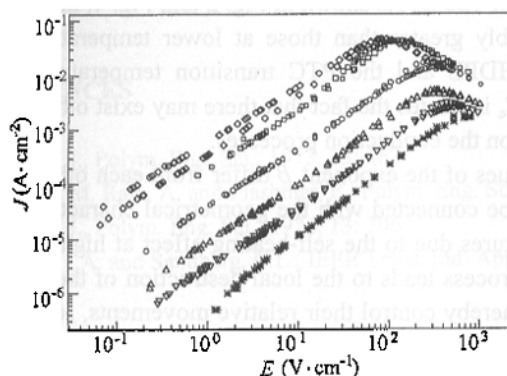


Fig. 1 Nonlinear J - E characteristics in the self-heating equilibrium state for HDPE/GP composites with initial resistivity of 1.64 ($\diamond$), 6.95 ($\square$), 25.3 ($\circ$), 92 ($\triangle$), 488 (∇) and 1225 ($*$) KΩcm

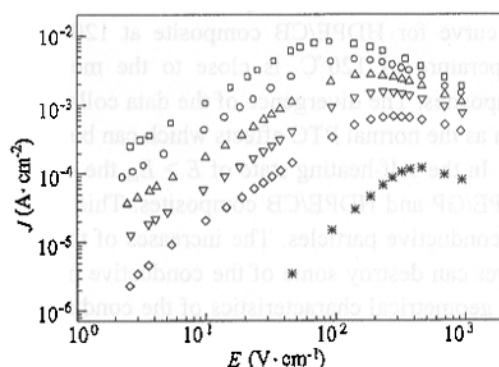


Fig. 2 Nonlinear J - E characteristics in the self-heating equilibrium state for HDPE/CB composites (CB volume fraction 0.082) at ambient temperature of 19 ($\square$), 40 ($\circ$), 58 ($\triangle$), 78 (∇), 100 ($\diamond$) and 120 ($*$) °C

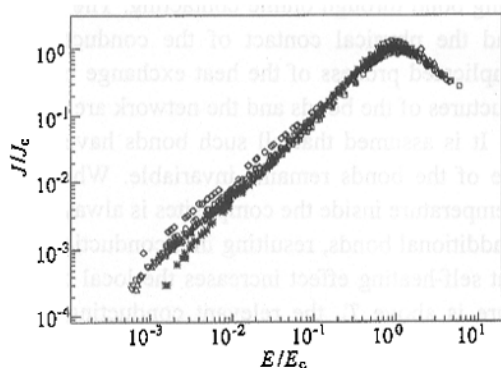


Fig. 3 Scaled J - E characteristics in the self-heating equilibrium state for HDPE/GP composites with initial resistivity of 1.64 ($\diamond$), 6.95 ($\square$), 25.3 ($\circ$), 92 ($\triangle$), 488 (∇) and 1225 ($*$) KΩcm

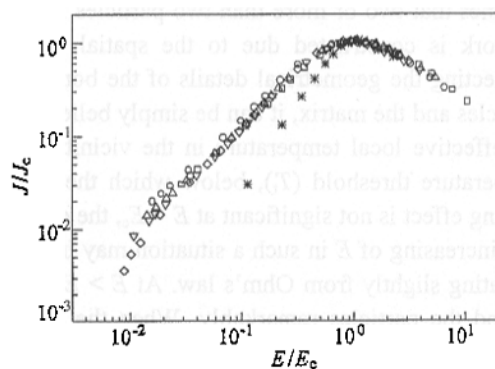


Fig. 4 Scaled J - E characteristics in the self-heating equilibrium state for HDPE/CB composites (CB volume fraction 0.082) at ambient temperature of 19 ($\square$), 40 ($\circ$), 58 ($\triangle$), 78 (∇), 100 ($\diamond$) and 120 ($*$) °C

The scaled J - E curves can be divided into two different sections. The J - E relationships in the two sections can be approximately described as $J/J_c = (E/E_c)^\alpha$ and $J/J_c = (E/E_c)^\beta$, respectively, on the basis of scaling laws. Least-square-fitting the experimental data to the two equations above gives $\alpha = 1.12 \pm 0.02$ and $\beta = 0.82 \pm 0.02$ for HDPE/GP composites with various GP contents, and $\alpha = 1.10 \pm 0.02$ and $\beta = 0.68 \pm 0.02$ for HDPE/CB composites at various ambient temperatures.

It is interesting to notice that the experimental values of the exponent α for the two systems are almost the same. However, the difference of about 20% for the experimental values of the exponent β is comparatively large

for the two systems. It is believed that the former critical exponent may be related to the overall structure of the network, but the later may be related to the geometrical characteristics of the conductive particles. When $E < E_c$, the electrical power of the composites is too small to produce significant self-heating behavior. The changes of the local temperatures around the particles are negligible, which can not affect the physical characteristics of the conducting pathways formed by the physical contact between GP or CB particles. The conduction characteristics under $E < E_c$ are consequently independent of the geometrical details of the conductive particles, resulting in a universal exponent α of about 1.10.

It is also noted that the data coincidence under $E < E_c$ is poorer than that under $E > E_c$, especially for the situation of HDPE/CB composite at an ambient temperature of 120°C. As shown in Fig. 2 and Fig. 4, the slope of the curve for HDPE/CB composite at 120°C is considerably greater than those at lower temperatures. The temperature of 120°C is close to the melting point of HDPE and the PTC transition temperature of the composites. The divergence of the data collapse under $E < E_c$ indicates the fact that there may exist other factors such as the normal PTC effects which can be super-imposed on the conduction processes.

In the self-heating state of $E > E_c$, the experimental values of the exponent β differ from each other for the HDPE/GP and HDPE/CB composites. This difference may be connected with the geometrical characteristics of the conductive particles. The increases of the local temperatures due to the self-heating effect at high electrical power can destroy some of the conductive pathways. This process leads to the local destruction of the network. The geometrical characteristics of the conductive particles thereby control their relative movements, resulting in the exponent β being dependent on the compositions of the composites.

Reversible Thermal Fuse Model

It was found that the nonlinear J - E characteristic in Fig. 1 is reversible. When the field decreases gradually, J decreases almost in the same track of field increasing. Taking the reversible J - E characteristic and the above-mentioned scaling laws into consideration, a reversible thermal fuse (RTF) model is suggested to describe the nonlinear conduction behavior in the self-heating equilibrium state for conductive composites. This model assumes that two or more than two particles form a conducting bond through ohmic contacting. The conducting network is constructed due to the spatial organization and the physical contact of the conducting bonds. Neglecting the geometrical details of the bonds and the complicated process of the heat exchange between the particles and the matrix, it can be simply believed that the structures of the bonds and the network are involved in the effective local temperature in the vicinity of the bonds. It is assumed that all such bonds have a uniform temperature threshold (T_b), below which the physical nature of the bonds remains invariable. When the self-heating effect is not significant at $E < E_c$, the effective local temperature inside the composites is always below T_b . The increasing of E in such a situation may introduce some additional bonds, resulting in a conduction behavior deviating slightly from Ohm's law. At $E > E_c$, the significant self-heating effect increases the local temperature around the particles remarkably. When the local temperature is above T_b , the relevant conducting bonds are disrupted. Accordingly, the current flow must redistribute to the other possible bonds and make them breakdown gradually. The bonds disrupt randomly in the conducting network, but the summation of the broken bonds depends on the electric field applied and the corresponding local temperature of self-heating. There exists a rule of statistical thermodynamics which controls the changes in the microstructures of the network for the sake of adaptation to the surroundings. The network transforms its microstructure in almost the same physical fashion due to its initial structure (initial resistivity). Because of the self-temperature control characteristics of polymer PTC composites, the local temperature never exceeds T_m of the matrix when the filler contents are not much higher than the percolation threshold, or the ambient temperature is below T_m . Consequently, the changes of the network are only caused by the short-range rearrangement of the bonds. With decreasing E , the local temperature decreases gradually. The volume shrinkage of the matrix exerts internal stress on the particles, rehabilitating the thermally broken bonds in the reverse way of increasing of E . The limited short-range transformations of the spatial architecture of the network result in the reversible J - E characteristics in a self-heating equilibrium state.

CONCLUSIONS

The nonlinear conduction behavior occurring in a self-heating equilibrium state is determined by a mechanism, which is independent of initial resistivity of the composites. Scaling laws describing the J - E characteristics are established by using the data collapse method. It was found that the critical exponents α and β are independent or dependent on the geometry of conductive particles, respectively. A RTF model is suggested to interpret the physical origination of the nonlinear J - E characteristics. The local microstructure transformations of the conducting network resulting from the limited volume expansion and shrinkage of the matrix are believed to be responsible for the reversible nonlinear J - E characteristics.

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