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Electrical-thermal switching effect in high-density polyethylene/graphite nanosheets conducting composites

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Abstract The nonlinear response in high-density polyethylene/graphite nanosheets conducting composites under increasing applied voltage is investigated. Under sufficient applied constant voltage, the resistance increases initially due to Joule heating effect and then eventually reaches a steady value with a characteristic thermal relaxation time τ_h, which decreases as the applied field increases. The switch value, namely the ratio of the resistance under steady condition to the resistance of sample in linear regime, gradually increases with the increasing applied field. The threshold voltage (V_0) at which the resistance start to increase with time scales with linear regime resistance (R_0) of the sample as $V_0 \sim R_0^x$, with the exponent $x = 0.78 \pm 0.05$. All the curves of R/R_0 vs. V/V_0 collapse to a similar curve with the function $R/R_0 = 1 + \alpha(V/V_0)^{\theta}$. The results reveal that the threshold voltage value decreases with increasing graphite nanosheets content in the composites.

Introduction

The application of finite force (electrical, mechanical) in disordered systems usually results in a nonlinear response [1]. The electrical nonlinear conductivity of composites consisting of conductive filler and insulator polymer matrix is of significant interest because of the wide spread application of this material, such as current-limiting thermistors, self-regulating heating elements, static electricity dissipation devices, etc [2–4]. The nonlinear conduction in conductor-filled polymer composites usually arises from two effects, negative coefficient of resistance effect and positive coefficient of resistance effect under applied field. The first case referring to resistance decrease resulting from tunneling conduction effect was investigated early in many systems under low applied field, especially focusing on nonlinear enhancement near the percolation threshold [5–8]. The latter one refers to the resistance increase induced by joule heating effect under sufficient applied filed [3, 4, 9–15], associated with the temperature increase and expansion of polymer in conducting composites' body when the whole composite is heated via the network of conducting filler when the sufficient current flows through. Such process is also called self-heating effect which is intriguing for researchers due to the composite application. When the temperature in composites closes to the melting point of the polymer matrix, it can be seen that the electrical resistance of the composites increase abruptly, exhibiting a strong positive temperature coefficient of resistance (PTCR) effect. Contrary to precipitous increase in resistance resulting from external heat [16], PTCR effect induced by self-heating is more complicated with strongly time-dependent and non-isothermal process [9]. The increase of macroscopic resistance in composites resulting from self-heating induced decay of current across them with time [14], so this conducting composite can be utilized as current limitation in circuit protection. Recently it was demonstrated that conductor-filled polymer composites could be fashioned into "polymer current limiter" devices that rapidly and reversibly switch from a low to high resistance state when high current densities flow through them [13]. Such composites also were used as heating elements possessing several advantages such as self-adjusting heat output by environment temperature and simple fabrication [14].

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The behavior of conducting composites under applied field have been studied in other systems, but seldom focus on in detail the thermal relaxation behavior in the self-heating process and the relation of switching value and the applied voltage value. The self-heating in composites filled with graphite nanosheets (GNs) have been studied by our group, showing the phenomenon and interpreting in a single sample with increased applied constant voltage [15]. The electrical-thermal (ET) switching effect in composites driving from the thermal relaxation process is related to the fraction of conductive filler and the value of applied field, so the research on composites with large range of filler fraction is necessary. In this article, experimental data on resistance thermal relaxation behavior in details under applied increasing constant voltages are shown here. The resistance of sample reaches the saturated situation ultimately under increasing applied field when the thermal equilibrium is established between heat generation from self-heating and heat dissipation to surrounding. The ratio of the resistance under steady condition to the resistance of sample in linear regime rises with the increasing applied voltage. At a composition of the filler far above the percolation threshold, the resistance of a composite sample increases with time due to Joule heating effect as applied constant voltage pass through the sample beyond the threshold value .The value of threshold voltage (V_0) under which the resistance starts to increase scales with linear regime resistance (R_0) of the sample as $V_0 \sim R_0^x$, with the exponent $x = 0.78 \pm 0.05$. All the curves of R/R_0 vs. V/V_0 collapse to a similar curve with the function $R/R_0 = 1 + \alpha(V/V_0)^\theta$ where $\alpha \approx 0.15$ and $\theta \approx 2.2$. The macroscopic switched state is then a result of a dynamic-stationary state of fast switching and slow reconnection of the corresponding junctions. The threshold voltage is strongly dependent on the GNs content in the system. The results reveal that the threshold voltage value decreases with increasing GNs content in the composites. A reasonable explanation is given that the threshold voltage value becomes smaller as interparticle tunneling barriers become narrower with the increase in the GNs content.

Experimental procedures

The conducting filler used in the elaboration of composites consists of GNs, the average diameter of which is 12.5 μm and the thickness of which is close to 51.5 nm. Detailed procedures and conditions for elaboration of GNs were described in our previous paper [17]. High-density polyethylene (HDPE) ($\rho = 0.95$ g/cm^3, melting point = 120 °C) was supplied by Petrochemical Ind. Co. Ltd. (Korea). Briefly, preweighed HDPE and GNs were melt-blended using single-screw extruder at 140 °C for several minutes to achieve a uniform dispersion. The obtained compound was further heat treated at 130 °C for 2 h and cooled down to room temperature in the oven.

Measured samples were prepared with graphite particles concentrations ranging from 0.02 to 0.2 by weight. The (dc) electrical conductivity has been studied as a function of the concentration p of the GNs. The percolation model provides a good description of the experimental results. Below a critical concentration p_c(0.06), the resistivity of sample is close to that of the polymer matrix. Above and close to p_c, the conductivity increases as $\rho^{-1} \sim (p - p_c)^t$, where t is the conductivity exponent and t is 2.9, p_c is the percolation threshold in the classical percolation [18] .This behavior is attributed to the formation of an infinite percolating cluster of connected particles spanning the entire sample.

Measured samples were prepared with graphite particles concentrations ranging from 0.02 to 0.20 by weight. Samples were originally prepared in the shape of ribbons with a width of 10 mm and thickness of 2 mm. However, measurements were done at room temperature on samples of sizes 10 × 10 × 1 mm^3 with dc constant-voltage from Keithley2400. Two sides of the samples were pasted with silver paint and a sample was held between two circular brass electrodes slightly larger in diameter than those of the sample. A computer was used to acquire data. In a typical measurement, the voltage corresponding to a certain value would be turned on at time $t = 0$ and the bias across the sample be measured at an interval of time (usually 1 s) until it reached steady value. After that, samples are cooled down to the room temperature for the next measure.

Results and discussion

Thermal relaxation under constant voltage source

The behaviors of a sample resistance under increasing applied voltage are measured, as shown in Fig. 1. All the curves correspond to applied voltage value. R_0 represents the linear resistance of the sample under zero field [6]. At a low bias (2 V), the resistance always retains a steady value and is independent of time. As the applied field increases, the resistance increases with the time first and then reaches a steady value slowly. These results present also the time scale that is involved in the macroscopic process, namely, that the resistance increases with time, following applied voltage, for up to about several minutes, after which it saturates. This shows that under the conditions used, a macroscopic stationary ''switched'' state is reached. Macroscopic resistance increase in sample is induced by sufficient applied field which results in local Joule heating effect in the composite. The phenomenon is called positive temperature coefficient of resistance (PTCR) effect

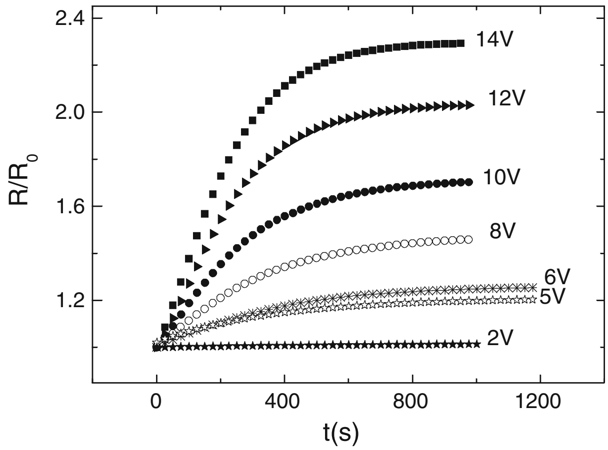

Fig. 1 Thermal relaxation of resistance of a sample with filler concentration 0.16 under increasing applied voltage. Many data points have been omitted for clarity

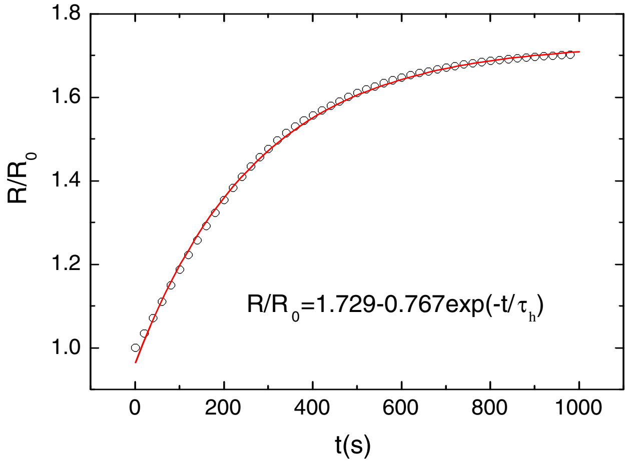

Fig. 2 A typical resistance curve of a sample with filler concentration 0.16 under a constant voltage of 10 V. Many data points have been omitted for clarity. The solid line is fit to a simple exponential $R/R_0 = 1.729 - 0.767\ \exp(-t/\tau_h)$, τ_h is the relaxation time, here $\tau_h = 274$ s

resulting from self-heating under applied field. The certain applied voltage value which results in the resistance starting to increase is called threshold field, above which the ratio of dynamic resistance to initial resistance raises to a higher value. Each ultimate stable state represents stationary hot ''switched'' state when an electric thermal equilibrium is established between dissipation and generation of heat for several minutes.

The resistance increases with time first and reaches a new stable situation slowly under the disturbance of applied constant field. This dynamic process of resistance increasing is thermal relaxation during self-heating under applied field, corresponding to a continuous temperature change with time. Figure 2 shows a typical relaxation curve during self-heating by 10 V. The curve is well described by a simple exponential function indicated by the solid line in Fig. 2. It may be recalled that the relaxation function *f*(*t*) is almost universally given by $f(t) \sim \exp[-(t/\tau)^{\alpha}]$, here t is the time, τ is the relaxation time constant, and α is an exponent. The exponential relaxation corresponding to $\alpha = 1$ occurs mostly in simple systems such as homogeneous ordered solids [19]. A simple exponential in the present case may be attributed to a long-time relaxation behavior. In systems with characteristic time scales such as percolating networks, the relaxation function may change from a stretched exponential at short times to a simple exponential at long times [20, 21].

All resistance relaxation curves are fitted by the relaxation function $R/R_0 = k_1 - k_2\ \exp(-t/\tau_h)$. k_1, k_2, and τ_h are treated as fitting parameter. In fact, k_1 is the approximate value of R/R_0 at ultimate steady situation in the relaxation process. The relaxation time (τ_h) in several samples of different compositions against constant voltage are shown in Fig. 3. The result reveals that τ_h decreases with the increasing applied voltage for all samples. A higher applied field induces faster change in resistance of a sample, so that the relaxation time becomes shorter. The relaxation time is short to microsecond order of magnitude under extreme high voltage in some other composites, corresponding to a fast current limiting process [11–13]. So under low power; the resistance presents a low switching value and slow current limiting process. There is the trend of shorter in relaxation time under same applied field for samples with higher filler fraction. But it is not obvious in the samples with high filler fraction.

The resistance relaxation under constant current is different from the process in our case. Under constant current condition, the relaxation time diverges at the point of

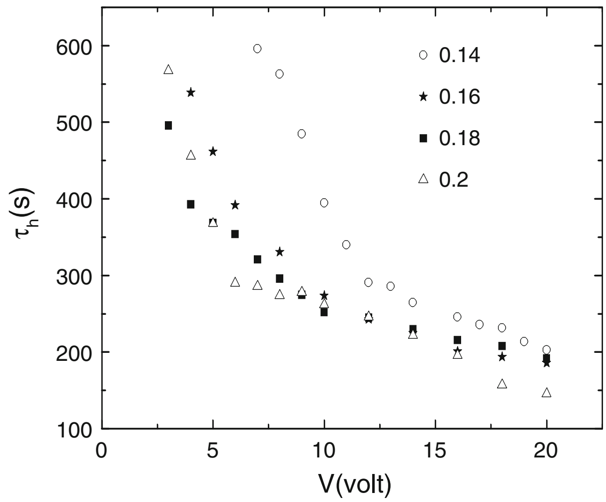

Fig. 3 Relaxation time vs. voltage in various samples

critical breakdown current value I_B [19], corresponding to a critical transition of steady to unsteady state. But under increasing applied constant voltage, the resistance of sample always increases first and then reaches a steady state with certain relaxation time, corresponding to the current passing through the sample decays with time in this process. The increase in resistance limits the current to a moderate value in the relaxation process which is the origin of conducting composite acting as current-limiter, self-regulating heating elements, static electricity dissipation devices, etc.

The ET switching effect in HDPE/GNs conducting composites

The basic manifestation of the macroscopic ET switching effect is that the application of a voltage beyond some threshold value yields a large increase of macroscopic resistance. This effect is exhibited in Fig. 4 which shows the switching value as the function of applied voltage. Six curves shown here represent different compositions of the composites. Each point represents an ultimate stable value of thermal relaxation of resistance under constant voltage source. When the fraction is closed to the percolation threshold, the resistance increases first and then decreases under increasing applied field, resulting from the competition between tunnel conduction and Joule heating effect. For the samples with fraction far beyond the percolation threshold, the resistance always increases under applied field. The critical fraction is called p_J which is a fraction characteristic of the system, referring to the samples which only have $R/R_0 \geq 1$ for all fields [10]. As shown in Fig. 4, the nominal GNs fraction of samples ranging from 0.1 to 0.2 are above or near p_J which is approximately 0.14 in the system.

For the samples with fraction above p_J, the ratio keeps a constant value independent of applied voltage, under low electric field. When the electric field overcomes a certain value, the resistance starts to depend on the applied voltage and increases ($R/R_0 > 1$). The transition from linear regime to nonlinear regime is shown in Fig. 4. V_0 sets the voltage scale value of nonlinearity .The certain value of electrical field is called threshold value, which is dependent on the original resistance determined by the filler fraction and the two competing effects: Joule heating induced by applied field and heat dissipation relying on the surroundings. Considering that all samples were measured under the same condition, the relationship of voltage value V_0 and R_0 are investigated singly. It was found that the threshold voltage value V_0 scaled with R_0; R_0 is the linear regime resistance of a sample. A log-log plot of threshold field value V_0 vs. R_0 is shown in the inset of Fig. 5. The straight line fit indicates that V_0 scaled with R_0 as $V_0 \sim R_0^x$, with the exponent $x = 0.78 \pm 0.05$.

To better analyze the dependence of resistance on the applied bias, Fig. 5 shows the semi-log plot of the relative variation of resistance (R/R_0) as a function of V/V_0 for the sample with different R_0. All curves collapse to a similar curve. A scaling relation is found between R/R_0 and V/V_0, where R_0 is the linear regime resistance and V_0 is threshold value for the onset nonlinearity. R/R_0 scales with V/V_0 in the whole region of applied voltage as $R/R_0 = 1 + \alpha(V/V_0)^{\theta}$, here α and θ are treated as fitting parameter as shown in Fig. 5. A similar relation was found in CB-HDPE system under constant current condition [19] .The experimental

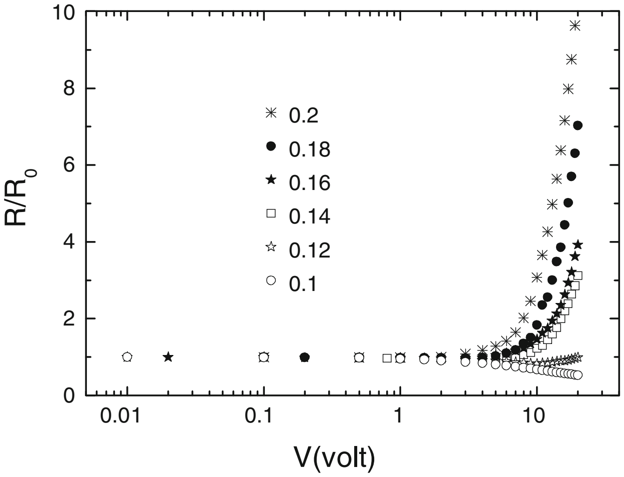

Fig. 4 Semi-log plot of the ratio of resistance as a function of the field for different samples of HDPE/GNs .The GNs fraction p of each sample is as indicated

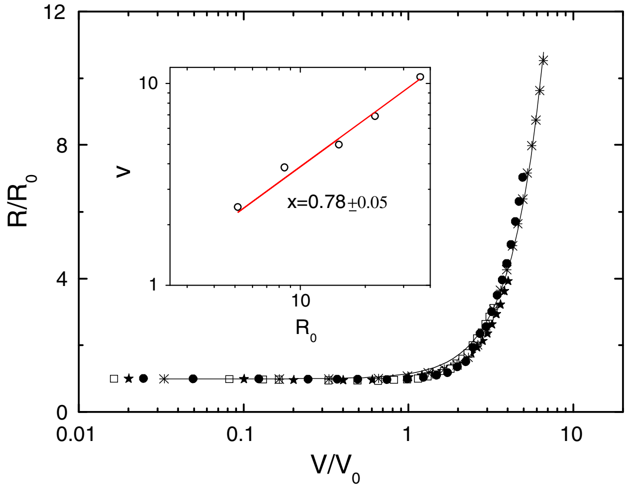

Fig. 5 Scaled plot of normalized resistance vs. scaled field of data in Joule regime .The solid line is a fit to the data according to $R/R_0 = 1 + \alpha(V/V_0)^{\theta}$, $\alpha \approx 0.15$, $\theta \approx 2.2$. Inset: Log-Log plots of $V_0 \sim R_0^x$. The solid line is the power law fit to the data with the exponent as indicated

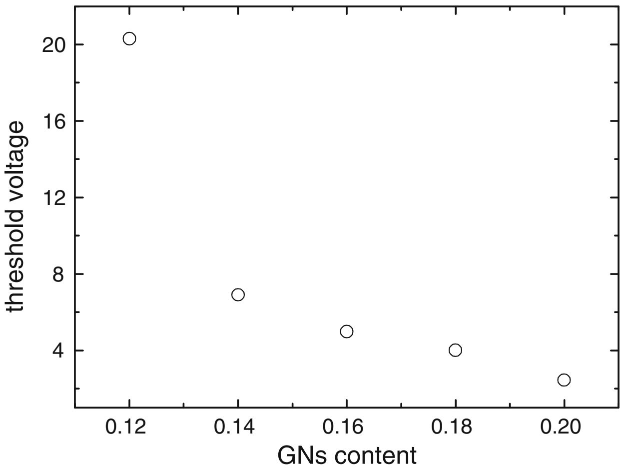

Fig. 6 The dependence of the threshold voltage on the GNs content

results are also consistent with the theoretical results from Monte Carlo (MC) simulations [22].

As mentioned above, the threshold voltage value V_0 scaled with R_0. R_0 is relevant to the composites' composition in percolation conduction network. Figure 6 shows the dependence of the threshold voltage on the GNs content. The results reveal that the threshold voltage value decreases with increasing GNs content in the composites. For the sample with $p < p_J$, PTCR effects take place hardly because samples with lower conductive filler exist tunneling effect offsetting of Joule heating effect, so the threshold voltage is extraordinarily large (see Fig. 4). For the sample ($p \geq p_J$), the increasing conducting filler denotes a larger number of contacts and smaller volumes of polymer matrix material embedded with the network of conducting GNs .The interparticle tunneling barriers become narrower with the increase in the GNs content. This holds two effects. Firstly, due to the smaller corresponding resistance, the current and heat dissipation in the junctions (for a given bias) are larger in the case of the higher GNs content. Alternatively, the narrower junctions require a smaller Joule heating for the fusing due to the smaller amount of the polymer material in them.

The macroscopic ET switching state is the statistic result about the dynamic microcosmic switched state in the percolation network. Under applied constant voltage, the current is carried by percolation paths of the conducting particles and the heat is produced. The fuse of polymer matrix between the GNs or their aggregation represents a switch-off state under sufficient heat. When the local heating heat dissipates, the polymer is cooled slowly and the junctions between conducting fillers reconnect. The macroscopic switched state is, then, a result of a dynamic-stationary state of fast switching and slow reconnection of the corresponding junctions. The investigation of the switching behavior in such composites by employing conducting atomic force microscopy had convicted these results and also indicated that the PTCR effect is mainly driven by the change in interparticle resistance [23].

Conclusions

Many applications of these conducting composites rely on the complete understanding of the physical properties. The fundamental physical problems associated with ET switching effect in high-density polyethylene/GNs conducting composites are studied here. For the application of the conducting composites acting as electrical element in electrical industry, the parameters, such as threshold voltage, switching value, and relaxation time under defined applied field, etc. are crucial. Such ET switching effect induced by self-heating effect under applied field is concerned with heat production and transfer process, so monitoring of composites' temperature on dynamic switching state process is useful to understand ET switching phenomenon deeply. Considering power and external condition as well as relevant materials' physical properties, such as thermal conductivity etc, future works need to establish the available model to predict such behaviors in the composites.

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