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Conductive switching behavior of epoxy resin/micron-aluminum particles composites

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Abstract: Epoxy resin (ER)/micron-aluminum particles (MP) composites with different filling concentration of spherical particles were fabricated. The nonlinear conductive behavior of ER/MP composites under increasing applied voltage using the improved V-I method was investigated. Under sufficient high intensity applied constant voltage, the obvious conductive switching behavior of samples with volume fraction 12.7%, 16.9% and 18.9% was found. The conductivity of ER/MP composites increase up to 3–4 orders of magnitude when the conductor-insulator transition occurs. The switching threshold voltage decreases with the increase of volume fraction of MP in the composites. The results show that the ER/MP composites with conductive switching properties are of great potential application in electromagnetic protection of electron devices and systems.

Keywords: conductive paths; conductive switching behavior; conductor-insulator transition; tunnel effect.

1 Introduction

Polymer matrix containing micro/nanometer metal, graphite and other conductive particles have excellent mechanical, electrical and other properties (1–4). The conductor-insulator transition is a well-known phenomenon observed in heterogeneous composites as the extreme change of certain physical properties within a rather narrow concentration range of conductive particles. When the filling concentrations reach a percolation threshold of the conductive particles, the conductivity of composites shows a sharp increase (5).

The research and application of heterogeneous composites filled with conductive particles have attracted plentiful attentions. A sharp change of conductivity has also been found in the composites filled with conductive particles under the strong applied voltage excitation (6, 7). Kiesow and co-workers (8) observed a reversible electronic switching effect in plasma polymer films with embedded silver nanoparticles. White studied reversible resistive switching behavior of silver nanowire-polystyrene nanocomposites with increasing voltage at room temperature (9, 10). Heterogeneous composites filled with conductive particles, with conductive switching properties, have a wide range of applications such as overcurrent protectors, sensors, electromagnetic protection of electron devices and so on.

Actually, the conduction mechanism of polymer composites is complex (11–16). Two theories, namely, the conduction pathway theory and tunnel effect theory or electric field emission theory, are considered the most important theories (17–20). The correspondent relation of tunneling current density, resistivity and electric field intensity was given by Sherman et al. (21), Voet (22), Ezquerra and Kulescza (23) and Simmons (24). The nonlinear conduction behavior in epoxy resin (ER) with graphite nanosheets has been studied and the nonlinear random resistor network (NLRRN) and the dynamic random resistor network (DRRN) models proposed by Gefen et al. (25) were given to explain the nonlinear characteristics by Chen (26, 27). For conductor-insulator transition composites, the tunnel effect theory is considered as the rational conduction mechanism for the sharp change of conductivity excited with the strong applied voltage. However, there is still no theoretical model that can explain and predict the conductive switching properties of conductor-insulator composites completely.

In this paper, considering the advantages of aluminum powder, such as relatively great conductivity, low density and cheap price, the conductive switching behavior of ER/MP composites under increasing applied voltage was investigated. Under sufficient high intensity applied constant voltage, the samples with certain volume fraction of particles show obvious conductive switching effects. Meanwhile, the quantum tunneling theory is used to analyze and explain the repeatable conductive switching behaviors of ER/MP composites.

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2 Sample preparation and measuring circuit

The composites comprising ER and conducting micron-aluminum spherical particles were synthesized in the form of a cylindrical shape. The conducting filler utilized is aluminum particles [Baijujie Science and Technology Instrument Co., Ltd (Shenyang, China) with purity not less than 99.99%] with a mean diameter of about 4 µm (Figure 1) which was measured by a KYKY-EM6200 Scanning Electron Microscope (SEM) (KYKY Technology Co., Ltd., Beijing, China) and a Bettersize 2000 Laser Particle Size Analyzer (Bettersize Instruments Ltd., Dandong, China). In Figure 1A, it can be seen that the shape of micron-aluminum particles (MP) is spherical. The size and size distribution of particles was measured, and the typical diameter was about 3.4 µm. The range of particle size distribution MP were shown in Figure 1B. In Figure 1B, the horizontal axis is the particle size range, and vertical coordinate is the cumulative volume fraction. It can be seen that median diameter (D50) of aluminum particles is 3.57 µm, cumulative percentage of particles diameter from 3 µm to 5 µm is 46.3%.

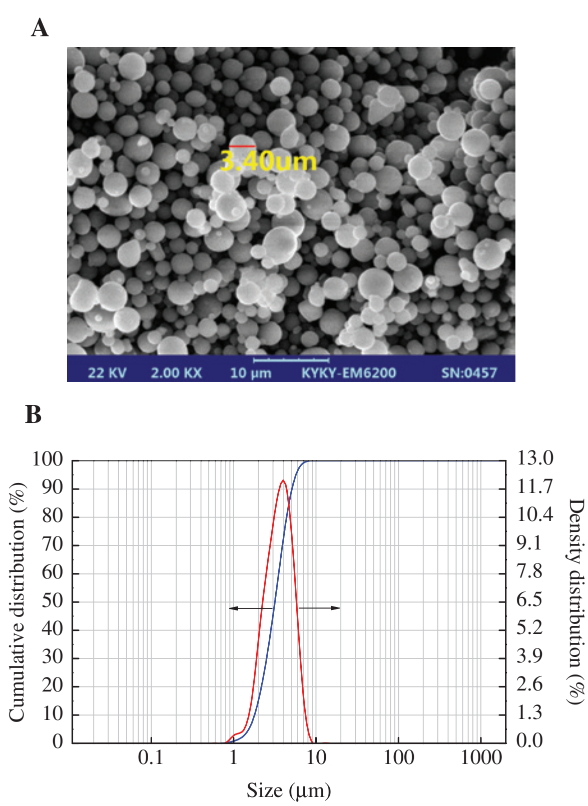

Figure 1: Micron-aluminum particles of (A) SEM image and (B) particle size distribution graph.

It is well known that Al particles are easily oxidized in the open atmosphere, so the oxidation of the MP was measured. The MP were placed in air for 0–48 h, respectively. The six samples were analyzed by an energy dispersive spectrometer (EDS) and the results are shown in Table 1. The results show that, the atomic percentage of the oxygen element of sample No. 1 was only 0.40%, the content of oxygen in MP in the open atmosphere environment tends to be stable after 24 h, indicating that the atoms on the surface of MP can oxidize, but the process of oxidation is very slow. During the experiment, MP exposure time in the open atmosphere environment was <10 min, indicating that the oxidation of MP was not significant. For conductor-insulator composites, the minute oxidation of MP will not affect the conductive switching behavior of ER/MP composites.

The MP were mixed with high purity alcohol (Yongda Chemical Reagent Co., Ltd., Tianjin, China) in a certain proportion and then ultrasonically treated for degreasing. The silane coupling agent (Chuanshi Chemical Co., Ltd., Nanjing, China) was added and stirred for 30 min for surface modification. The pretreated particles were vacuum-dried, incorporated into the ER in an oil bath at 60°C and then stirred for 2 h. The polyamide resin (Hui-Sheng Electronic Materials Co., Ltd., Chuzhou, China) was added to the mixture and then stirred for 10 min. The mixed material was placed in a vacuum oven for 10 min to remove bubbles. The mixture was then transferred to a sample mold mounted on a rotating holder in an oven. The holder was set to rotate at 5 rpm (to prevent sedimentation of the filler) and the oven temperature kept at 60°C for 10 h. The diameter of round samples was about 40 mm and the thickness was about 5 mm.

There is no standard method for measuring and evaluating the conductive switching behavior of composites. The conventional voltmeter-ammeter method cannot be used to test the big variation range of conductivity (several orders of magnitude) under high applied voltage and the accuracy, reliability, repeatability and safety of the measurement system should also be considered. For resistance measurements for the samples, an improved test system based on the voltmeter-ammeter (V-I) method was

Table 1: The element content in micron-aluminum particles.

Time (h)	0	0.5	6	12	24	48
O (Weight %)	0	0.24	0.86	1.47	1.74	1.84
Al (Weight %)	100.00	99.76	99.14	98.53	98.26	98.16
O (Atomic %)	0	0.40	1.44	2.46	2.90	3.06
Al (Atomic %)	100.00	99.60	98.56	97.54	97.10	96.94

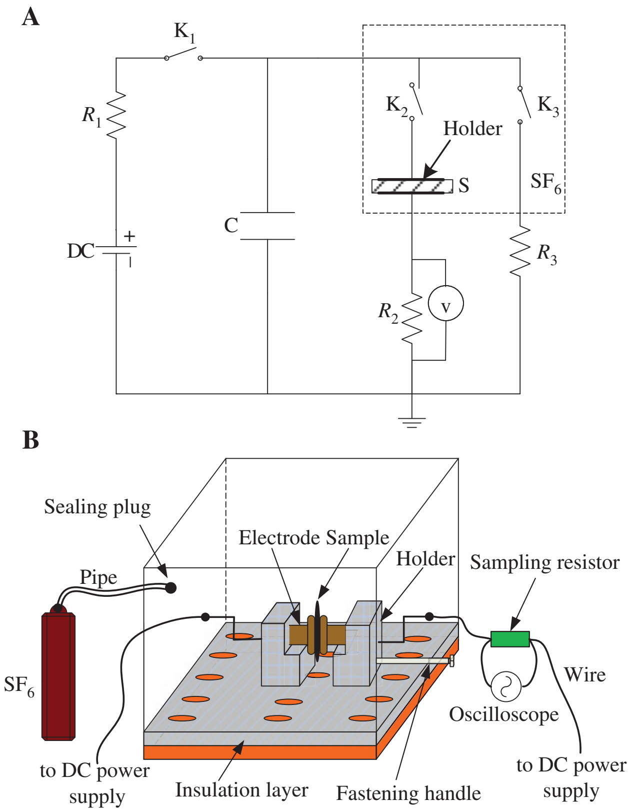

Figure 2: Measuring circuit and experimental setup.
(A) Circuit for conductivity under applied voltage: R_1-current limiting resistor, R_2-sampling resistor, R_3-discharge resistor, S-sample and DC-regulated power supply and (B) experimental setup.

developed (see Figure 2A). K_1, K_2 and K_3 are remote control switches. For protecting NHWY6000-2 DC power supply (Nova Power Instruments Ltd., Jinan, China), a large capacitor is used as the voltage source. To ensure good electrical contact, the silver conductive paint is pasted onto both surfaces of the sample after polishing. The sample (S) and sample holder were placed inside a glass box filled with SF_6 for avoiding discharge between electrodes (holder) (see Figure 2B). Firstly, close the switch K_1, DC power supply charges the capacitor C. After charging, disconnect K_1 and close the switch K_2, the capacitor C discharges the sample. The conductivity and applied voltage of the samples can be calculated by the recorded data. The study of the conductivity nonlinear behavior consists of applying a gradually increasing applied voltage from zero to about the switch-on voltage.

3 Results and discussion

The electrical properties of samples depend on the content and distribution of the conductive particles. The microstructures of samples and dispersed morphology of conductive particles in matrix were observed by SEM, as shown in Figure 3. In Figure 3, the white bright spots in the SEM micrograph are MP on the surface of specimen. The MP in the composite did not show obvious agglomeration. The distance of the MP decreases with the increases of the filling volume concentration. In Figure 3D, it can be seen that although there is local contact between MP in the sample, there is no complete conduction pathway in the composite.

The relationship between conductivity and applied voltage of the samples was shown in Figure 4. To insure the repeatability, each sample was measured twice. For comparison, the conductivity of the sample as a function of the applied voltage has been normalized by the factor σ_0 ($=10^{-7}$ S/m), which stands for the conductivity of the sample without the application of voltage. The conductivity-voltage curves of the composites exhibited three regions. Under low voltages, the conductivity of samples is very small, which implies that free electrons are very few and the conductive pathway is not formed in composites. The conductivity of the sample with the volume fraction of 10.4% remains intrinsically constant with gradually increasing applied voltage from zero to about 1.3 kV. The conductivity of the samples with a volume fraction of 12.7% and 18.9% sharply changes by about 10^3–10^4 times higher when the applied voltage is about 1.0 kV and 0.4 kV. However, for the samples with volume fractions of 12.7%, 16.9% and 18.9%, the conductivity remains nonlinear when the voltage exceeds a critical value, but the growth rate is significantly slowed down. It is also found that conductive switching property is very reproducible. Conductive switching behaviors become more obvious in the second measurement.

The results show that the conductivity of composites performs an obvious conductive switching characteristic within a certain filling concentration range. The conductive switching behavior of the proposed ER/MP composites can be explained such that, with the increase of the applied voltage, the conductive networks can be formed resulting from the quantum tunnel effect in which electrons can hop through the gaps. According to the quantum tunneling theory, Simmons derived a formula for the tunnel current density flow through a generalized barrier which can be expressed as follows (16, 24):

$$J = J_0\left\{\varphi_0 \exp\left(-A\varphi_0^{1/2}\right) - (\varphi_0 + eV)\exp\left[-A(\varphi_0 + eV)^{1/2}\right]\right\} \quad [1]$$

where $J_0 = e/2\pi h(\beta\Delta s)^2$, $A = (4\pi\beta\Delta s/h)(2m)^{1/2}$, φ_0 is the mean height of barrier, m and e are the mass and charge of electron, β is the correction factor, Δs is the width of the barrier. According to the general formula of the tunneling conduction equation, the tunnel current density is exponentially

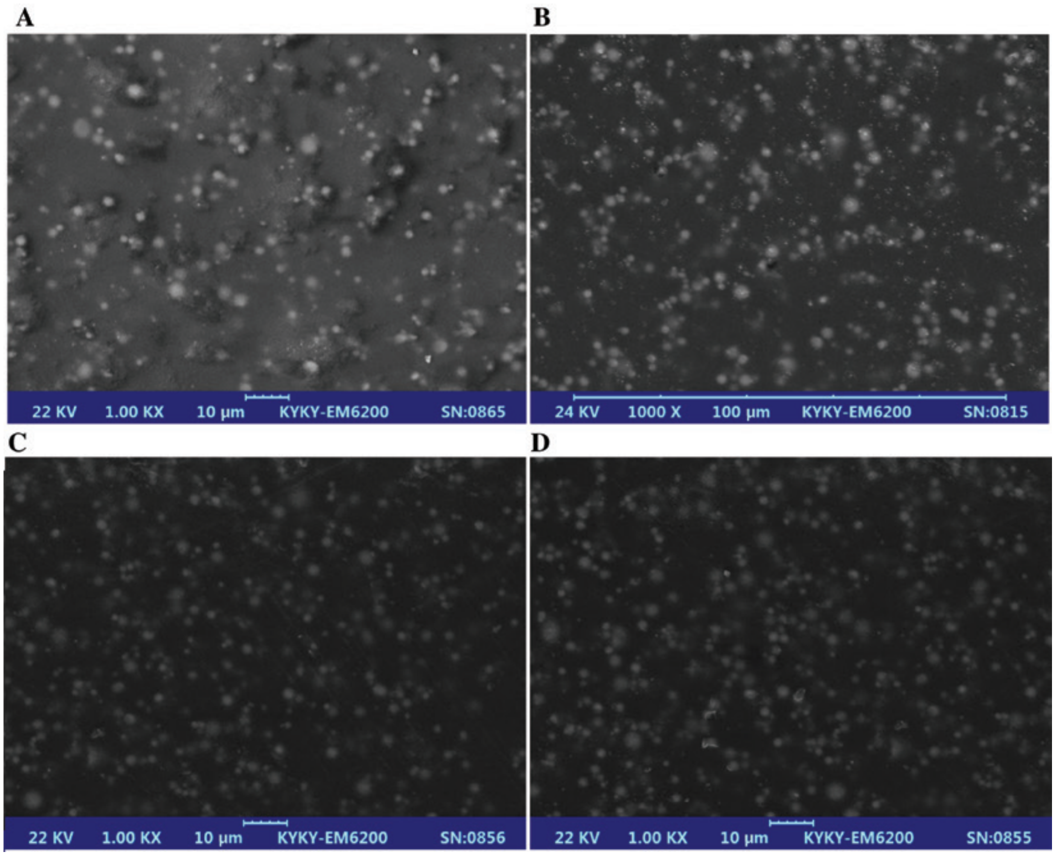

Figure 3: SEM images of ER/MP composites: (A) volume concentration of 10.5%, (B) volume concentration of 12.7%, (C) volume concentration of 16.9% and (D) volume concentration of 18.9%.

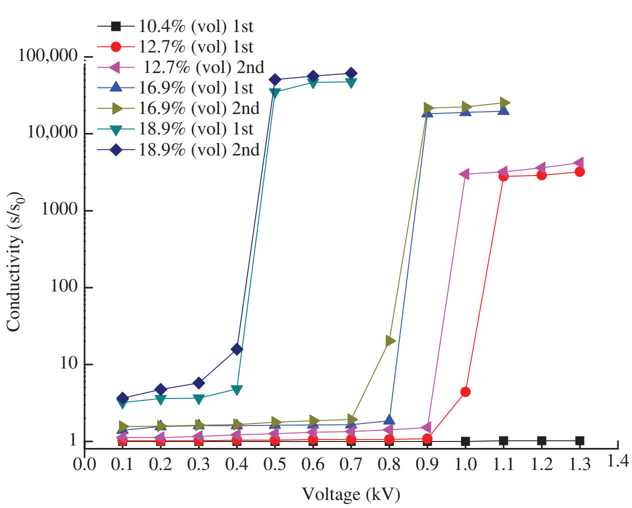

Figure 4: Conductivity-voltage curve of ER/MP.

related to the applied voltage. The higher the concentration of conductive particles in the composite material, the smaller the spacing of the conductive particles. Under applied voltage, the potential of the electrons in the conductive particles can be significantly increased. When the voltage reaches a critical level, the electrons in the conductive particles have sufficient energy, a large amount of electrons hop to the adjacent conductive particles, generate tunnel currents and form conductive paths. The conductivity of the composite materials is exponentially increased. As the voltage exceeds the critical level, the hopping electron tended to be nearly saturated and meanwhile, the growth rate of conductivity is significantly slowed down.

The results demonstrate that higher filling concentration will lead to shorter distance between the conductive particles inside the composite, lower energy required to penetrate the barrier and lower switch-on voltage being needed. The conductive behaviors of materials prepared in this paper is more sensitive to applied voltage and have greater nonlinear coefficients than those in the literature (26).

4 Conclusions

The conductive switching behavior of ER/MP composites under increasing applied voltage was investigated. With the increase of filling volume concentration of conductive particles, two distinct conductivity curves were observed with the increases of applied voltages. The samples with volume fractions of 12.7%, 16.9% and 18.9% show obvious conductive switching effects, and the conductivity magnitude of ER/MP composites increases for 10^3–10^4 times during the conductor-insulator transition. The switching threshold voltage value decreases with the increasing volume fraction of MP in the composites. The conductive switching behavior can be explained by formation of the conductive network resulting from the quantum tunnel effect where electrons can hop through the gaps under sufficient high applied constant voltage. The results show that the ER/MP composites with conductive switching properties have great potential applications in electromagnetic protection of electron devices and systems. The comprehensive adjustment of switch-on voltage and conductivity of the ER/MP composites will be investigated in our future research.

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