Nonlinear Conductive Behaviour of Silver Nanowires/Silicone Rubber Composites

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Abstract. Silver nanowires with an average length of 10 μm and diameter of about 90 nm have been synthesized by polyol reduction of silver nitrate in the presence of polyvinylpyrrolidone(PVP). Silver nanowires (AgNWs)/silicone rubber (SR) composites have been made by mixing silver nanowires into silicone rubber. The nonlinear response of AgNWs/SR composites under high electric field is investigated. The nonlinear Conductive behavior of composites is considered as a competitive process of several effects. From the perspective of the microstructure of composites, the conductive path is established by the quantum tunnel effect between silver nanowires. The influence factors on the conductivity of composites are discussed and analyzed. The results show that the AgNWs/SR composites with nonlinear conductive properties are of great potential application in electromagnetic protection of electron device and system.

1. Introduction

The unique thermal, optical, electrical, magnetic, catalytic and sensitive properties of silver nanowires have attracted a great deal of interest from chemists, physicists and material scientists. In particular, silver nanowires have high specific surface area and surface activity [1, 2]. The polymer matrix composites filled with silver, graphene and other conductive particles have excellent mechanical, electrical and other properties [3-5]. When the filling concentrations reach a percolation threshold, the conductivity of composites shows a sharp increase. When the conductive particles concentrations less than and closed to percolation threshold, the conductivity of composites has a special nonlinear conductive characteristic. Composites filled with conductive particles, with a special nonlinear conductive characteristic, have a wide range of applications such as overcurrent protectors, sensors, electromagnetic protection of electron devices and so on.

The conductive mechanism of polymer matrix composites is very complex [6-8]. The nonlinear conductive behavior of composites under strong field is a hot and difficult academic research in recent years. The conduction mechanisms of polymer composites have been discussed theoretically and technically. The correspondent relation of tunneling current density, resistivity and electric field intensity was given by Sherman, Voet, Ezquerra and Simmons, et al [9-12]. Beek and co-workers considered that when the distance between conductive particles is less than 10 nm, an internal electric field can be generated from strong electric field between these conductive particles [13]. The electrons can be induced to the neighboring conductive particles by internal electric field, and the tunneling current density formula is described the form:

$$J = AE^{n}\exp(-B/E). \tag{1}$$

Where E is electric field intensity, A, B, n are constants. Actually, the conduction mechanism of polymer composites is complex. It is generally believed that the conductive process of composite materials is the combined effect of several conductive mechanisms, and the conductive mechanisms that play a leading role in different situations are also different.

At present, the main methods for synthesizing one-dimensional silver nanowires including wet chemical synthesis, electrochemical deposition, hydrothermal method, template method and polyol method. Among them, the polyol method has the advantages of simple preparation method, relatively fast reaction rate and mild conditions And so on. In this paper, the Synthesis silver nanowires by the method of polyol and nonlinear conductive behavior of AgNWs/SR composites were studied.

2. Experimental Section

2.1. Materials
Ethylene glycol(AR) (EG) and Ethanol absolute(AR) were purchased from Tianjin Yongda Chemical Reagent Co.,Ltd. PVP was purchased from Aladdin Industrial Iorporation. Silver nitrate(AR) and Tetraethyl orthosilicate(AR) (TEOS) were purchased from Sinopharm Chemical Reagent Co.,Ltd. Silicone rubber was purchased from Shanghai Silicon Mountain Macromolecular Materials Co.,Ltd. Dibutyltin dilaurate were purchased from Tianjin Bodi Reagent Co.,Ltd. Scanning Electron Microscopy(SEM) was carried out with a Zeiss Gemini 300FE-SEM.

2.2. Sample Preparation
The preparation procedure of the Ag nanowires was described as follows: Firstly, 0.2 g of PVP and 25 ml EG were stirred for 4~5 h until completely dissolved. After that, 0.25g silver nitrate was added and stirred for about 1h. 3.5 ml 600 μM $FeCl_3$/EG solution was added to the mixture and stirred for about 5 minutes until the mixture is homogeneous. The mixture was poured into a 250 ml round bottom flask and placed in oil bath at 130°C for 5 h. When the reaction finished, the AgNWs suspension was diluted with ethanol (200 mL) and ultrasound for about 30 min. After that, the AgNWs suspension was centrifuged at 3500r/min for about 15 min, and the supernatant was removed. This procedure was repeated twice to remove the EG and excess PVP. The SEM images were obtained using Zeiss Gemini 300FE-SEM.

Add KH-550 to silver nanowires and ultrasonic treatment; the treated silver nanowires were freeze -dried, and then added to the silicone rubber directly. Cross-linking agent TEOS and catalyst dibutyltin dilaurate were added to the mixture in a certain percentage and then stirred 10min. The samples were put into vacuum oven to remove bubbles during the curing process. Finally, the samples were poured into the mold, and vulcanized after 24 hours.

2.3. Measurements
Under high electrical fields, samples testing cannot be performed using conventional test methods, as The composites conductivity has a nonlinear characteristic, and the accuracy, reliability, repeatability, and safety of the measurement system are also take into account. A test system based on electrostatic high voltage source and copper electrode fixture was designed, as shown in Figure 1. In order to protect NHWY6000-2 DC power supply (Nova Power Instruments Ltd., China), a large capacitor is used as the electric field source. In the circuit, R_1 is used as current limiting resistor. The electric current passing through the sample was collected with multimeter. To avoid any skin effect, the surfaces of the sample are polished with 1500-grit sandpaper, and silver conductive paint is used to ensure good electrical contact. The study of the conductivity nonlinear behavior consists of applying a gradually increasing applied voltage.
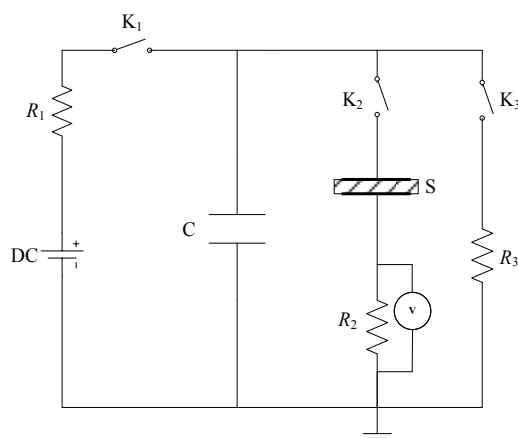
Figure 1. Measurement circuit for conductivity under high electric field: R_1-current limiting resistor, R_2-sampling resistor, R_3-discharge resistor, S-sample and DC-regulated power supply.

3. Results

The microstructure of silver nanowires was observed by scanning electron microscope (SEM), as shown in Figure 2. The heated ethylene glycol solution has the ability to reduce the metal ions in the metal salts to metal atoms. Fe^{3+} as a control reagent for oxidative etching regulates the transition from monocrystalline seeds to twinned seeds. During the growth of silver nanowires, PVP as a surfactant can not only make the silver nanowires grow anisotropically along the {1, 1, 1} plane, but also inhibit the agglomeration of nuclei in the early stage of the reaction. In Figure 2, the average length of silver nanowires was about 10μm and the average diameter was about 90 nm.
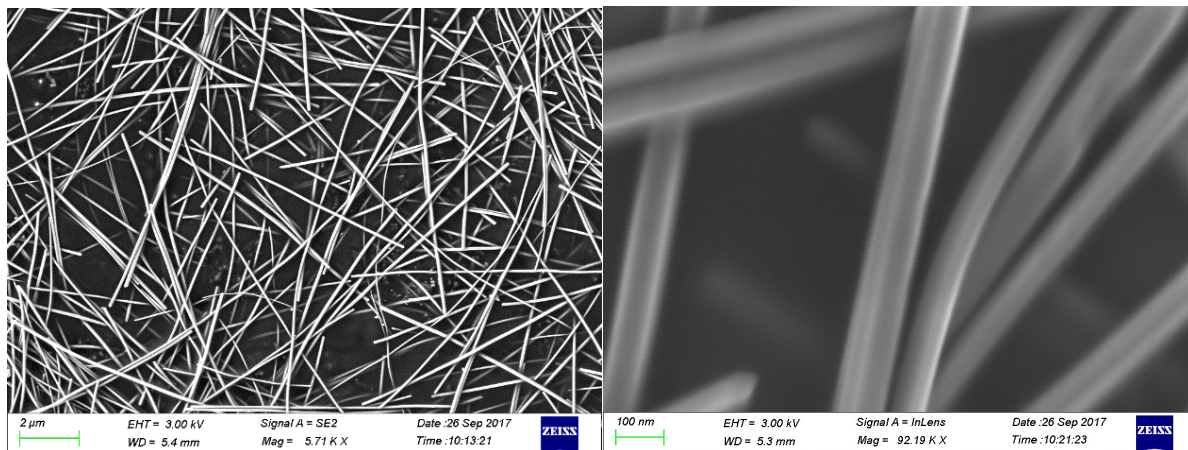
Figure 2. SEM images of silver nanowires.

Silver content in the composite samples was measured by the potentiometric titration. It can be seen from Figure 3, as the concentration of the silver nanowires increases, the conductivity of composites increases. The conductivity of sample with the Volume fraction of 0.68% is very small. With the increase of electric field intensity, the conductivity of composite remains intrinsic constant, that is, free electrons are very few and conductive pathway is not formed in composites. The conductivity of the sample with volume fraction of 1.05% increased about 10 times with the electric field intensity is about 10kV·m^{-1} to 14kV·m^{-1}. When the electric field intensity exceeds 14kV·m^{-1}, the conductivity remains nonlinear, but the growth rate is significantly slowed down. The conductivity of the sample with volume fraction of 1.31% increased about three orders of magnitude with the electric field intensity is about 7kV·m^{-1} to 11kV·m^{-1}. When the electric field intensity exceeds 11kV·m^{-1}, the conductivity remains nonlinear, but the growth rate is also significantly slowed down. For the sample

with volume fraction of 2.06%, the conductivity is much greater than others. As the electric field intensity increased, the conductivity increased slowly. The results show that when the concentration of conductive particles in the composite material closes to percolation threshold, the spacing of the conductive particles is very small. The larger the filling concentration, the shorter distance between the particles, lower energy required to penetrate the barrier, the larger growth rate of conductivity. As the electric field intensity exceeds the critical level, the hopping electron tended to be nearly saturated and meanwhile, the growth rate of conductivity is significantly slowed down.
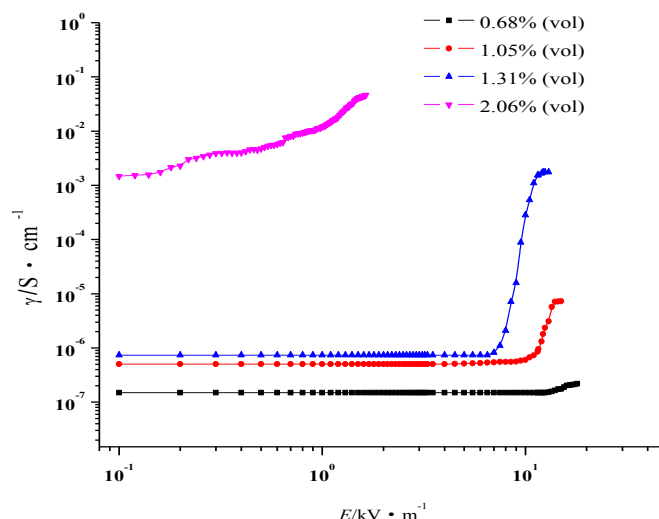
Figure 3. Conductivity-electric field intensity curve of composites.

4. Conclusions

The nonlinear DC response in AgNWs/SR composites under increasing electric field intensity was investigated. With the increase of Volume concentration of conductive particles, the samples show obvious conductive nonlinear effects. The nonlinear conduction behavior of the composites is considered as a competitive process of several effects. With the increase of applied electric field intensity, the conductivity of composites increased gradually, and moreover, the increased rate increases. The conductive behavior of composites is often the result of many conductive mechanisms acting together and competing. Theoretical modeling of quantum tunneling based on microcosmic conditions of materials can reasonably explain the nonlinear conduction behavior of many composites. In the next step, we should get the quantum tunneling effect model on the basis of the experiment.

5. References

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