Electrical properties of nano-silver/polyacrylamide/ethylene vinyl acetate composite

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Abstract Nano-Ag particles/polyacrylamide (PAM) composites were synthesized by γ irradiation method and then blended with ethylene vinyl acetate (EVA). Dielectric behaviors of the Ag/PAM/EVA composites are investigated as a function of both the concentration and size of Ag particles. When concentration of the Ag fillers is rarely low, dielectric anomalies were first observed in contrast to the traditional percolation theory. As concentration of Ag increases, volume resistivity and breakdown field strength are enhanced, loss tangent (tan δ) reduced and dielectric constant kept invariable. In addition, the above variation became larger when the diameter of the Ag nano-particles is smaller. Such dielectric anomalies may be understood by considering the unique “Coulomb Blockade Effect” of the nano-sized Ag particles.

Keywords nano-silver (Ag), dielectrics, composite, electrical property.

1 Introduction

Metal-polymer composites have attracted much attention because they can possess high dielectric constant while retaining flexibility of the polymer matrix[1−3]. With this feature, the metal-polymer composites have broad applications such as electrostrictive materials, charge-storage capacitor and gate dielectric of semiconductor devices[4−6]. In view of these applications, previous investigations are most concentrated on enhancing dielectric constant and reducing percolation threshold of the composites. The composites studied are correspondingly those with high filler concentration, e.g., near 17 vol% (0.17 volume fraction)[1], 9 vol%[2] and 20 vol%[3], etc.

The metal-polymer composite undergoes a metal-insulator transition at a certain concentration of its metallic phase (i.e., the percolation threshold), which is often characterized by an abrupt drop of resistivity and a divergence of the real part of the dielectric constant[2]. Such transition is attributed to the formation of the continuous conductive network in the composites and is commonly studied with the famous power law of the percolation theory. In this paper, we report an interesting phenomenon that when the content of the conductive filler is at a certain low concentration, the dielectric behavior of the metal-polymer composite exhibits characteristics in contrast to the percolation theory, i.e., as the concentration of Ag increases, the volume resistivity and breakdown field strength enhanced, loss tangent (tan δ) reduced and dielectric constant kept invariable. In addition, the above variation became larger when the diameter of the Ag nano-particles is smaller.

2 Experiment

The AgNO₃ solutions with different concentration (0.01~0.13 M) are mixed with 3 M acrylamide monomer and radical scavenger and then irradiated with 3 × 10⁴ Gy in the field of a 2.59 × 10¹⁵ Bq ⁶⁰Co γ-ray source. The diameter of the Ag nano-particles can be well controlled by either the reaction ratio or the time of radiation. The obtained gelatinous solid mixtures are dried in oven at 100 °C for 72 h and milled into grains with a diameter smaller than 45 µm.

The polyacrylamide (PAM) is known as a hard and brittle material thus the above Ag/PAM composites cannot be hot-molded into samples that are appropriate for dielectric measurements. Thus, ethylene vinyl acetate (EVA) (modified PE, vinyl acetate is 28%) is selected as stick matrix to form the final composite. At this time, the Ag concentration of Ag/PAM/EVA composite can be well controlled by either the reaction ratio or the time of radiation. The mixture of PAM and EVA is selected as the control sample for the dielectric measurements.

Ag/PAM and EVA are blended together on a HAAKE-90 rheometer at 130 °C with a rotor speed of 60 r/min for 10 min, and then molded with a hot-pressing procedure at 170 °C. The final samples are square plate with a side length of 100 mm and a thick-
ness of about 1 mm. Aluminum foils were pasted onto both side of the samples using vaseline to form three-electrode system for the electrical measurement according to the IEEE standard. Resistance of the sample is measured by high resistance meter ZC36. Strength of the breakdown field is measured by power frequency voltage instrument. The parameters $\tan \delta$ and $\varepsilon_r$ are measured by QS-36 Schering bridge.

3 Results and discussion

Fig.1 shows a transmission electron microscope (TEM) photo of Ag/PAM/EVA composite with Ag concentration of 0.05wt%. From the photo it is evident that the Ag nano-particles with an average diameter of about 20 nm dispersed uniformly in solution. Fig.2 shows XRD pattern of the nano-composite. It can be seen that the sample is composed of two phases, i.e., the metallic silver as indicated by diffraction peaks (111), (200), (220), (311) and non-crystalline polyacrylamide.

Nano-sized particles tend to agglomerate because of their high surface energy[7]. Thus, it is quite difficult to prepare nano-particles with both tiny size and homogeneous dispersion. Traditionally, the polymer matrix and metal nano-particles are synthesized separately and then hybridized physically to form polymer-metal nanocomposites, which may lead to the non-uniform dispersion of the metal particles in the polymer matrix. In addition, the nano-particles in the composite prepared by such procedures usually agglomerated and the diameter of them often exceeds 100 nm[8].

In the presented synthesizing procedure, the metal salt and organic monomer are mixed homogeneously at the molecule level in the solution, which made the formation of crystalline metal nano-particles and polymerization of monomers proceeded simultaneously. The macromolecular chains of the polyacrylamide on the surface of Ag nano-particles prevent them from agglomerating. Thus a homogeneous dispersion of nanocrystalline metal particles in the polymer matrix is realized perfectly.

Fig.3 shows the volume resistivity (hereinafter, the resistivity) of the Ag/PAM/EVA composites plotted versus the weight concentration of Ag measured at both room temperature and cryogenic temperature. The average diameter of the Ag nano-particles in the composites studied is about 10 nm. At room temperature, when the content of Ag is below $2 \times 10^{-2}$ wt%, the resistivity varies little compared with pure EVA. When the content of Ag is between $2 \times 10^{-2}$ wt% and $5 \times 10^{-2}$ wt%, the resistivity rises obviously and reaches a peak value when the content of Ag is $5 \times 10^{-2}$ wt%. The value of the peak is $4.5 \times 10^8 \ \Omega \cdot m$, which is almost 4 times larger than that of EVA matrix ($0.8 \times 10^8 \ \Omega \cdot m$). Nevertheless, the resistivity of the composite decreases gradually when the content of Ag is more than 0.025%. At cryogenic temperature (77 K), the resistivity curve resembles that measured at the room temperature with a peak value of $9 \times 10^{13} \ \Omega \cdot m$. Compared with the resistivity of pure EVA at cryogenic temperature ($1.5 \times 10^{13} \ \Omega \cdot m$), it is 6 times larger. In order to study the effect of the particle size on the dielectric behavior of the Ag/PAM/EVA composites, the resistivity of composites with Ag particles of 20 nm in diameter is also measured as a function of the weight fraction of Ag at both room temperature and cryogenic temperature, as shown in Fig.4. It clearly exhibits the similar characteristics with that of the composites with 10 nm Ag nano-particles, while only the enhancement of the resistivity is a little smaller than that of the composites with 10 nm Ag nano-particles. The