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Ultrahigh dielectric loss of epsilon-negative copper granular composites

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ABSTRACT

Loss materials have great potential applications in electromagnetic wave absorption and attenuation. In this paper, we report an epsilon-negative composite that has very high dielectric loss (tan $\delta \sim 100$@10 MHz). This percolative polymer composite is filled with spherical micron-sized copper particles. Below the percolation threshold, conductivity spectra showed obvious frequency dispersion and conformed to the Jonscher's power law, indicating hopping conduction. When composites reached up to percolated state, the conduction mechanism changed to electron-like conduction. It is suggested that the electron transfer between copper particles leads to a very high loss of the composites.

1. Introduction

Recently, epsilon-negative (ENG) materials with negative permittivity (ε) but positive permeability (μ) whose electromagnetic features are distinct from the conventional materials have drawn extensive attentions, especially in microwave frequency region. ENG can be obtained in metamaterials with artificial constructed arrays of split-ring resonators and thin metal wires [1]. Simultaneously, attributed to the formation of random metallic networks, random composites successfully achieved ENG such as Ag/Al_2O_3, Ni/Al_2O_3 [2–8]. Majority of the researches have been focused on the real part of permittivity and to enable the creation of an ENG material. However, there are very few research works that have paid attentions to the application of ENG materials in electromagnetic-wave absorption and attenuation [9,10].

Loss materials have been widely used in microwave electronics for suppression of electromagnetic interference (EMI) and electromagnetic compatibility (EMC) purposes, e.g., microwave absorbing coated on the exterior surfaces of military aircrafts and vehicles. In order to avoid detection by radars, zero-reflection is demanded, which requires proper dielectric permittivity at a given frequency. Hence, it is significant to tune the dielectric constant and dielectric loss to obtain both specific frequency-matching and attenuation characteristics [11–16]. In this letter, we show a ENG material with relatively low dielectric constant and high dielectric loss.

Polymers have a very low concentration of free charge carriers, and thus are non-conductive and transparent to electromagnetic radiation. The conductivity of the composite materials predominantly depends on the content and properties of the conductive filler. The most general approach to description of charge transport in composites is provided by the percolation theory, which responds the influence of the content of conductive particles [17–21]. The randomly distributed metal fillers form clusters (conducting networks) within the matrix. The conduction network becomes continuous as the conductive component content exceeds percolation threshold. When the conductive component content beyond but near percolation threshold, ENG appear as a result of the plasma oscillation of conduction electrons provided by the conductive component.

In this work, we are introducing a copper/epoxy granular composite with significantly high dielectric loss. Because size and shape both play an important role in influencing the electric property [18,22], spherical micron-sized copper particle were chosen as the conductive filler due to its unique shapes and perfect conductivity. Special attention is paid to elucidation of the negative permittivity appeared in the composites with copper contents of 60 vol%.

2. Material and methods

The copper granular composites were prepared by mixing different volume fractions concentrations of 1 μm copper powders with bisphenol a epoxy resin (thermosetting resin) using hot compression molding method. All the samples were homogenized by being cryomilled (ball-milled at liquid nitrogen temperature) for 5 min. The homogenized mixture was compacted in a mold with a 30 MPa pressure for 10 min at 100 °C.The composites with

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14 vol%, 28 vol%, 40 vol%, 55 vol% and 60 vol% copper content were prepared, and denoted as Cu14, Cu 28, Cu 40, Cu 55 and Cu 60, respectively.

The cryomilling was carried out by a cryomill (Retsch, Germany). The microstructure of bulks was investigated by SU-70 field emission scanning electron microscopy (FESEM). The impedance properties of the sample at room temperature in the frequency range from 10 MHz to 1 GHz were determined using Agilent E4991A precision impedance analyzer (Agilent Technologies) equipped with 16453A dielectric test fixture. In order to determine the permittivity vs. frequency or various kinds of dielectric parameters, the dielectric test fixture of 16453A was used under AC voltage 100 mV, and the samples were processed into square discs (16 mm × 16 mm × 2 mm). During the measurement, the real part (ε_r') and imaginative part (ε_r'') of permittivity were calculated by $\varepsilon_r' = Cd/\varepsilon_0 A$ and $\varepsilon_r'' = d/RA2\pi f\varepsilon_0$, where d is the sample thickness, C is the capacitance, R is the resistance, A is the electrode plate area, f is the frequency and ε_0 is the absolute permittivity of free space (8.85×10^{-12} F/m). The frequency dispersions of the real part of ac conductivity was determined by $\sigma'_{ac} = d/RA$, where d is the sample thickness and R is resistance, A is the electrode plate area.

3. Results and discussion

The SEM images of copper powders are shown in the inset of Fig. 1(**b**). Compared with traditional sheet-shape particles, the copper powders show spherical shape. It can be observed that the size of spherical copper powders is 1 μm. The frequency dispersions of the real part of ac conductivity at frequency range from 10 MHz to 1 GHz are shown in Fig. 1(**a**). The increasing of the

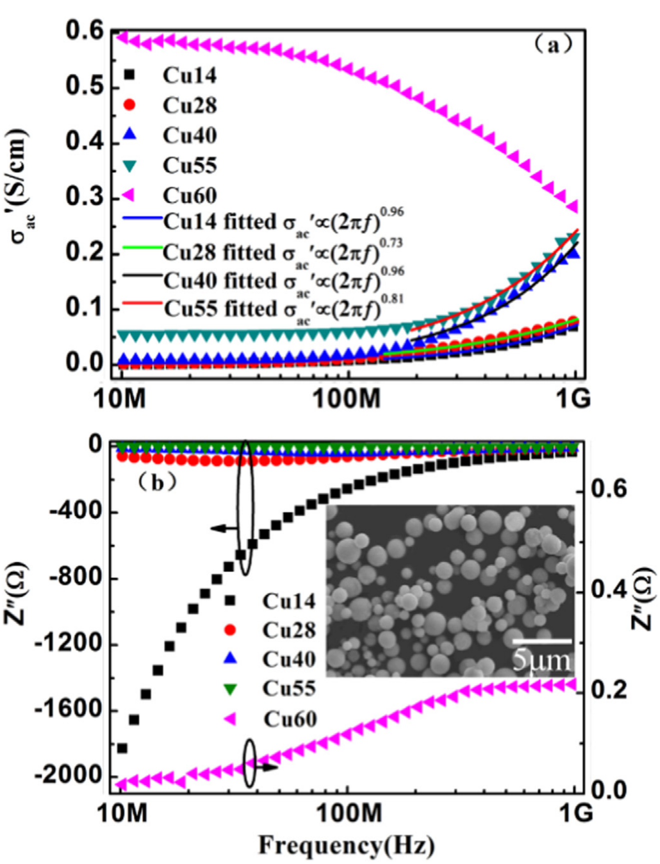

Fig. 1. Frequency dependence of ac conductivity σ′ac (a) and reactance (b) for copper granular composite.

copper content results in the improvement of conductivity. It also can be found that the frequency dispersion behavior of the conductivity within a certain range of frequency, represents an extension of the universal law, namely, the Jonscher power law in the form of $\sigma'_{ac}(f) \propto (2\pi f)^n$ with a different power-law index of n ($0.5 < n < 1$). The $\sigma'_{ac}(f)$ exhibits a characteristic of plateau in the low-frequency regime and a frequency dispersion in the high-frequency regime with an onset frequency that is a function of the materials. The σ_{ac} of Cu14, Cu 28, Cu 40 and Cu 55 are proportional to the frequency and the fitted results (shown as the solid line in Fig. 1(**a**)) are in good agreement with Jonscher power law. The value of the exponent n is 0.96, 0.73, 0.96 and 0.81, respectively, shows that the conductive mechanism is hopping conduction. That is electrons implement macroscopic conductivity via hopping between adjacent copper under the effect of high frequency electric field.

When copper content exceeds the percolation threshold (in samples Cu 60), the conductivity is inversely proportional to frequency due to the skin effect of conduction electrons, which is similar to the free electron conduction. The formula of skin depth is described as $\delta = 2/\sigma_{dc}\mu\omega$, where δ is the skin depth, ω is angular frequency ($\omega = 2\pi f$), σ_{dc} is dc conductivity, and μ is static permeability of composites. With the increase of frequency, the skin depth would reduce, leading to the enhancement of skin effect, so the σ_{ac} gradually decreases and the conductive mechanism changes from hopping to metal-like conduction.

The frequency dependencies of reactance Z'' for the composites were also investigated. Inductance L is determined by conductive electrons in metallic networks, while capacitance C is determined by polarized electrons.

As shown in Fig. 1(**b**), the reactance of composites with low copper content (Cu14, Cu28, Cu40, Cu55) are negative, indicating a capacitive character. By contrast, the reactance of Cu60 is positive which manifest an inductive character. Inductance L is determined by conductive electrons in metallic networks, while capacitance C is determined by polarized electrons. The capacitive-inductive transformation also indicates the existence of the percolation threshold.

The dielectric spectra of copper granular composite with different copper contents are presented in Fig. 2. It can be seen from Fig. 2(**a**) that, the real permittivity ε_r' is positive because the electrons are localized for the metallic region isolated by epoxy and increases upon increasing content. Meanwhile, ε_r' value decreases as the frequency switched from 10 MHz to 1 GHz.

Accordingly, the dielectric loss tangent ($\tan\delta$) can be calculated as $\tan\delta = 1/2\pi f RC$, where δ is the dielectric loss angle, C is the capacitance, R is the resistance, f is the frequency. The copper granular composite below percolation threshold show dielectric loss tangent in the range of 0.02–0.1 due to the weak polar polymer matrix material.

Fig. 3(**a**) shows the negative permittivity of copper granular composite with high copper content. Negative permittivity was usually considered to realize by continuous conducting metal wires. Electrons in the thin conducting wires resonate with the parallel electric field and give negative permittivity below the plasma frequency. In composites with low metallic content, electrons were localized in isolated metallic region because the copper particles were surrounded by disordered epoxy regions. Electrons remained localized within the domain to form mini capacitors rather than hop to adjacent metallic regions. While in Cu60, copper was dispersed well and formed a continuous conducting pathway. Electrons were delocalized and allowed to make long-range movements. Thus, the dielectric constant became negative, showing inductive behaviors.

Theoretically, the plasma-like negative permittivity behavior can be described by Drude model, which gives a frequency