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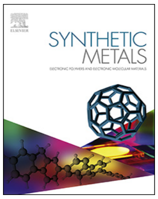

Regulation mechanism of negative permittivity in poly (p-phenylene sulfide)/multiwall carbon nanotubes composites

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ABSTRACT

Negative permittivity behavior has attracted extensive attention recently owing to its remarkable properties and potential for developing metamaterials. In this paper, the relative complex permittivity and ac conductivity of poly (*p*-phenylene sulfide)/multiwall carbon nanotube composites were investigated. Both the negative permittivity and ac conductivity behaviors could be explained by Drude model which was attributed to the low frequency plasmons. Small negative values of permittivity have been observed by controlling the multiwall carbon nanotubes contents, meanwhile the weakly negative permittivity possessing good frequency stability. This work provides an alternative to achieve tunable and weakly negative permittivity for the polymer based composites.

1. Introduction

Nowadays metamaterials with negative permittivity or/and permeability have catalyzed plenty of potential applications in various radio, microwave and optical devices, because of their novel physical phenomena, such as inverse Doppler effect, negative refraction, and perfect absorption etc. [1–5]. Negative permittivity is mostly associated with negative refractive [6], invisibility cloaking in electromagnetism or optics and new high-k capacitances [7–9]. As matter of fact, the negative permittivity has already been implemented by collective oscillations of free electrons in metals in ultraviolet and visible spectrum which is known as plasmons [10]. However, at lower frequency, the permittivity of metal is essentially imaginary, and negative permittivity behaviors are unusual seen in naturally occurring materials. This have been changed since 1996 with the idea of realizing the low frequency plasmons at GHz band in periodic thin wires [11]. Then a structure containing 3D network of thin wires exhibits low frequency plasmons at GHz which shows negative permittivity below the plasma frequency [12]. However, for metamaterial, negative permittivity derived from the periodic structure, rather than materials' property. Hence, negative permittivity established from intrinsic characteristic of materials attracted substantive attention from material researchers.

Zhong et al. [13] achieved negative permittivity in polyetherimide/carbon nanofiber composites sweep through a frequency range of 0.1 kHz–3 MHz. Our group first reported negative permittivity in 10MHz-1 GHz frequency range in cermet due to the conductive networks formed beyond the percolation threshold [14,15]. Tsutaoka et al. notarized low frequency plasmons state in Cu/YIG granular composites with negative permittivity when the Cu contents above the percolation threshold [16]. Gu et al. [17,18] and Qiu et al. [19–21] also did a monumental amount work in polymer based composites with negative permittivity. Inspired by recent progress in intrinsic metamaterials, there are still much challenges in practical application. Such as negative permittivity is strongly sensitive to the frequency, which is undesired in many electronic devices. In addition, extremely negative permittivity blocks the impedance matching for microwave applications and perfect absorption. On the above basis, we focus on realization of the weakly negative permittivity with frequency nearly independent.

Poly (*p*-phenylene sulfide) (PPS) is an engineering plastics which is widely applied in commercial and industrial fields due to its outstanding thermal stability, excellent corrosion resistance, good flame resistance, and non-toxic [22,23]. Great progress has been made to improve its performance by addition of fillers into PPS, especially carbon nanotube (CNT) is extensively used as reinforcement fillers on account of its extraordinary electrical, thermal and mechanical properties [24]. For instance, single-walled carbon nanotubes were

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homogeneous dispersed in PPS matrix with increasing thermal conductivity and mechanical behavior [25]. Also improved compatibility of the PPS with other polymers was found through adding multi-walled carbon nanotubes (MWCNTs) [26–28]. However, the dielectric property of PPS/MWCNTs composites is rarely studied, not to mention the negative permittivity behavior. High aspect ratio of CNT helps in attaining the percolation threshold at very low filler concentrations, so a percolation threshold about 2 wt% was reported in PPS/MWCNTs composites [29]. And as a side benefit, negative permittivity could be extensive tuned due to the low percolation threshold

In this paper, the PPS/MWCNTs composites were prepared by hot-press processing. And we focus on the negative permittivity behavior of this percolative composites. The fundamentals of negative permittivity have been investigated, and effects of MWCNT contents on permittivity, ac conductivity and reactance are discussed in detail.

2. Experimental

2.1. Materials and sample preparation

Matrix materials PPS powders were purchased from Ticona (6165A6NC, America), the average powder dimension of PPS is about 10–15 μm. MWCNTs were supplied by Chengdu Organic Chemicals Co. Ltd. without any further purification. Each MWCNT was about 10–20 μm length and 50 nm in outside diameter. Purity was over 98% based on the manufacturer's specification. PPS with different mass ratio of MWCNTs (from 20 wt% to 60 wt%) were mixed completely by a high-energy ball milling (CryoMill, Retsch, Germany) with a speed 20 r/s and 4 min. Then the mixed powders were hot-pressed in a mold with a vent at the bottom at 300 °C and 30 MPa. The voids are removed by10 mines pressure maintaining and the voids in melted polymer are crowd into the flow channel module slot. The pressed cylindrical disks were 15 mm in diameter and about 2 mm in thickness. Dense composites of PPS with the density of 1.34 $g.cm^{-3}$ (20 wt% MWCNTs), 1.35 $g.cm^{-3}$ (30 wt% MWCNTs), 1.37 $g.cm^{-3}$ (40 wt% MWCNTs), 1.39 $g.cm^{-3}$ (50 wt% MWCNTs), 1.41 $g.cm^{-3}$ (60 wt% MWCNTs) are obtained.

2.2. Characterization and electrical measurement

The microstructures of samples were investigated by an SU-70 field emission scanning electron microscopy (FESEM). The chemical compositions were performed using Fourier transform infrared (FTIR) spectra (IRPrestige-21, Shimadzu, Japan) with KBr pellets method.

The dielectric property, ac conductivity and reactance were examined by Agilent E4991 A RF Impendence/Materials Analyzer equipped with 16,453 A test fixture. The complex permittivity and ac conductivity were calculated from following equation,

$$\varepsilon_r{}' = \frac{Cd}{\varepsilon_0 A} \tag{1}$$

$$\varepsilon_r{}'' = \frac{d}{RA2\pi f\varepsilon_0} \tag{2}$$

where d is sample thickness, C is the capacitance, A is the electrode plate area, ε_0 is the vacuum dielectric constant (8.85×10^{-12} F m^{-1}), R is the resistance, and f is the frequency of the electric field.

3. Results and discussion

Fig.1a shows the FTIR spectra of samples with the range of 400–2000 cm^{-1}. The peaks centered at 1639 and 756 cm^{-1} region assigned to typical MWCNTs [30]. In addition, the peaks at 1730 and 1449 cm^{-1} are corresponding to the vibrational modes of MWCNTs [31,32]. The characteristic peak at 1074 cm^{-1} is due to the telescopic vibrations of sulfoxide and the feature peaks at 1182 and 544 cm^{-1} are from C—S bonds vibrations, which indicate the presence of PPS [23,33]. As stated above, PPS/MWCNTs composites were successfully prepared. Also the fractured cross-surface morphology of PPS with different mass ratio of MWCNTs are showed in Fig.1(b–d). MWCNTs are uniformly distributed in the PPS matrix and partially interconnected. It is obvious that numerous conductive pathways are formed. As mentioned previously, the percolation threshold in PPS/MWCNTs composites is around 2 wt% [29], which means the samples in this paper are all exceed the percolation threshold. The conductive networks are ubiquitous in SEM images which support the speculation. We can see some of MWCNTs formed as bundles in percolative composites. Increased bundle radius and electrical conductivity are contributing to form conductive pathways, which are beneficial to achieve negative real part of permittivity [34].

The dielectric spectra are shown in the Fig. 2. Negative permittivity behaviors (Fig. 2a) appeared as expected when percolation networks were established [35–37]. And weakly negative permittivity is emerged in PPS/MWCNTs composites with 20 wt% and 30 wt% MWCNTs contents. In fact, impedance matching is highly based on the permittivity close to the permeability. However, the value of permeability is always small, especially the negative permeability, so a low magnitude of negative permittivity is desired in practical application [38,39]. In addition, low frequency dispersion phenomenon is also discovered in PPS with 20 wt% and 30 wt% MWCNTs composites. For example, the negative permittivity is about −859 (@10 MHz) and it is still about −270 (@1 GHz) in PPS-20 wt% MWCNTs composites. However, for PPS-60 wt % MWCNTs composites, the negative permittivity is about −108068 (@10MHz) but only −2257 (@1 GHz), the variation is more than 50 times. The negative permittivity very sensitive to frequency is particularly undesirable in practical application. With increasing of MWCNTs contents, the absolute values of negative permittivity increased. From above discussion, the negative permittivity can be tuned by controlling conductive filler contents. And it seems the conductive fillers near but beyond the percolation threshold is more likely to achieve a weakly negative permittivity [40]. As is well known, dielectric loss mainly includes polarization loss and conductive loss. It obviously dielectric loss increases with higher MWCNTs contents, which mainly comes from the increasing conductivity loss (Fig.2b). The solid lines in Fig. 2a are fitted by the Drude model which gave the relationships between the complex permittivity and frequency [15]. Drude model is a classical theory to describing the negative permittivity behaviors of conductor or semiconductor [11,14–18]. The expressions are shown as following:

$$\varepsilon_r(\omega) = 1 - \frac{\omega_p^2}{\omega^2 + i\omega\omega_\tau} \tag{3}$$

$$\omega_p = 2\pi f_p = \sqrt{\frac{n_{eff}e^2}{m_{eff}\varepsilon_0}} \tag{4}$$

where ω is angular frequency ($\omega = 2\pi f$), ω_τ is the collisional frequency and inverse of relaxation time ($\omega_\tau = 1/\tau$), ω_p is the plasma frequency. And n_{eff} is effective concentration of the conduction electrons, m_{eff} is the effective mass of the electron. The experimental data were consistent well with the Drude model.

It has been widely accepted that the negative permittivity properties of percolative composite are highly based on their electrical conductivities. Pure PPS is highly insulated (about 10^{-16} $(\Omega\,cm)^{-1}$ [41]) with a positive permittivity. Electrical conductivity was improved by orders of magnitude when the conductive filler near percolation threshold. And the ac conductivity at low frequency is approximately equivalent to the dc conductivity. As show in Fig. 3, the conductivity of all samples in this paper are considerably larger than the pure PPS, which verified MWCNTs content exceed percolation threshold. In addition, ac conductivity shows a metal-like behaviors in Fig. 3, and it increased with increasing MWCNTs contents at lower frequency. With