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Existence of negative permittivity in carbon coated iron nanoparticle - PDMS composites

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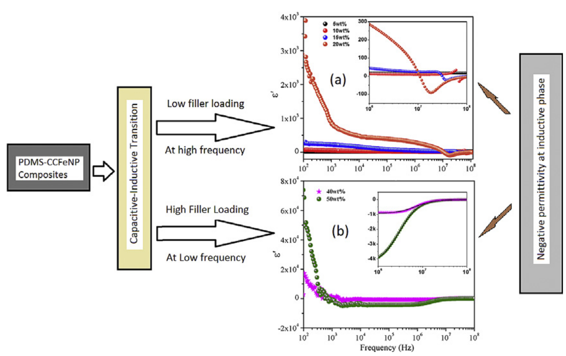
HIGHLIGHTS

- The ε' for the PDMS-CCFeNP composites varied inversely with frequency.
- Later permittivity switched from positive to negative for the composites.
- The switching frequency was very low for composites with high filler loading.
- The capacitive-inductive transition was observed at switching frequencies.
- For higher filler loading composites σ'_{ac} decreased with increase in frequency.

GRAPHICAL ABSTRACT



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ABSTRACT

We prepared polydimethylsiloxane (PDMS)-carbon coated iron nanoparticle (CCFeNP) composites (varying filler content) to investigate the dielectric behaviour, in the frequency range 100 Hz–100 MHz. The sample structures were studied by means of Transmission Electron Microscopy (TEM), Scanning electron microscopy (SEM) and X-ray diffraction (XRD). The ac conductivity, impedance, permittivity and dielectric loss of PDMS-CCFeNP composites were analysed. The real part of permittivity/epsilon (ε') for the cured composites varied inversely with frequency and switched from positive to negative. The 10 wt% composites exhibit negative permittivity at higher frequency, whereas for 50 wt% permittivity switches from a highly positive to negative at very low frequency and remained negative thereafter. The shifting of switching frequency towards lower frequencies with increasing filler loading is attributed to the increased inductive nature of the composites. The unique frequency dispersion of permittivity is explained by interband transition and Drude model (multiband nature of the electronic excitations). The well dispersed filler particles in PDMS matrix gave the high permittivity of 833 for 30 wt% composite at 1 kHz. The frequency dependence of real part of ac conductivity (σ_{ac}') and impedance studies were carried out to elucidate the capacitive-inductive transition and dielectric resonance in the composites.

1. Introduction

Double negative (DNG) metamaterials, exhibiting negative permittivity as well as negative permeability values have been

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reported in the past. The nonexistence of metamaterials in nature has evoked researchers' interest negative index materials. Veselago was the first to theoretically explain, the concept of negative index materials in 1968 [1]. But the realization of metamaterials in artificially designed structures took after a long time in 2001 [2]. Subsequently, large number of metamaterials consisting of array of wires and rings were proposed to exhibit negative permittivity and permeability [3,4]. Negative index materials are of great interest due to their unique properties arising from the ordered arrangement of structured unit cells. However, polymers reinforced with conductive fillers without periodic array also exhibit negative permittivity and permeability. Exploration of polymer composites to manipulate various properties of polymers has begun long back and in the past one decade many researchers have reported a large number of epsilon negative (ENG) materials with polymer matrix composites. Though the contribution of polymers, in realizing the negative value of permeability or permittivity is rarely discussed anywhere. An enhanced dielectric property with negative permittivity has been achieved by many like Xi Zhang et al. in cnt-polypropylene nano composites [5] and in polyimide/carbon nanotube composites by Yiyi Sun et al. [6]. The epsilon negative property in composite materials embedded with metallic fillers is mainly due to the plasma oscillation of delocalized electrons or due to the interband transitions of localized electrons [7–11]. The presence of metallic fillers in polymer matrix not only enhances the dielectric property, also gives rise to negative permittivity [8]. Negative properties in such composites depend on composition, dimension and distribution of filler materials in the polymer matrix. The graphitic carbon envelope over the iron nanoparticle protects iron from oxidization and degradation, keeping its properties intact. Number of features of PDMS, like flexibility and thermal stability makes it a better matrix material for composites.

In spite of extensive research on dielectric properties of polymer composites, the dielectric behaviour of PDMS-CCFeNP composites has not been studied so far. In this work ac conductivity, impedance, permittivity and dielectric loss of PDMS-CCFeNP composites were studied and analysed. Carbon coated iron nanoparticles when embedded in PDMS matrix enhanced the permittivity of the polymer matrix by great extent and resulted in negative permittivity over a certain frequency range. Composites with negative permittivity find wide applications in designing highly functional compact antennas, highly sensitive sensors, and high resolution super lenses which can overcome the diffraction challenges [12–16]. The epsilon negative materials (ENG) are also of great importance when combined with a Mu negative (MNG) i.e. negative permeability materials to give a double negative material [17,18].

2. Experimental

2.1. Fabrication of PDMS-CCFeNP composites

Iron-nanoparticles covered with graphitic carbon matrix were synthesized in laboratory by pyrolysis of ferrocene at 980 °C in the presence of argon gas. PDMS (Sylgard 184 Silicone Elastomer kit) purchased from Dow Corning Corporation, USA consisting of base and curing agent was used. The curing agent contains a platinum-based catalyst that catalyses the addition of the Si–H bond across the vinyl groups, forming Si–CH_2–CH_2–Si linkages. Toluene was used as solvent to dissolve PDMS and to disperse CCFeNPs. The PDMS composites were fabricated by solvent casting method, which involves two steps Fig. 1. At first the PDMS base was dissolved in toluene by magnetic stirring (450 rpm) for 15 min. The carbon coated iron particles were dispersed in toluene by ultrasonication at room temperature. In the second step the PDMS solution and dispersed particles were mixed together and sonicated for few hours. The curing agent was added in a ratio 1:10 with the base and the mixture was manually mixed for about 10 min. The obtained homogenous mixture was poured into a flat bottom dish and thermally treated for 1 h at 100 °C. The composites with varying weight percentage of CCFeNP were fabricated. Free standing films of thickness about ~250 μm with uniformly dispersed nanoparticles were obtained by this method.

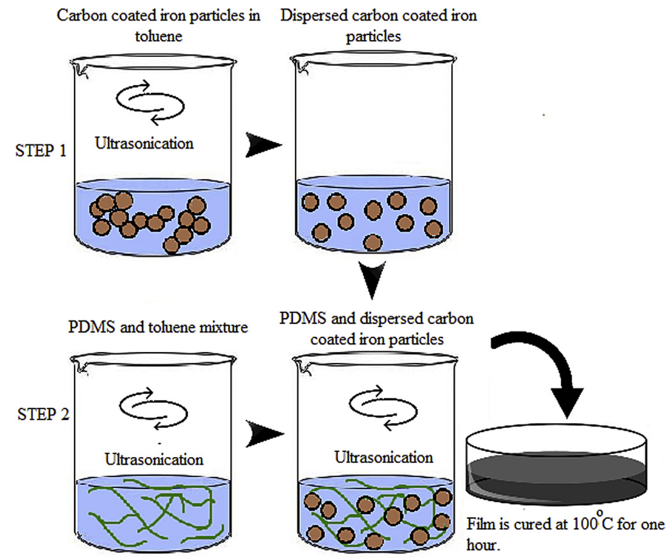

Fig. 1. Fabrication process of composites.

2.2. Characterization

Structural analysis of CCFeNPs was conducted on FEI Tecnai F30S-twin TEM. The morphological study of the nanocomposites was studied by SIRION FESEM. The X-ray diffraction measurements of CCFeNPs and PDMS-CCFeNP composites were measured on Rigaku X-ray diffractometer, Japan with the K_α ray of Cu with the wavelength of 1.5418 Å.

Agilent 4294A impedance analyser was used to study the dielectric properties of fabricated composites over a frequency range of 100 Hz-100 MHz. Impedance measurements were conducted at room temperature on the 1 cm × 1 cm film sandwiched between two parallel plate silver electrodes. During the measurements the real and imaginary parts of permittivity and ac conductivity were determined from the following equations

$$\varepsilon' = \frac{Cd}{A\varepsilon_0}$$

$$\varepsilon'' = \frac{d}{RA\varepsilon_0\omega}$$

The real part of ac conductivity $\sigma_{ac}' = \frac{d}{RA}$ (in S/m).where, $\varepsilon_0 = 8.85 \times 10^{-12}$ F/m is the permittivity of the free space and $\omega = 2\pi f$ the angular frequency in Hz, d is the thickness of the sample in meter, R is the resistance in ohms, C is the capacitance in Farad, and A is the area of the electrode plate in m^2.

3. Results and discussion

3.1. TEM analysis

The sample for TEM analysis was prepared by sonicating the