Materials Letters 210 (2018) 309–313

Contents lists available at ScienceDirect

Materials Letters

journal homepage: www.elsevier.com/locate/mlblue

Polydimethylsiloxane-multiwalled carbon nanotube composite as a metamaterial

Hitha D. Shetty [a,b,*], Ananya Patra [a], V. Prasad [a]

[a] Department of Physics, Indian Institute of Science, Bangalore 560012, India
[b] Department of Physics, Nitte Meenakshi Institute of Technology, Bangalore 560064, India

ARTICLE INFO

Article history:
Received 13 July 2017
Received in revised form 28 August 2017
Accepted 13 September 2017
Available online 14 September 2017

Keywords:
Carbon nanotubes
Polymer nanocomposites
Negative permittivity
Low dielectric loss

ABSTRACT

Negative permittivity is an exceptional property of metamaterials, which makes them unique class of artificial materials with numerous applications ranging from cloaking to wave filters. In this paper we report about the PDMS (Polydimethylsiloxane)–MWcnt (Multi wall carbon nano tube) composite beyond percolation, as a metamaterial with high negative permittivity. Percolated composite showed high negative permittivity of −2376.62 at 2541.401 Hz and low tangent loss of −0.065 at 1 MHz. The conductivity spectra followed Jonscher's power law, indicating hopping conduction for composites below percolation threshold. Beyond percolation, networking between the MWcnts formed large number of conductive paths resulting in free electron conduction. The impedance studies showed the capacitive-inductive transition in the percolated composite with inductive phase exhibiting negative permittivity.

1. Introduction

The study of metamaterials has gained popularity, as permittivity and permeability are the important parameters to decide the electromagnetic properties of materials. The unavailability of natural metamaterials, led to the invention of artificially designed metamaterials with ordered arrangement of structured unit cells by researchers like D R Smith [1]. They were named as double negative materials (DNM), as both permittivity and permeability were negative. But it got interesting, when polymers reinforced with cnts without periodic arrangement turned out as DNMs. Recently polypyrrole/cnt and polyaniline/cnt composites were reported by Xuechen Kou et al. and Xiuchao Yao et al. to exhibit DNM properties [2,3]. DNMs are useful in designing perfect lens, sensitive antennas and cloak of invisibilities. On the other hand the metamaterials with single negative parameters, like permittivity are also of importance because of their interesting properties and applications [4,5]. The existence of conductive fillers in polymer matrix imparts unique dielectric property to the composite depending on the size, type and distribution of reinforced materials. The carbon nanotubes, when embedded in polymer matrix forms conductive networks inside the matrix. Beyond percolation they contribute large number of free electrons and the plasma oscillation of delocalized electrons gives rise to negative permittivity [6,7]. Thus MWcnts with their excellent properties are the perfect filler materials to tailor the properties of the polymer matrix [8,9] according to our needs whereas; thermally stable, flexible PDMS is good candidate as a matrix material.

2. Materials and method

PDMS kit consisting of base and curing agent was purchased from Dow Corning Corporation, USA. The curing agent contains a platinum-based catalyst that catalyzes the addition of the Si-H bond across the vinyl groups, forming Si-CH_2-CH_2-Si linkages. Multi-walled carbon nanotubes were purchased from Sigma Aldrich. Toluene from Merck was used as the solvent. PDMS composites with varying MWcnt loading were prepared by solvent casting method. Different weight percent samples were prepared according to the equation

$$wt(\%) = \frac{M_{cnt}}{M_{CNT} + M_p + M_{CA}} \times 100$$

where M_{CNT}, M_P and M_{CA} are the masses of MWcnt, PDMS and curing agent respectively. An exact quantity of MWcnts was dispersed in 5 ml toluene by ultrasonication. PDMS solution was prepared in 5 ml toluene, mixed with dispersed MWcnts and sonicated for few hours at room temperature. Resulting solution was mixed manually with curing agent at 10:1 wt ratio and poured into a flat bottom dish to get thermally cured free standing films of

* Corresponding author at: Department of Physics, Indian Institute of Science, Bangalore 560012, India.
E-mail address: shetty_hitha@yahoo.co.in (H.D. Shetty).

http://dx.doi.org/10.1016/j.matlet.2017.09.051
0167-577X/

uniform thickness of ~300 μm. Homogeneous dispersion of MWcnts has been achieved without the use of surfactants. The good dispersion of MWNTs within the PDMS matrix is attributed to the toluene used. The dispersion of MWcnts in toluene by ultrasonication will result in adsorption of toluene by the MWcnt surface via non-covalent interactions (π -π stacking). This helps the interaction between MWcnts and long polymer molecules, and hence MWNTs get dispersed uniformly.

The morphological study of the nanocomposite was studied by SIRION field emission scanning electron microscope. The X-ray diffraction measurements were taken on Rigaku X-ray diffractometer, Japan with the K_α ray of Cu with the wavelength of 1.5418 Å. Raman analysis for samples was carried out in Horiba LabRam instrument using a laser source of wavelength 532 nm. FTIR spectra were obtained by Perkin Elmer FTIR spectrometer. Dielectric studies were examined on Agilent 4294A impedance analyzer over a frequency range of 100 Hz–1 MHz. 1 cm × 1 cm film of PDMS-MWcnt composites were sandwiched between two parallel plate silver electrodes for the dielectric property measurement. The real and imaginary parts of permittivity were determined from the following equations $\varepsilon' = \frac{Cd}{A\varepsilon_o}$ and $\varepsilon'' = \frac{d}{RA\varepsilon_o\omega}$. The ac conductivity $\sigma'_{ac} = \frac{d}{RA}$ S/m, where, $\varepsilon_o = 8.85 \times 10^{-12}$ F/m permittivity of the free space, $\omega = 2\pi f$ 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

The SEM images of PDMS composites Fig. 1(a) with 2 and 4 wt% of MWcnts are shown for surface and cross section. The images for both 2 and 4 wt% show the well dispersed MWcnts in the PDMS matrix. Remarkable morphological changes were not observed with increase in MWcnt loading.

Fig. 1(b) shows X-ray diffraction pattern for PDMS-MWcnt composite shows the characteristic peak of PDMS located at 11.63° attributing to its tetragonal phase. The peaks at 25.85^0 and 44.17^0 corresponds to (0 0 2) and (1 0 0) plane of carbon in MWcnts. Peaks attributed to PDMS become less intense and those corresponding to MWcnts become more intense with increase in MWcnt loading.

Raman spectra in Fig. 1(c) shows increase in intensity of the characteristic peaks for MWcnts the D-peak and G-peak with increase in MWcnt loading, indicating good dispersion of MWcnts in the PDMS matrix. The peaks attributed to the PDMS decrease in intensity with increasing MWcnt loading.

The FTIR spectra show the characteristic bands of the PDMS-MWcnts composites in Fig. 1(d). The peaks found between 1412 cm^{-1} and 1259 cm^{-1} correspond to —CH3 deformation vibration in PDMS. The peak stretching from 1009 cm^{-1} to 1060 cm^{-1} corresponds to Si—O—Si symmetrical deformation.

—CH3 rocking peaks and Si–C bands are observed in 841–856 cm^{-1} and 780–800 cm^{-1} region respectively. Slight decrease

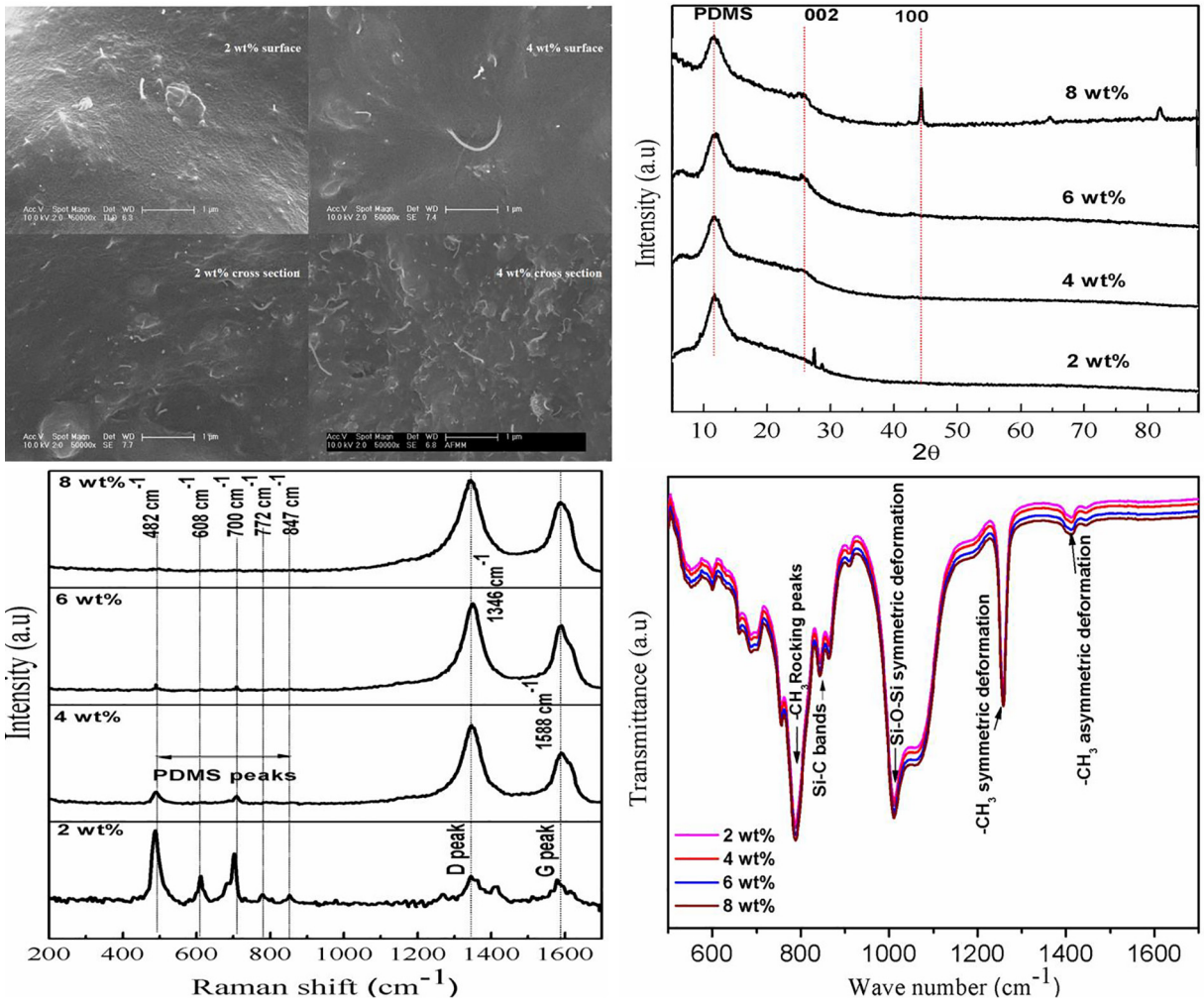

Fig. 1. a) SEM images b) XRD c) Raman and d) FTIR spectra for PDMS-MWcnt composites.