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Dielectric relaxation and ac conductivity behavior of carboxyl functionalized multiwalled carbon nanotubes/poly (vinyl alcohol) composites

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ABSTRACT

We study the dielectric relaxation and ac conductivity behavior of MWCNT-COOH/Polyvinyl alcohol nanocomposite films in the temperature (T) range 303–423 K and in the frequency (f) range 0.1 Hz–1 MHz. The dielectric constant increases with an increase in temperature and also with an increase in MWCNT-COOH loading into the polymer matrix, as a result of interfacial polarization. The permittivity data were found to fit well with the modified Cole-Cole equation. Temperature dependent values of the relaxation times, free charge carrier conductivity and space charge carrier conductivity were extracted from the equation. An observed increment in the ac conductivity for the nanocomposites was analysed by a Jonscher power law which suggests that the correlated barrier hopping is the dominant charge transport mechanism for the nanocomposite films. The electric modulus study revealed deviations from ideal Debye-type behavior which are explained by considering a generalized susceptibility function. XRD and DSC results show an increase in the degree of crystallinity.

1. Introduction

From last few decades, researchers have shown interest in polymer nanocomposites due to their potential for broad applications [1]. Traditional polymers generally have low modulus and are non conductive in nature. Thus, carbon black, graphite, or metal particles are generally utilized as conductive fillers for polymers to get desired properties for different electronics applications. Conductive micro scale fillers are added to polymers in expansive volume fractions to enhance electrical conductivity. This high filler loading leads to low mechanical strength, low ductility and additionally the poor processability of polymer composites. So the choice of suitable conductive filler is critical to plan a conductive composite for specific application. To overcome the limitations of micro fillers in polymer composites, nanometric size fillers have gained interest because of their high aspect ratio, high surface area, and high interfacial attraction with polymer matrix. Addition of conductive nanoparticles to the polymer matrix may tune its physical or electrical properties, extensively useful in the fields such as electromagnetic shielding, electrostatic dissipation and charge storage capacitor systems [2–6]. On account of their high aspect ratio, high conductivity with high mechanical strength and high thermal stability, carbon nanotubes (CNTs) are considered as perfect candidates for conductive fillers.

Poly(vinyl alcohol) (PVA), a transparent thermoplastic with good film formation property, dielectric strength and charge storage capacity, is getting increasing attention in electronic industries [7]. With the addition of CNTs to PVA matrix, one can get a conductive polymer nanocomposite with unique properties, which can be utilized as multifunctional materials for diversed applications [8,9]. Dielectric materials have long been examined and widely applied in power and electronic industries [10–12]. They demonstrate polarization and conducting phenomena under an applied electric field through charge migration. Because of their insulating nature, charge in dielectric materials is confined in the dielectric molecular or local space, which brings about local migration under the electric field and produces induced dipole moment [11]. There are few reports on the variation of the dielectric relaxation and alternate current (ac) conductivity with various conducting particles doped PVA polymer [3,13]. Very few give the information regarding the electrical and dielectric properties of CNT/PVA composites.

However, to the best of our knowledge, the effect of MWCNT-COOH in a PVA matrix has not yet been reported. Since, the inclusion of CNTs can enhance the conductivity of the polymer matrix; the main objective of this study is to investigate the effects of MWCNT-COOH on the dielectric properties of PVA and also to understand the polarization mechanism as well as the ac conduction mechanism in the temperature range 303–423 K and in the frequency range 0.1 Hz–1 MHz.

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2. Materials and methods

PVA in powder form (Molecular weight 14,000, density 1.31 g/cm^3) was supplied by BDH Chemicals. MWCNT-COOH (prepared by Chemical Vapor Deposition technique, purity 95%, outer diameter 8–15 nm, inner diameter 3–5 nm, length 0.5–2 μm, Electrical conductivity σ_{CNT} > 100 S/cm, and density 2.1 g/cm^3) utilized in this study were procured from Chengdu Organic Chemicals (Chinese Academy of Science, China) and were used as received.

Nanocomposite films were prepared by solution casting method. Distilled water was used as a common solvent. Different weight percentages of MWCNT-COOH from 0% to 5% were added to PVA. In a typical procedure, required amount of PVA and an exact amount of MWCNT-COOH were dissolved in distilled water by heating upto 70 °C with continuous stirring. Thin films were prepared by casting the viscous and homogeneous solution onto a leveled optically flat petri dish in an oven. The thickness of the composite films was between 55–100 μm. The samples containing 0%, 1%, 2%, 3% and 5% CNTs were prepared, which will be noted as P0, P1, P2, P3, and P5 respectively.

3. Experimental techniques

The temperature and frequency dependent electrical measurements were performed on the samples with the help of Broadband Dielectric Spectrometer (Novocontrol Technologies Germany-Concept 80). The sample was placed in a furnace where the measurement temperature was varied in the range from 30 to 150 °C (303–423 K) in 10-degree steps. The ac applied voltage was 1 V and the measurements were done in the frequency ranging from 0.1 to 1 MHz using an alpha Analyzer. Scanning electron microscopy (SEM) images were taken on a Field emission gun-scanning electron microscope (FEG-SEM) Jeol Inc., JSM-7600F, operated at 5 kV. Infrared spectra of MWCNT-COOH and nanocomposite were recorded utilizing Perkin Elmer Infrared Spectrophotometer (Model name-Spectrum 100 series) in the range of 4000–400 cm $^{-1}$ with a resolution of 4 cm $^{-1}$. The X-ray diffraction profile was taken in the 2θ range of 5–30°with the help of an Advance ECO XRD System diffractometer, with CuK_α radiation source (λ=1.54059 Å). Differential Scanning Calorimetry (DSC) measurements were carried out in the temperature range 30–300 °C in a nitrogen atmosphere, using a Perkin–Elmer Pyris 6 apparatus. Both cooling and heating rates were 10 °C/min. The weight of the samples was kept at approximately 7 mg. It is noted that all the examined samples were formerly heated from room temperature to 300 °C, at10 °C/min, and kept to that temperature for 5 min in order to remove any previous thermal history.

4. Results and discussion

4.1. Scanning Electron Microscopy analysis

Fig. 1 shows SEM micrographs of PVA, MWCNT-COOH and composite sample P1. The image with MWCNT-COOH shows a nanotube bundle. The micrographs of P1 was taken in a cross section view which were prepared by breaking off the sample indicates that the individual nanotubes are agglomerated and shows non uniform dispersion within the matrix. The bright spots in the images are of CNTs due to their high electrical conductivity.

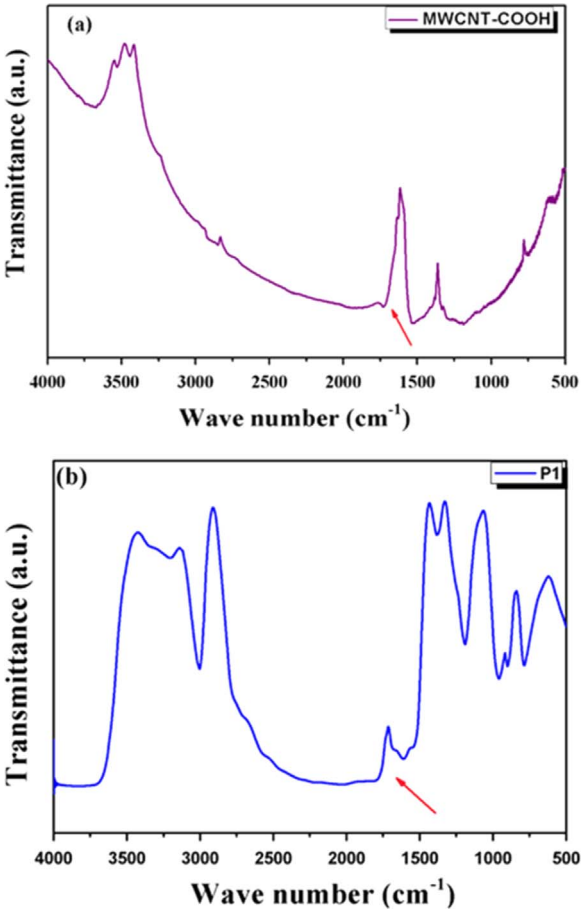

Fig. 2. FT-IR spectra of (a) MWCNT-COOH and (b) P1.

4.2. FT-IR analysis

Fig. 2(a) shows the FT-IR spectrum of the MWCNT-COOH. The peak seen at approximate around 1700 cm^{-1} is assigned to the carbonyl stretching vibration while the broad peak at around 3250–3400 cm^{-1} are assigned to the presence of OH group. This confirms the presence of COOH group in MWNT which is shown by an arrow in the figure. A weak broad peak around 1700–1725 cm^{-1} is seen in the spectrum of composite sample P1 Fig. 2(b) which corresponds to the carboxyl C=O

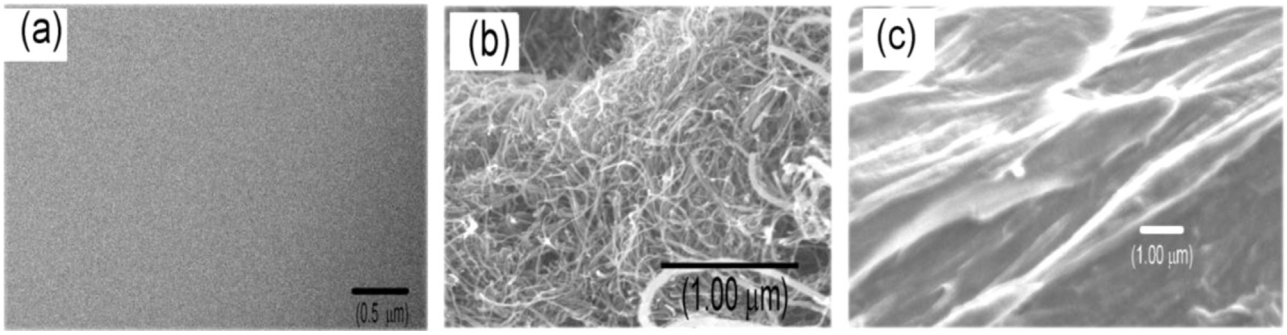

Fig. 1. SEM images of the (a) PVA (b) MWCNT-COOH and (c) P1.