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Characterization, charge transport and magnetic properties of multi-walled carbon nanotube–polyvinyl chloride nanocomposites

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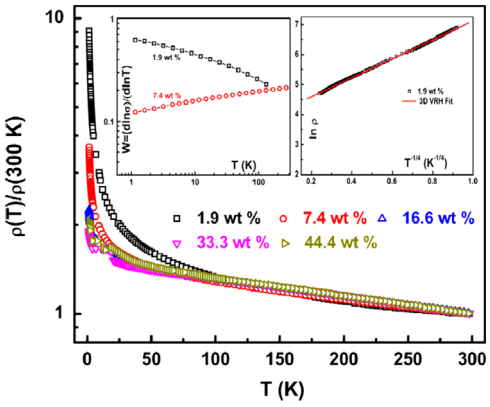
HIGHLIGHTS

- Good quality MWCNT–PVC nanocomposites (0.1–44.4 wt%) are prepared and characterized.
- The $\rho(T)$ of MWCNT–PVC nanocomposite of 1.9 wt% follow the 3D VRH model.
- The $\rho(T)$ of higher (7.4 and above) wt % nanocomposites seem to follow power law.
- Exchange bias is observed due to interfacial interaction between Fe_3C and core Fe nanoparticles.

GRAPHICAL ABSTRACT



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ABSTRACT

Multi-walled carbon nanotube (MWCNT)–polyvinyl chloride (PVC) nanocomposites, with MWCNT loading up to 44.4 weight percent (wt%), were prepared by the solvent mixing and casting method. Electron microscopy indicates high degree of dispersion of MWCNT in PVC matrix, achieved by ultrasonication without using any surfactants. Thermogravimetric analysis showed a significant monotonic enhancement in the thermal stability of nanocomposites by increasing the wt% of MWCNT. Electrical conductivity of nanocomposites followed the classical percolation theory and the conductivity prominently improved from 10^{-7} to 9 S/cm as the MWCNT loading increased from 0.1 to 44.4 wt%. Low value of electrical percolation threshold ~0.2 wt% is achieved which is attributed to high aspect ratio and homogeneous dispersion of MWCNT in PVC. The analysis of the low temperature electrical resistivity data shows that sample of 1.9 wt% follows three dimensional variable range hopping model whereas higher wt% nanocomposite samples follow power law behavior. The magnetization versus applied field data for both bulk MWCNTs and nanocomposite of 44.4 wt% display ferromagnetic behavior with enhanced coercivities of 1.82 and 1.27 kOe at 10 K, respectively. The enhancement in coercivity is due to strong dipolar interaction and shape anisotropy of rod-shaped iron nanoparticles.

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1. Introduction

Advancement in the synthesis of nanomaterials has revived the research interest towards their possible use in the fabrication of nanocomposites [1,2]. The nanocomposites are prepared by adding filler of nanometer dimensions in the host matrices, most often the polymers serve as host. Nanocomposites have attracted many researchers across the world, which is due to the fact that the physical properties of host materials can be easily tailored by addition of the nanoscale materials appropriately. For example, inclusion of small amount of magnetic nanoparticles into a nonmagnetic material can result into a magnetic material [3]. Similarly, the electrical conductivity of an insulating polymer matrix can be tailored in a particular range by the appropriate addition of conducting filler materials [4]. Ideally, a conducting filler material should have low density and high aspect ratio so that a finite conductivity can be achieved with inclusion of minimal amount of additive material. However, the selection of both suitable filler and host material is very important for the nanocomposite fabrication towards a particular application.

Carbon black, metal particles, graphitic nanoparticles and carbon fibers are traditionally used as conducting filler materials for the fabrication of polymer composites [5–7]. Over the past two decades, carbon nanotubes (CNTs) have become one of the most promising candidates to be employed as reinforcing material in nanocomposites due to their extraordinary properties including low density, high aspect ratio and electrical conductivity, superior mechanical and thermal properties [1,8]. Thus inclusion of small quantities of CNTs within the polymer matrix can improve the mechanical strength, electrical conductivity and thermal stability of the host material prominently and offer multi-functionality, when compared with traditional fillers [4]. CNT based nanocomposites have significant advantages in broad range of applications such as field emission, gas sensors, electromagnetic interference shielding and actuators [9–11].

However, the fabrication of CNT based nanocomposites is not straightforward since the Van der Waals interactions between CNTs hinder the effective unbundling. This leads to inhomogeneous dispersion of CNTs due to segregation in the polymer matrix which adversely affects the properties of the nanocomposites. Thus the most important aspect in preparing the nanocomposites with CNT is to achieve high degree of dispersion in polymer matrix [12]. In order to achieve uniform dispersion of CNTs throughout the matrix, use of surfactants like sodium dodecyl sulfate, sodium dodecylbenzene sulfonate, and N-methyl-2-pyrrolidone has been reported [13,14]. From both fundamental and applications point of view, the CNT–polymer nanocomposites are fantastic electrical systems in which the charge transport depends on the thickness of insulating pathways separated by random network of 1D conducting materials.

In this work, we report the fabrication of multi-walled carbon nanotube–polyvinyl chloride [MWCNT–PVC] nanocomposites with different weight percent (wt%) of MWCNTs. The as-prepared nanocomposites are characterized by X-ray diffraction (XRD), electron microscopy, and thermogravimetric analysis (TGA). Temperature dependence of resistivity of MWCNT–PVC nanocomposites is studied to probe the conduction mechanism as a function of MWCNT content in the temperature range of 300–1.4 K. Furthermore, the magnetic properties of MWCNT and MWCNT–PVC nanocomposite of higher wt % are studied and compared.

2. Experimental

2.1. Materials

PVC, in powder form (molecular weight ~62,000, purchased from Sigma Aldrich), was used for the fabrication of nanocomposites. MWCNTs were synthesized by pyrolysis method using ferrocene and benzene mixture [15]. Tetrahydrofuran (THF; supplied by Fisher scientific, India) was used as solvent to dissolving PVC and dispersing MWCNTs.

2.2. Preparation of nanocomposites

MWCNT–PVC nanocomposites were prepared by a two step solution processing and casting method. The first step involves the dispersion of MWCNT in THF by ultrasonication and preparation of PVC solution in THF (200 mg in 10 mL) in separate beakers. The next step involved the mixing of these two solutions by ultrasonication for several minutes. Finally, the homogenous mixture was carefully poured to a specially modified optically flat bottom beaker and the solution was then allowed to dry under ambient conditions for 48 h. The MWCNT–PVC nanocomposite films of different wt% were prepared by varying the content of MWCNT and keeping the same amount of PVC for all samples. The free standing films of diameter ~4 cm and thickness around ~150–250 μm were obtained by carefully peeling the films from the bottom of the beaker.

2.3. Characterization

Bruker D8 Advance instrument (with Cu $K_{\alpha 1}$ radiation of wavelength 1.5406 Å) is employed to obtain the XRD pattern of the films. Morphology of the nanocomposites was studied by the SIRION high resolution scanning electron microscope (SEM) equipped with a Schottky field emission source, and high resolution FEI Technai F30 transmission electron microscope (TEM). The NETZSCH TG 209 F1 TGA-equipment was used to study thermal stability of the MWCNT–PVC films.

Nanocomposite films of different wt% were cut into 5 mm × 5 mm dimensions for electrical conductivity measurements using Van der Pauw geometry. The electrical contacts were made by using fine enameled copper wire of 38 AWG (0.1 mm diameter) on the sample with conductive silver paint and the conductivity was calculated by using the following formula, $\sigma_{dc} = \ln 2/\pi hR$; where h and R are the thickness and measured resistance respectively. The two probe method was used for measuring the resistance of low wt% samples (< 1 wt%). The temperature dependent resistivity measurements were carried out in a Janis variable-temperature system (from 300 to 1.4 K), using Keithley 2000 multimeter and Keithley 220 programmable current source. Appropriately chosen constant currents (in the range of 0.1–10 μA) were applied to the current leads on the sample to avoid any sample heating at low temperatures. Magnetization hysteresis loop measurements were

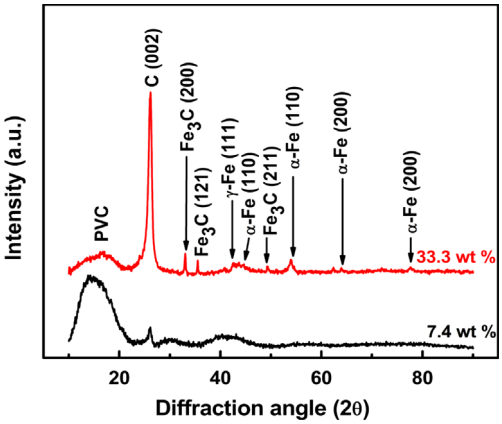

Fig. 1. XRD patterns of MWCNT–PVC nanocomposites of 7.4 wt% and 33.3 wt% of MWCNTs.