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Carboxyl-functionalized MWCNT doped poly(o-toluidine) nanohybrids: Synthesis, characterization with AC electrical and dielectric properties

Arup Choudhury*

Department of Chemical Engineering & Technology, Birla Institute of Technology, Mesra, Ranchi 835-215, India

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ABSTRACT

Nanohybrids of protonic acid doped poly(o-toluidine) (POT) with carboxyl-functionalized multi-walled carbon nanotubes (MWCNT-COOH) were synthesized by in situ chemical oxidation polymerization in the absence of any added acid. Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) showed that carboxylic groups had been introduced onto the surface of MWCNT. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) showed that a thin layer of POT is well coated on the surface of MWCNT-COOH with a thickness of ~19 nm. Based on π–π* electron and H-bonding interactions between functional groups of o-toluidine monomer and those of MWCNT-COOH, o-toluidine molecules were adsorbed and polymerized on the surface of nanotubes. AC conductivity and dielectric properties of POT/MWCNT-COOH nanohybrids were measured at 100 Hz–1 MHz and a temperature range of 25–125 °C. Upon increasing the concentration of MWCNT-COOH an increase in the AC conductivity, dielectric permittivity and loss tangent of host POT are observed. The presence of polarons and bipolarons are responsible for the frequency dependence of AC conductivity in these nanohybrids. The variation of AC conductivity with frequency has been described by the power law. The decrease in activation energy is observed with increasing concentration of MWCNT-COOH in the nanohybrids. The incorporation of 4 wt% MWCNT-COOH into POT matrix resulted in around ten-fold increase in dielectric permittivity with a negligible effect on loss tangent at 100 Hz. The permittivity is found to be stable up to 75 °C and then increase gradually with increasing temperature.

1. Introduction

Electro-active polymer composites with excellent dielectric performance have received extensive importance for their potential applications. Both high permittivity and low dielectric loss are desired for the composites with electrically conductive fillers to enhance microwave absorption capacity and, also to achieve high energy density for realistic capacitor applications [1–4]. Functional polymer composites have ability to meet the above mentioned requirements. The use of various conductive fillers such as metallic powder, ceramic and carbon black have been extensively explored and shown to improve the electrical conductivity and dielectric properties of the composites [5–9]. High filler content is usually needed to achieve high values of dielectric permittivity for the purposed applications, which might cause deterioration of mechanical properties and processability of the polymers. Carbon nanotubes (CNTs) have excellent nanoporosity properties, unique electronic structure, and extremely large aspect ratio (100–1000) [10,11] and polymers containing very low concentration of CNTs have high dielectric permittivity [12]. It has been reported that CNT sheets are more effective in providing EMI shielding compared with graphite and carbon black sheets over broad frequency range due to their better electron transmission [13]. High thermal conductivity of the CNTs could also promote the dielectric stability over a wide range of temperature.

Among these polymer/CNT nanocomposites, combination of intrinsic conducting polymers (e.g., polyaniline, polypyrrole, polythiophene, poly(phenylene vinylene)) and CNT have attracted considerable attention because of their unique electrical properties as well as extensive application in electronic devices [14–19]. Several methods have been developed to synthesize these CNT-reinforced conducting polymer nanohybrids, including electrochemical [20] and chemical [21] polymerization of monomer solution containing different CNT contents. However, pristine CNTs are difficult to disperse in common organic solvents or polymeric matrices owing to their inherent chemical inertness, structural rigidity, and strong van der Waals interactions. Therefore, in this study, an attempt has been made to disperse multi-wall carbon

* Tel.: +91 9430 732461; fax: +91 651 2276184.
E-mail address: arup@bitmesra.ac.in

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nanotubes (MWCNTs) into the conducting polymer matrix by chemical functionalization of MWCNTs. A homogeneous dispersion of functionalized filler particles into polymer matrix could ensure strong interfacial interaction between the fillers and the polymer, thus opening the way to charge transfer process, and improving the electrical and dielectric properties of the nanocomposites.

In particular, a considerable progress has been made in designing and fabricating polyaniline (PANI)/CNT nanohybrids due to their unique electrical properties as well as extensive application in electronic devices [14,15,22]. However, the major disadvantage of PANI is its insolubility in common organic solvents and its infusibility. The combination of CNTs with methyl-substituted polyaniline could offer an attractive possibility to enhance the solubility or processability of resultant nanohybrid. In addition, the methyl-substituted polyaniline, i.e., poly(o-toluidine), exhibit fast switching time between the oxidized and the reduced states, which is an additional advantage over parent polymer [23].

In this study, nanohybrids of doped poly(o-toluidine) with COOH-functionalized MWCNTs were synthesized by in situ chemical oxidation polymerization without using any other protonic acid. The structural characteristics of the functionalized MWCNTs and as-prepared nanohybrids were examined by Raman spectroscopy, XPS, X-ray diffraction (XRD), SEM and TEM. The AC conductivity and dielectric properties of MWCNT-COOH doped poly(o-toluidine) nanohybrids as a functions of MWCNT-COOH ratio, applied frequency and temperature were measured and discussed.

2. Experimental

2.1. Materials

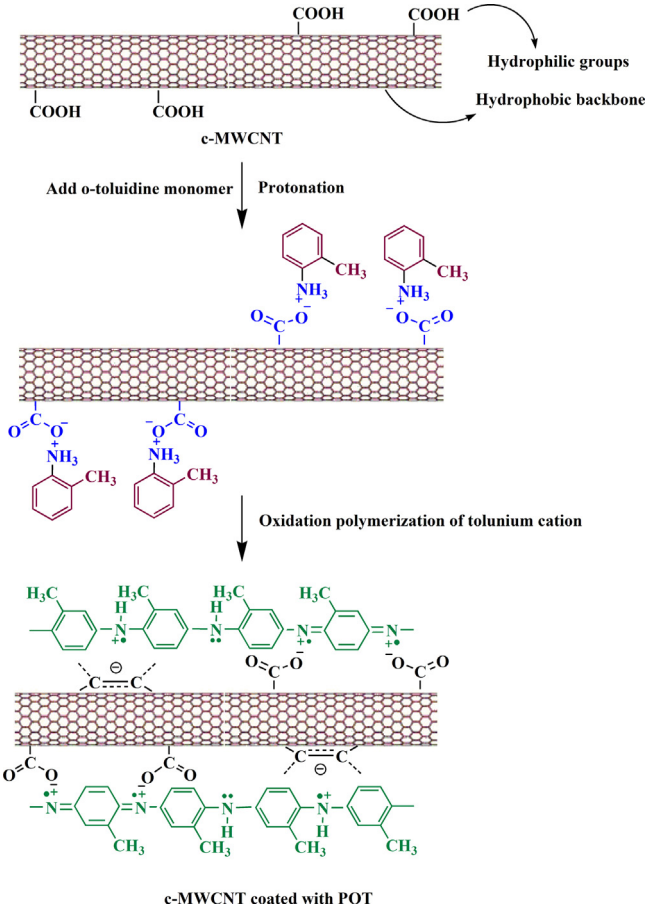
The o-toluidine (monomer, purity 98%) was obtained from Aldrich Chemical Co. as analytical grade and used as received. The multi-walled carbon nanotubes (purity 95%, diameter = 10–15 nm, length = 0.1–10 μm, density = 1.7–2.1 g/cm^3 batch 05225JA) were used as received from Aldrich. Reagent grade concentrated H_2SO_4 and HNO_3 (Merck India Ltd.) were used without further purification. Ammonium persulfate (APS) was bought from Merck India Ltd. The deionized (DI) water was used for the synthesis and washing purpose.

2.2. Functionalization of pristine MWCNT

The MWCNTs were functionalized following the route reported by Choudhury [24]. Briefly, 1 g of pristine MWCNTs was suspended in 250 ml concentrated sulfuric acid/nitric acid mixture (3:1, v/v) for 1 h with the ultrasonicator. The resultant mixture was then refluxed under magnetic stirring at 90 °C for 12 h. After cooling to room temperature, nanotubes were subsequently washed with DI water to obtain an acid-free nanotube suspension. Finally, a dry powder of carboxyl-functionalized MWCNTs (MWCNT-COOH) was obtained by filtering the nanotube suspension through 0.2 μm porous Teflon filter paper followed by drying under vacuum at 70 °C for 12 h. The extent of functionalization was determined by back titration with a freshly prepared aqueous solution of NaOH (0.05 M) as described by Solhy et al. [25]. The amount of acidic functions on the nanotube surfaces was found to be 8.6 mmol/g. Hence, MWCNT surface was successfully functionalized through the acid oxidation process.

2.3. Synthesis of MWCNT-COOH doped poly(o-toluidine) nanohybrids

Poly(o-toluidine)/MWCNT-COOH nanohybrids were prepared according to following procedure. Initially, various weight percentage of MWCNT-COOH (0.5, 1, 2, and 4 wt%) were ultrasonicated



Scheme 1. Schematic illustration of formation of POT/MWCNT-COOH nanohybrids.

in 100 ml DI water for 1 h to obtained dispersed suspensions. After that, the o-toluidine monomer (0.25 M) was slowly added to the above MWCNT-COOH suspension with constant stirring followed by ultrasonication for another 15 min. The o-toluidine monomer adsorbed onto the hydrophilic end of the MWCNT-COOH through formation of a thin layer of tolunium cations. The chemical polymerization of the adsorbed o-toluidine monomers on the MWCNT-COOH surfaces was started with the addition of aqueous APS [$(NH_4)_2S_2O_8$] solution (0.5 M) to the pre-cooled (4 °C) monomer–CNT mixture under constant stirring for 30 min. After 12 h, a good degree of polymerization is achieved and the suspension was in dark green. The site-selective interaction between the quinoid rings of POT and the MWCNT-COOH leads to POT deposit onto the surface of MWCNT-COOH. The formation mechanism of POT/MWCNT-COOH nanohybrids is illustrated in Scheme 1. The POT/MWCNT-COOH nanohybrids were obtained by filtering the green suspension and washing with distilled water and ethanol to remove residual oligomers. Finally, the nanohybrids were dried in a vacuum oven at 70 °C for 24 h. The crude yield of the nanohybrids under present experimental conditions was around 70%, indicating no adverse effects of the functionalized MWCNTs on the polymerization process. To prepare the pure polymer, the same procedure was undertaken in the absence of MWCNT-COOH.

2.4. Characterization methods

XPS study was conducted on a VG Microtech 2000 ESCA system using Al Kα radiation (1486.6 eV photons). The X-ray source was operated at 14 kV and 20 mA. All samples were grounded into fine powder before being mounted on standard sample holders by