



Electrical properties and glass transition temperature of multiwalled carbon nanotube/polyaniline composites

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ARTICLE INFO

Article history:

Received 28 January 2012

Received in revised form 1 March 2012

Available online 4 April 2012

Keywords:

PANI;

Electrical properties;

Functionalized carbon nanotube;

Glass transition temperature

ABSTRACT

Polyaniline (PANI) was synthesized and doped with 0, 2, 4 and 16 wt.% of pure and functionalized multiwall carbon nanotubes (MWCNTs) by “in-situ” polymerization. Measurement of temperature dependence of electrical resistivity showed a reduction in the resistivity of the composites at all temperatures. The reduction was increased by increasing the wt.% of MWCNTs. This decrease was more for the composites containing functionalized MWCNTs and was more prominent for temperatures below 150 K. The glass transition temperature (T_g) of the pure and doped PANI was measured using electrical resistivity measurements. It was observed that by increasing the amount of functionalized MWCNTs in PANI, its T_g increases. Temperature dependence of resistivity of pressed pure PANI showed that by increasing the pelletization pressure, the bulk electrical resistivity decreased but the T_g increased.

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1. Introduction

Carbon nanotubes (CNTs) have been widely studied due to their superb properties such as unusually high strength and stiffness, flexibility, thermally stable and low density. These properties accompanied by their high aspect ratio make CNTs ideal for various potential applications such as filler for polymeric composites. Comparing with composites containing conducting nanoparticles, CNT composites show high electrical conductivity at a low concentration of CNTs. In order to use the CNTs as dopant in various substances, they require to be well dispersed. This is due to their large surface area and strong van der Waals forces which can form strongly bound aggregates [1–3]. The chemical functionalization of CNTs is a technique to improve their dispersion in different matrices such as polymers. Functionalized CNTs are also easier to disperse in organic solvent and water, which can improve the dispersion and homogeneity of the CNTs within a polymer matrix [4–10].

Many polymers have been doped with CNTs for various target applications. Among them, polyaniline (PANI), a conducting polymer with molecular formula C_6H_7N , has achieved extensive importance for having good environmental stability, electrical conductivity and reversible control of conductivity both by charge transfer doping and protonation [4,11]. PANI is also used in electromagnetic shielding, corrosion inhibitors and “smart windows” due to its electrochromic

properties. It shows a whole range of colors as a result of their many protonation and oxidation forms [12].

Polymer molecules can have different kinds of motions depending on the polymer structure. The T_g of polymers is a way of understanding the molecular motion of a polymeric system. The degree of molecular motion is of fundamental concern when considering adhesion, cohesion, and other properties of polymers. Many physical properties including thermal expansion coefficient, heat capacity, resistance to mechanical shock and electrical characteristics can be changed by passing through T_g . PANI has high intra-chain rigidity coupled with strong inter-chain hydrogen bonding and dipolar interaction due to its crystalline structure. Thus, the detection of its molecular motion and therefore its glass-to-rubber transition temperature (T_g) becomes quite difficult with the available methods of measurement.

The T_g is determined using different techniques such as differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA) and dilatometry [13]. It seems that the measurement of temperature dependence of resistivity is a very good and near accurate technique for T_g measurement of conductive polymers because any motion of polymer chains can affect the motion of electrons resulting in an increase in resistivity.

MWCNT/PANI composites with different wt.% ratios of pure and functionalized MWCNTs were synthesized by “in-situ” polymerization and the properties of two sets of samples were compared. The samples were characterized using XRD, SEM and Raman spectroscopy. By measuring the electrical resistivity of the composites as a function of temperature using a standard four-probe technique, the effects of pure and functionalized MWCNTs on the electric resistivity of PANI were investigated. The T_g of composites was deduced from the resistivity curves.

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2. Experimental

2.1. Composite preparation

MWCNTs used in this study were synthesized using chemical vapor deposition (CVD). The MWCNTs were acid treated as described below to remove impurities such as metallic catalysts and to introduce functional groups such as carboxylic acid and hydroxyl groups to their surfaces. Initially, the MWCNTs were ultrasonically treated in concentrated HCl for 1 h in an ultrasonic bath. The samples were then filtered using a 0.45 μm Teflon filter paper and washed with deionized water until the rinsing water was of neutral and then dried in an oven at 100 $^{\circ}\text{C}$ for 24 h. Afterward the MWCNTs were ultrasonically treated with a 3:1 mixture of concentrated $\text{H}_2\text{SO}_4:\text{HNO}_3$ at room temperature for 30 min. Then, the oxidation reaction was carried out in a one necked, round bottomed glass flask, equipped with reflux condenser, magnetic stirrer and thermometer which was mounted in the preheated water bath. The reaction was carried out at 80 $^{\circ}\text{C}$ and refluxed for 8 h. After that, the sample was filtered using a 0.45 μm Teflon filter paper and was washed with deionized water until the pH value was around 7.0. The samples were then dried at 100 $^{\circ}\text{C}$ in 24 h. The composites of doped PANI with pure and functionalized MWCNTs were synthesized via in situ chemical oxidation polymerization. In a typical synthesis experiment, 0, 2, 4 and 16 wt.% of pure or functionalized MWCNTs were dissolved in 50 ml of 1.0 M HCl solution and ultrasonicated for 2 h, separately. Then, they were transferred into one necked, round bottomed glass flask with an ice bath. Aniline monomer also dissolved in 100 ml of 1.0 M HCl solution and then was added to the above MWCNT suspension. A 50 ml of 1 M HCl solution containing 1.96 g ammonium persulfate (APS) was slowly added dropwise into the individual suspension with constant mechanical stirring at a reaction temperature of 0–5 $^{\circ}\text{C}$ for 30 min. The reaction mixture was stirred for 8 h at 0–5 $^{\circ}\text{C}$. In the next step, the resultant green suspension, indicating the formation of insoluble PANI in its emeraldine form, was filtered and rinsed several times with deionized water and acetone. The powder obtained was dried at 70 $^{\circ}\text{C}$ in 20 h.

2.2. Structural and morphological analysis

The Raman spectroscopy, X-ray diffraction and SEM measurements were utilized to characterize the structure of MWCNTs, functionalized MWCNT/PANI and pure MWCNT/PANI composites. Raman spectra were performed under Alpha Thermo Nicolet dispersive Raman spectrometer using 532 nm of an Nd:YLF laser, at the spectra range of 500–4200 cm^{-1} , resolution 4 cm^{-1} and 32 scans in 3 min. The powder X-ray patterns were carried out using a PW-1840 Philips diffractometer at room temperature utilizing $\text{Cu K}\alpha$ radiation wavelength of $\lambda = 1.5418 \text{ \AA}$. The peak position and intensities were obtained between 10–80 $^{\circ}$ with a velocity of 0.02 $^{\circ}$ per second. The structural and morphological characterization of composites, were performed by measuring SEM using a Philips XL30 scanning electron microscope.

2.3. Electrical resistivity measurements

The temperature dependence of resistivity was measured using the standard four-probe technique from 427–113 K using a liquid nitrogen cryostat. In order to measure the resistivity, powders of PANI, pure MWCNT/PANI and functionalized MWCNT/PANI composites were pressed into bar shaped pellets under 380 MPa. The cross section and the length of all samples were the same. The effect of pelletizing pressure on T_g of PANI was also investigated by measuring the resistivity of samples which were pressed under 96, 380, 580, 770 and 1150 MPa.

3. Results and discussion

3.1. Raman spectroscopy analysis

Raman spectroscopy is a very useful technique to characterize material composition, sample temperature, and strain from analysis of the material specific phonon mode energies. The most prominent Raman active modes in CNTs are radial breathing modes (RBM) in the low frequency region and D, G and G' modes in the higher frequency region. While D, G, and G' modes are also found in graphite, the RBM mode which is seen at 100–300 cm^{-1} is a unique CNT mode and is only seen in single-walled carbon nanotubes. The D mode or disorder mode originates from structural defects and is seen at 1200–1400 cm^{-1} . The G mode or graphite mode corresponds to planar vibration of carbon atoms and is seen at 1500–1600 cm^{-1} . This mode appears in most graphite like materials. Therefore, the ratio of the I_D/I_G represents the degree of disorder in CNT structures. The G' mode is a second overtone of the defect induced D mode and is seen at 2500–2900 cm^{-1} [4,6,11,14,15].

Fig. 1 shows the Raman spectrum of pure and functionalized MWCNTs. Both spectra are the same which means the functionalization does not affect the graphite structure of the MWCNTs. As can be seen the ratio of I_D/I_G is bigger for the functionalized MWCNTs as expected. The oxidation of MWCNTs breaks some bonds and inserts chemical groups that can be interpreted as defects on the structure. Table 1 shows the peak position and the intensity ratio of I_D/I_G of the samples.

Fig. 2 shows the Raman spectroscopy of functionalized MWCNTs, PANI and the composite containing 2 and 4 wt.% of functionalized MWCNTs. For comparison, Fig. 2 also includes the spectrum of functionalized MWCNT, which contains D and G modes. For PANI and functionalized MWCNT/PANI composites, C–H bending of the quinoid ring at 1170 cm^{-1} , C–H bending of the benzenoid ring at 1230 cm^{-1} , C–N $^+$ stretching at 1330 cm^{-1} , and C–C stretching of the benzene ring at 1480 and 1590 cm^{-1} were observed, revealing the presence of the doped PANI structures [4,16,17]. On the other hand, with the increase of the wt.% of MWCNTs in the polymer matrix, the intensity of the peaks at 1330 and 1590 cm^{-1} was increased because they are very close to the D and G modes, respectively. This indicates a strong interaction between MWCNTs and PANI.

The formation mechanism of functionalized MWCNT/PANI composites is believed to arise from the strong interaction between aniline monomer and MWCNTs. The interaction could be due to both the π – π^* electron interaction between MWCNT and the aniline monomer and the hydrogen bond interaction between the carboxylic groups of functionalized MWCNTs and amino groups of aniline monomer. Such a strong interaction causes the adsorption of aniline monomer on the surface of MWCNTs. MWCNTs therefore serve as the template during the formation of composites. The polymer chains during their growing can possibly disentangle the MWCNT bundles

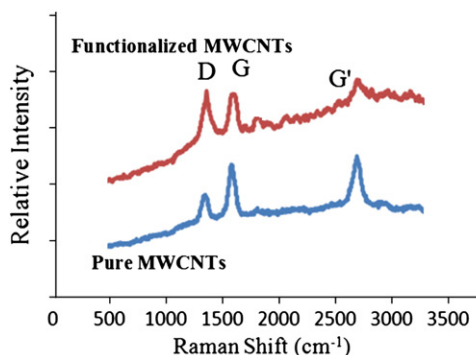


Fig. 1. Raman spectroscopy of pure and functionalized MWCNTs.

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