Properties of Polyacrylamide and Functional Multi-walled Carbon Nanotube Composite

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Abstract

In this study the structural and electrical properties of multi-walled carbon nanotube (MWCNT) reinforced polyacrylamide (PAM)-based composites were investigated. Two types of nanotubes were prepared and used i.e. acid functionalized MWCNT-COOH and amine-functionalized MWCNT-A. The nanocomposite was prepared using the solution cast technique. The samples were characterized using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), mechanical testing and electrical conductivity measurement. A comparative study has been made on the physical property of PAM/MWCNT-COOH and PAM/MWCNT-A nanocomposites. It was observed that the amine-functionalization of nanotube improved the filler dispersion into the polymer matrix. SEM photographs ascertain that the MWCNT-A nanoparticles were evenly dispersed in PAM matrix. The electrical conductivity of PAM/MWCNT-COOH was in the range of 0.03-0.5 S cm⁻¹, while PAM/MWCNT-A had higher electrical conductivity of 0.4 to 1.2 S cm⁻¹. The ultimate tensile strength of PAM/MWCNT-A nanocomposites was found to increase from 21-26 MPa, relative to PAM/MWCNT-COOH series (19-23 MPa).

Keywords: Polyacrylamide; carbon nanotube; amine-functionalization; SEM; electrical conductivity

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1. Introduction

Carbon nanotube (CNT) based nanocomposites are progressively being discussed as a reasonable choice to usual smart materials, as they present higher electronic features and superior sensitivity. The CNT is expected to strengthen the outstanding characteristics of polymer matrix leading to several advance applications [1-3]. For polymer composite strengthening, a number of research efforts have been employed [4-6]. As a result of research by Iijima in 1991, carbon nanotube has been discovered. The hexagonal arrays of carbon atoms in graphite sheets of carbon nanotube surface are perfect for strong interaction with other molecules [7]. The significances of carbon nanotubes are exceptional metallic, electronic, optoelectronic, mechanical, structural, semiconductor, and chemical large specific surface area, hollow and layered structures, and other enhanced physical properties. Carbon nanotube would contact future nanotechnology and nanoscience since it is a highly prospective material and has become accessible in macroscopic quantities. Carbon nanotube is categorized into two main types (i) single-walled carbon nanotube (SWCNT) and (ii) multi-walled carbon nanotube (MWCNT). The walls of carbon nanotube are not reactive, while their fullerene-like tips are known to be more reactive. Therefore the functionalization at end of carbon nanotube is used to produce functional groups (–COOH, –OH, or –CO). Carbon nanotube has several latent applications such as field emission, nano-devices, gas adsorption, composite strengthening, metal (ion) nanocomposites, and catalyst supports as they possess unique electrical properties, extraordinary mechanical features, large specific surface area, high chemical and thermal stability. The applications of carbon nanotube have also been broadly utilized in the numerous detection devices for example gas sensors, electrochemical detectors and biosensors with immobilized bio-molecules. Moreover their applications are encouraging in voltammetric and electrochemical stripping methods. The optical and electrical properties of the poly(3-hexylthiophene)/SWCNT composites have been studied and an enhancement of ~5 orders of magnitude in electrical conductivity was reported for a concentration of 30 wt.% SWCNT in polymer matrix [7-9]. However there are still several challenges in the polymer/CNT composite preparation because of the nanotube agglomeration. In order to optimally utilize CNT as a reinforcing component in polymer matrix, some unique treatment methods such as chemical or physical methods have been employed. Modification is important to attain enhanced CNT dispersal and good interface between polymer matrix and filler [10, 11]. Physical methods involve ultrasonication or milling to physically separate the tubes that are bundled together. Chemical methods involve employment of surfactant or chemical functionalization of the tube surface. This enhances the interfacial bonding between the polymer and nanotube and can avoid the tube aggregation. Several research groups have studied the electrical and mechanical features of polymer/CNT composites employing physically/chemically treated CNT [12, 13]. Functionalized nanotube is also usually easier to diffuse in solvents/organic solvents which may enhance the dispersal and homogeneity of the nanotube within the polymer [14, 15]. While property enhancement based on carboxylated functionalized MWCNT are not superior to amino (-NH2) functionalized SWCNT composites [16, 17]. In one study polyacrylamide/amo termined MWCNT composite displayed enhanced dispersion and improved interfacial interaction between polymer and nanotubes. The employment of covalent chemistry to join amines to nanotube is also anticipated to provide accessibility, excellent stability, and selectivity [18]. The generation of amino-functionalized MWCNT has been reported by chemical treatment of carboxylic acid introduced onto the MWCNT surface by chemical oxidation. To introduce amino groups on MWCNT surface via amide formation involves direct coupling of ethylene diamine with the carboxylic groups. Polyacrylamide was also explored as significant matrix for functional nanotube [19, 20]. In the present study, the preparation of polyacrylamide (PAM) and MWCNT composite films by solution cast technique has been reported. Acid-functionalized as well as amine-functionalized MWCNT were used as reinforcement. Later electrical, mechanical, and morphological properties of PAM/MWCNT composites were studied. Enhanced electrical conductivity was observed for the PAM/amine-functional MWCNT composites.
2. Experimental

2.1. Materials

Polyacrylamide (\(M_n\) 5×106,000,000-6,000,000), poly(ethylene glycol) diamine (average \(M_n\) 2,000), CNT, multi-walled (>98% carbon basis, ODxL 6-13nmx2.5-20 mm), and sodium dodecyl sulfonate (SDS) were purchased from Aldrich.

2.2. Instrumentation

Infrared spectroscopy (IR) spectra were taken at room temperature with a resolution of 4 cm\(^{-1}\) using Excalibur Series FTIR Spectrometer, Model No. FTSW 300 MX manufactured by BIO-RAD. The scanning electron microscopic (SEM) images were obtained by Scanning Electron Microscope S-4700 (Japan Hitachi Co. Ltd.). Stress-strain behavior was examined using a universal testing machine (Instron 4466) with a strain rate of 5 mm/min at 25 °C according to ASTM D638 standard method. The electrical conductivity of thin films was measured at room temperature and ambient atmosphere using the four-point method (Keithley 2401).

2.3. Acid functionalization of MWCNT (MWCNT-COOH)

Firstly, raw MWCNT was annealed at 400 °C for 0.5 h to remove the amorphous carbon content. The purified MWCNT were refluxed and sonicated at 70 °C in a mixture of 8 M sulphuric acid:5 M nitric acid (3:1). Then 500 mL of deionized water was added and mixture was filtered and washed several times with deionized water to obtain pH ~ 6 [20, 21].

2.4. Amine functionalization of MWCNT (MWCNT-A)

1g acid functionalized MWCNT was mixed with 0.5 g sodium dodecyl sulphate and added to 200 mL deionized water. The mixture was ultrasonicated for 4 h. 1g poly(ethylene glycol) diamine was added to the reaction mixture.
and refluxed for 6 h at 80 °C. The product obtained was put into 500 mL deionized water. The mixture was filtered and dried at 80 °C (Fig. 1). FTIR (cm⁻¹): 3320 (N–H stretching vibration), 3003 (Ar C–H stretching vibrations), 2944 (aliphatic C–H stretching vibrations), 1611 (carbonyl C=O stretching vibrations), 1525 (N–H bending vibration), 1270 (C–O stretching vibrations).

2.5. Synthesis of polyacrylamide/MWCNT composite (PAM/MWCNT-COOH and PAM/MWCNT-A)

The PAM/MWCNT composites were prepared by the solution cast technique using acid and amine-functionalized MWCNT. 0.5 g PAM powder was dissolved in 10 mL ethanol and mixed with MWCNT at different wt. % (1-5) (Fig. 2). Films were caste at 50 °C for 3 h.

![Fig. 2 Interaction between amine-functional MWCNT and PAM.](image)

3. Results and Discussion

3.1. Morphology of PAM/MWCNT composite

To study the surface morphologies of PAM/MWCNT-COOH and PAM/MWCNT-A composites, scanning electron microscopy studies were carried out. The SEM micrographs of PAM/MWCNT-COOH and PAM/MWCNT-A are given in Fig. 3A and Fig. 3B. Both of the composites series was observed with 2 wt. % filler loading to study the comparative affect. The acid-functionalized MWCNT was present somewhat in the form of agglomerates. Whereas the amine-functionalized MWCNT were dispersed more uniformly throughout the PAM matrix. The photographs confirmed much better dispersion of MWCNT-A in PAM matrix. In other words good dispersion for MWCNT-A was observed due to enhanced interfacial bonding between nanotube and polymer matrix.
3.2. Mechanical strength

The mechanical properties of PAM/MWCNT-COOH and PAM/MWCNT-A composites is shown in Fig. 4. The data is also tabulated in Table 1. Generally the mechanical properties of polymer/CNT composites depend on (i) nature of nanofiller; (ii) nanofiller loading; (iii) compatibility between the two phases; and (iv) relative concentration of two phases. Mechanical results also depicted that the properties increased with the MWCNT-COOH and MWCNT-A content. In PAM/MWCNT-COOH 1-5 composite the ultimate tensile strength was increased from 19-23 MPa, while in PAM/MWCNT-A 1-5 composites the values increased further to 21-26 MPa. Similarly the Young’s modulus for the PAM/MWCNT-A 1-5 series was found higher in the range of 399-544 MPa, compared with the acid-functional series (123-375 MPa). Results suggested that the mechanical property of the composites not only depends on the filler type and content, but also on the interfacial interaction between PAM and nanofiller [22, 23].
3.3. Electrical transport property

The d.c. electrical conductivity of PAM/MWCNT composite was measured using the four-probe technique (Table 2). The room temperature conductivity of the PAM/MWCNT-COOH 1-5 and PAM/MWCNT-A 1-5 composites at different loading is shown in Fig. 5. The electrical conductivity of neat PAM film was found as $1 \times 10^{-6}$ Scm$^{-1}$. The change in conductivity was observed for PAM/MWCNT-COOH 1-5 series in the range of 0.03-0.5 Scm$^{-1}$. The electrical conductivity was further increased from 0.4 to 1.2 Scm$^{-1}$ in PAM/MWCNT-A series. The noteworthy enhancement in conductivity suggested that the dispersion of nanotube was increased due to amine-functionalization. At 5 wt.% loading of poly(ethylene glycol)diamine functionalized MWCNT, the conductivity was several orders of magnitude higher than neat PAM film [24, 25].

![Figure 5: Room temperature electrical conductivity of PAM/MWCNT composite.](image-url)
Table 2 Electrical conductivity of PAM/MWCNT composites.

<table>
<thead>
<tr>
<th>Composition</th>
<th>Electrical conductivity (S cm$^{-1}$)</th>
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<tbody>
<tr>
<td>PAM</td>
<td>1×10$^{-6}$</td>
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<tr>
<td>PAM/MWCNT-COOH1</td>
<td>0.03</td>
</tr>
<tr>
<td>PAM/MWCNT-COOH2</td>
<td>0.2</td>
</tr>
<tr>
<td>PAM/MWCNT-COOH3</td>
<td>0.3</td>
</tr>
<tr>
<td>PAM/MWCNT-COOH5</td>
<td>0.5</td>
</tr>
<tr>
<td>PAM/MWCNT-A1</td>
<td>0.4</td>
</tr>
<tr>
<td>PAM/MWCNT-A2</td>
<td>0.5</td>
</tr>
<tr>
<td>PAM/MWCNT-A3</td>
<td>1.1</td>
</tr>
<tr>
<td>PAM/MWCNT-A5</td>
<td>1.2</td>
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</table>

4. Conclusion

In this attempt, PAM/MWCNT composites were prepared using solution casting technique. The influence of acid functionalization and amine functionalization of MWCNT on dispersion, mechanical, and electrical properties of nanocomposites has been studied. The results revealed that the room temperature electrical conductivity of nanocomposites was increase by several orders of magnitude compared with the neat PAM film. SEM micrographs showed good dispersion for poly(ethylene glycol)diamine functionalized nanotube. Amine-functionalization of nanotube actually improved the interfacial bonding between the filler and polymer matrix, which later affected the physical properties of novel nanocomposites.

References


