



# Amino acid-functionalized multi-walled carbon nanotubes for improving compatibility with chiral poly(amide-ester-imide) containing L-phenylalanine and L-tyrosine linkages



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## ABSTRACT

Amino acid functionalized multi-walled carbon nanotubes (f-MWCNTs)/poly(amide-ester-imide) (PAEI) composites were fabricated by solution mixing method. Proper functionalization and mixing strategy of MWCNTs provides the best opportunity for better distribution and bonding of nanoparticles to the polymer matrix. MWCNTs have been chemically modified with L-phenylalanine to improve their compatibility with L-phenylalanine based PAEI. Field emission scanning electron microscopy micrographs of composite revealed that f-MWCNTs made a good interaction with polymer chains by wrapping the polymer around them, and transmission electron microscopy results confirmed well dispersion with nano size of f-MWCNTs in the polymer matrix. In addition, thermal analysis showed good enhancement in thermal properties of composites compared to pure polymer. Thermal stability of the composites containing f-MWCNTs was enhanced due to their good dispersion and improved interfacial interaction between the amino acid based PAEI matrix and f-MWCNTs.

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## 1. Introduction

Throughout the previous century, there have been a lot of progress and researches in the field of polymer nanocomposite due to its high performance at low filler loading [1–3]. Homogeneous distribution and adhesion of fillers to the polymer matrix are important factors to improve desired performances. Introducing proper functional groups on the nanofiller's surfaces play a significant role in the development of their compatibility with the polymer matrix [4–6].

A widespread investigation on structure, physical and chemical properties of carbon nanotubes (CNTs) has been made. Recently, the goal of researches has been shifted from the synthesis, purification, and characterization of nanotubes to their new functionalization; therefore, the modification of CNTs has become an important subject these days [7–10]. Different groups or compounds can be attached to the sidewall of the CNTs by different mechanisms such as covalent functionalization to the nanotube ends or defects,

sidewall covalent functionalization, and noncovalent exohedral functionalization; for example, wrapping nanotubes by polymers [11]. Several techniques have been reported for the synthesis of functionalized CNTs, which commonly need an activation step to introduce covalent functionalities on the CNT surface. The most common method is creating carbonyl and carboxylic acid groups on the CNT surface by chemical oxidation. For more compatibility, activated CNTs are further functionalized with different approaches such as amidation or esterification of oxidized nanotubes. Modifications of CNT surface with silanes and carboxylate salts under basic conditions are additional techniques that have also been reported. In addition, non-covalent functionalization of CNTs can be accomplished by van der Waals forces or  $\pi$ - $\pi$  stacking interactions using surfactants, biomolecules, polynuclear aromatic compounds and polymers [12–17].

Embedding functionalized CNTs into polymer matrix leads to the enhancement of electrical properties, tensile strength and thermal stability due to their unique characteristics [11,18–22]. Functionalization not only causes good distribution of CNTs; but also causes polymers to bond to the CNTs by covalent, non-covalent and electrostatic interactions, which improve significant properties of polymers [11,23].

Herein, well-dispersed polymer/MWCNT composite has been explored through amino acid functionalized multi-walled carbon nanotubes (f-MWCNTs). In addition, L-phenylalanine was used for modification of MWCNTs to get more interactions and

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compatibility with L-phenylalanine containing poly(amide-ester-imide) (PAEI). The results of analyses revealed these facts.

## 2. Experimental

### 2.1. Materials

MWCNT (diameter 10–20 nm, length 30  $\mu\text{m}$ , purity >95 wt%), was purchased from Neutrino Co. (Iran). Other chemicals used in this study were obtained from Fluka Chemical Co. (Switzerland) and Merck Chemical Co. (Germany). *N,N'*-dimethylacetamide (DMAc), sulfuric acid ( $\text{H}_2\text{SO}_4$  98%), hydrogen peroxide ( $\text{H}_2\text{O}_2$ ), and hydrochloric acid (HCl), from Merck were used for the synthesis of mediators. DMAc as solvent were distilled over barium oxide under reduced pressure. Other reagents were used without further purification.

### 2.2. Measurements

Fourier transform infrared (FT-IR) spectra of the composites were recorded with a Jasco-680 (Japan) spectrometer at  $4\text{ cm}^{-1}$  resolution and they were scanned at wavenumber range  $400\text{--}4000\text{ cm}^{-1}$ . Thermogravimetric analysis (TGA) is performed with a STA503 win TA (Bahr-Thermoanalyse GmbH, Hüllhorst, Germany) at the heating rate of  $10^\circ\text{C min}^{-1}$  from  $25^\circ\text{C}$  to  $800^\circ\text{C}$  under nitrogen atmosphere. The X-ray diffraction (XRD) was used to characterize the crystalline structure of the composites. XRD patterns were collected using a Bruker, D8ADVANCE (Germany) diffractometer with a copper target at the wave length  $\lambda$  Cu  $K_\alpha = 1.54\text{ \AA}$  and a tube voltage of 40 kV and tube current of 35 mA, in the range of  $10\text{--}80^\circ$  at the speed of  $0.05^\circ/\text{min}$ . The MWCNT dispersion morphology on PAEI matrix was observed using field emission scanning electron microscopy (FE-SEM, HITACHI S-4160, Japan). Transmission electron microscopy (TEM) images were obtained using an EM208S microscope with an accelerating voltage of 100 kV. A MISONIX ultrasonic XL-2000 SERIES (USA) was used in some steps. Ultrasound was a wave with  $2.25 \times 10^4$  Hz frequency and 100 W power.

### 2.3. Oxidation of MWCNTs

Oxidized MWCNTs were synthesized through Hummers method [24]. MWCNT powders (0.5 g) were poured into cold ( $0^\circ\text{C}$ ) solution of concentrated  $\text{H}_2\text{SO}_4$  (12 mL) and  $\text{NaNO}_3$  (0.25 g).  $\text{KMnO}_4$  (1.5 g) was gradually added while stirring and cooling so that the temperature of the mixture was not allowed to reach  $20^\circ\text{C}$ . The mixture was then stirred at  $35^\circ\text{C}$  for 30 min; and distilled water (25 mL) was added. The temperature was raised to  $98^\circ\text{C}$  and was maintained at this temperature for 15 min. The reaction was terminated by adding a large amount of distilled water (70 mL) and then it was treated with 30%  $\text{H}_2\text{O}_2$  (2 mL). The mixture was filtered and washed with distilled water and 10% HCl solution in order to remove metal ions. The obtained oxidized MWCNT powders were dried at  $60^\circ\text{C}$ .

### 2.4. Functionalization of MWCNTs

Oxidized MWCNT powders (0.1 g) were dispersed in 10 mL of distilled water, and 0.3 g of L-phenylalanine and an equimolar amount of NaOH in 10 mL of distilled water were added. The mixture was stirred for 24 h at room temperature. At the end of the reaction, the colloidal dispersion was treated with ethanol, and the resulting precipitate was centrifuged, washed well with  $\text{H}_2\text{O}/\text{EtOH}$  mixture, and finally dried. For more dispersion, the solids were stirred and ultrasonicated in 5% HCl solution to change the

carboxylate groups into carboxylic acid groups. Then, the solids were collected and dried at  $60^\circ\text{C}$ .

### 2.5. Synthesis of poly(amide-ester-imide)

Poly(amide-ester-imide) was synthesized based on our previous research (shown in Scheme 1) [25].

### 2.6. Preparation of PAEI/f-MWCNT composites

To obtain homogeneous mixed PAEI/f-MWCNT solutions with preferred weight percentages of f-MWCNTs, a step-wise method was used. First, two solutions were prepared: PAEI was dissolved in DMAc, and f-MWCNTs were dispersed separately in DMAc and stirred for 1 day at room temperature. Then, both solutions were mixed to reach the desired weight percentages of f-MWCNTs (5, 10 and 15 wt%). The PAEI/f-MWCNT solutions were stirred for 1 day at room temperature to  $40^\circ\text{C}$ , and then ultrasonicated in ice bath for 1 h. To remove the solvent, PAEI/f-MWCNT solutions were poured into glass Petri dishes and uniformly heated at  $60^\circ\text{C}$ ; then, the solid composite was further dried in vacuum at  $160^\circ\text{C}$  for 8 h. Appearance of a uniform color indicates the good distribution of f-MWCNTs in the polymer matrix.

## 3. Results and discussion

### 3.1. Preparation of PAEI/f-MWCNT composites

Finding a good way to incorporate MWCNTs within polymer matrix is a crucially important step in fabricating high performance composites. Achieving this goal needs homogenous dispersion of MWCNTs in the polymer matrix based on strong interfacial interactions. The major limitation is debundling and aggregation of MWCNTs in the polymer matrix due to their good intramolecular van der Waals forces and hydrophobic nature. Constructions of functional groups on nanotube surfaces effectively accomplish their interaction with polymer matrix. Undoubtedly, the most applied chemical modification is surface treatment with strong inorganic acids to form oxygen-containing functional groups (Fig. 1). Furthermore, for more interactions and compatibility between MWCNTs and polymer matrix, based on existence of L-phenylalanine in polymer structure, oxidized MWCNTs were functionalized with L-phenylalanine (Fig. 1). In this way, better covalent and hydrogen bonding will occur between f-MWCNTs and polymer functional groups, and the polymer wraps the f-MWCNTs more suitably.

Quite a lot of studies have been conducted on the properties of polymer/CNT composites with CNT content from 1 to 15 wt%, and good results have been obtained and reported [26–28]. Based on these, 5–15% of f-MWCNT contents in the composites were selected. The composite containing different amounts of f-MWCNTs (5, 10, 15 wt%) in PAEI matrix was obtained by dissolving in DMAc with vigorous stirring, followed by ultrasonication process for an hour, and then by evaporating the solvent to form a new series of chiral composites. Membrane based on polymer composites was made by casting method, which was transparent, homogeneous and brittle.

### 3.2. Characterization of f-MWCNT and PAEI/f-MWCNT composites

#### 3.2.1. FT-IR analysis

To confirm the functionalization of MWCNTs and the presence of functional groups on the prepared products, samples were analyzed by FT-IR. Similar to graphene oxide fabricated by Hummers

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