Efficient surface modification of MWCNTs with vitamin B₁ and production of poly(ester-imide)/MWCNTs nanocomposites containing L-phenylalanine moiety: Thermal and microscopic study

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Abstract. A simple and efficient method was presented for chemical functionalization of multi-walled carbon nanotubes (MWCNTs) with vitamin B₁. Poly(ester-imide) (PEI) based nanocomposites were prepared by the incorporation of different amounts of modified MWCNTs (5, 10, 15 wt%) into a chiral and biodegradable PEI by solution blending and ultrasonic dispersion methods. The chiral PEI was produced by a step-growth polymerization of chiral diacid with 4,4'-thiobis(2-tert-butyl-5-methylphenol). Spectroscopic and microscopic techniques were used to examine the chemical structure, morphology and thermal stability of the functionalized MWCNTs and the obtained nanocomposites. The microstructure study revealed the homogeneous dispersion of modified MWCNTs throughout the PEI matrix. Thermogravimetric analysis results confirmed that the heat stability of the prepared composites was improved compared to the pure PEI.

Keywords: polymer composites, multi-walled carbon nanotubes, functionalization, vitamin B₁, ultrasonic process

1. Introduction

Carbon nanotubes (CNTs) have attracted many basic research efforts since their discovery in 1991 [1]. They have an exceptional structure with superior physical and chemical properties as well as excellent mechanical performance. Owing to these properties, they have been widely used in nanoelectronic devices, actuators, air and water filters, chemical sensors, biosensors, drug delivery, phototherapy, etc. [2–4]. They can serve as a promising reinforcement phase incorporated into a polymer matrix to prepare high-performance polymer nanocomposites [5–10].

It has been found that the as-produced CNTs tend to agglomerate together due to the high aspect ratios and very strong van der Waals forces between the nanotubes. Therefore, poor dispersion, the lack of solubility and weak chemical compatibility with the polymer matrix have become a bottleneck in the application of CNTs [11]. Mechanical methods such as ultrasonication and high-shear mixing as well as chemical methods including non-covalent and covalent functionalization were among the commonly used methods to prevent CNTs aggregation and achieve good dispersion in the polymer matrix. The chemical functionalization of CNTs not only

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enhances the dispersion ability of CNTs in solvents and composites, but can also improve the compatibility of CNTs with the composite matrix [3, 12, 13]. Ultrasonic irradiation is widely used to dispersing nanoparticles and colloids, functionalization of CNTs and produce nanocomposites, nanomaterials, and nanoforms of chemical compounds [14]. The chemical effects of ultrasound derive from acoustic cavitation. The ultrasonic cavitation can generate bubble collapse and high-energy inter-particle collisions, producing intense local heating and high pressures together with implosion shock waves and micro jets in the liquid medium. The combined effect is able to provoke chemical reactions on the CNTs [15].

Poly(ester-imide)s (PEI)s show good mechanical properties, high thermal stability, facile processing and electrical insulation [16–18]. This class of polymers brings together the desirable characteristics from both polyesters and polyimides. These properties make them suitable for different applications in printed circuit boards, engineering thermoplastics, electronic devices, membranes, and adhesives, [19–21] being a promising matrix candidate for hybrid materials.

In this paper, the attaching of thiamine hydrochloride (vitamin B₁) on carboxylated-multi-walled carbon nanotubes (MWCNTs-COOH) was carried out under ultrasonic irradiation. The chiral PEI was prepared by a direct polycondensation of equimolecular amounts of aromatic diol and natural amino acid based diacid. The different loading levels of functionalized MWCNTs (5, 10, 15 wt%) were effectively dispersed in the aromatic polymer through ultrasonic irradiation to prepare MWCNTs reinforced polymer nanocomposites. The structure and morphology characterization as well as thermal stability of the modified MWCNTs and the obtained nanocomposites were investigated by FT-IR spectroscopy, thermogravimetric analysis (TGA), X-ray diffraction (XRD), transmission electron microscopy (TEM), and field emission scanning electron microscopy (FE-SEM).

2. Experimental

2.1. Materials

MWCNTs-COOH synthesized by thermal chemical vapor deposition process (CVD), having inner diameter of 5–10 nm, outer diameter of 10–20 nm, purity >95 wt%, carboxyl content of 2.00 wt% and length

~30 μm were used. Other solvents and chemicals were reagent-grade quality, achieved commercially from Aldrich Chemical Co. (Milwaukee, WI), Fluka Chemical Co. (Buchs, Switzerland), Riedel-deHaen AG (Seelze, Germany) and Merck Chemical Co. (Germany). Pyromellitic dianhydride (benzen-1,2,4,5-tetracarboxylic dianhydride) (1) was purified by recrystallization from acetic anhydride followed by sublimation. N,N-dimethylformamide (DMF) and N,N-dimethylacetamide (DMAc) were distilled over barium oxide under reduced pressure. Thiamine hydrochloride, 4,4'-thiobis(2-tert-butyl-5-methylphenol) (TTMP) and L-phenylalanine were used as obtained without further purification.

2.2. Measurements

FE-SEM images were obtained at 15 kV using a HITACHI S-4160 instrument (Tokyo, Japan). TEM analyses were performed using a Philips CM 120 operating at 100 kV (Germany). The XRD patterns of the samples were recorded using a Philips X'PERT MPD with a copper target at 40 kV and 35 mA and $\text{Cu K}\alpha \lambda = 1.54 \text{ \AA}$ in the range 10–80° at the speed of 0.05 °C/min. TGA data were taken on a STA503 instrument (Bahr-Thermoanalyse GmbH, Hüllhorst, Germany) in a nitrogen atmosphere at a rate of 20 °C/min. FT-IR spectra were recorded with a Jasco-680 (Tokyo, Japan) spectrometer at a resolution of 4 cm^{-1} and scanned at wavenumber range of 400–4000 cm^{-1} . The spectra of solids were obtained using KBr pellets. Band intensities were assigned as weak (*w*), medium (*m*), shoulder (*sh*), strong (*s*) and broad (*br*). The reaction was carried out on MISONIX ultrasonic liquid processors, XL-2000 SERIES (Raleigh, NC, USA). Ultrasound was a wave of frequency $2.25 \cdot 10^4 \text{ Hz}$ and power of 100 W.

2.3. Monomer synthesis

N,N'-(pyromellitoyl)-bis-L-phenylalanine diacid (3) as an optically active monomer was prepared based on our previous research (Figure 1) [22].

2.4. Polymerization procedure

Optically active and biodegradable PEI was synthesized by the direct polycondensation of equimolecular amounts of aromatic diol (4) and chiral diacid (3), using TsCl/DMF/Py as a condensing agent (Figure 1) [23].

Figure 1. Synthetic route used to prepare the PEI

2.5. Thiamine functionalized MWCNTs (Tm-MWCNTs)

The MWCNTs-COOH was chemically modified with vitamin B₁ as shown in Figure 2. 100 mg of vitamin B₁ was dissolved in 10 mL of H₂O. Then the MWCNTs-COOH (50 mg) and 0.10 mL of conc. HCl were added to this solution and the whole mixture was ultrasonicated for one hour. After irradiation, the mixture was centrifuged, washed thoroughly with water, and dried under vacuum to give the product of Tm-MWCNTs.

2.6. Preparation of the PEI/Tm-MWCNTs nanocomposites

The different amounts of functionalized MWCNTs (5, 10, 15 wt%) were dispersed in DMAc solvent and stirred for 1 day at 30–40 °C. Then, the PEI was added into this solution and ultrasonicated in a water bath for 1 h. Finally, the obtained suspension was poured into glass Petri dishes, followed by solvent evaporation at room temperature. The obtained nanocomposites were further dried under vacuum at 120 °C for 6 h to remove the remaining solvent.

3. Results and discussion

3.1. Fabrication of Tm-MWCNTs

Weakly dispersed CNTs often weaken the performance of CNTs-based composites materials. Chemical modification of the CNTs is essential to achieve a sufficient interfacial adhesion and obtain the advantage of exceptional properties of the CNTs to prepare polymer composites with enhanced performance [24]. In this work, the surface of MWCNTs-COOH was chemically functionalized with vitamin B₁ as a biological molecule, under ultrasonic irradiation. Vitamin B₁ is a water-soluble vitamin, pharmaceutically and biologically important compound. It plays a major role in the carbohydrate metabolism and good health of the body, mainly in terms of emotional health and well being [25, 26]. The carboxylic acid groups on the surface of MWCNTs could be reacted with the hydroxyl group of vitamin B₁ to form ester groups. The vitamin B₁ is expected to interact with different polar groups on the surface of MWCNTs through van der Waals, hydrogen bonding, electrical and hydrophobic interaction. Also, the aromatic structure of vitamin B₁

Figure 2. Chemical attachment of vitamin B₁ to MWCNTs-COOH

could provide the possibility for π - π interactions with the delocalized π -bonds on the CNTs wall (Figure 2). The modification of CNTs surface with vitamin B₁ is anticipated to reduce the tendency of CNTs to aggregate, increase its dispersion in solvents and improve interfacial interaction between polymer matrix and the Tm-MWCNTs.

3.2. Preparation of PEI/Tm-MWCNTs nanocomposites

The novel nanocomposites were prepared by mixing the appropriate amounts of functionalized MWCNTs and the optically active PEI under ultrasonic irradiations. CNTs functionalization and ultrasonication were used as useful methods to improve the interfacial interaction between MWCNTs and PEI matrix leading to efficient MWCNTs dispersion [27–31]. The obtained PEI contains heteroatoms with high-electron density, such as sulfur, nitrogen, and oxygen in its molecular structure, which provide the possibility for hydrogen bonding, van der Waals, electrical and hydrophobic interaction with different polar groups on the surface of modified MWCNTs. Also, the aromatic structure of PEI prefers to form π - π interactions with the delocalized π -bonds on the CNTs wall, as well as pyrimidine and thiazole ring of vitamin B₁ attached on the CNTs surface. Figure 3 illustrates possible interactions between the PEI chains and Tm-MWCNTs.

3.3. FT-IR spectroscopy

Figure 4 shows the FT-IR spectra of MWCNTs-COOH, Tm-MWCNTs, vitamin B₁, PEI and nanocomposites with 5, 10 and 15 wt% of Tm-MWCNTs. For MWCNTs-COOH, a characteristic peak at wave-number of 3454 cm⁻¹ corresponded to the O-H stretching mode of the carboxylic acid groups and the absorption peaks at 2852 and 2922 cm⁻¹ could be related to C-H stretching vibrations of MWCNTs-COOH defects [32]. The peaks at 1629 and 1431 cm⁻¹ could be assigned to the C=C aromatic ring stretching of the CNTs backbone [33] (Figure 4 curve (a)). For functionalized MWCNTs, the appearance of new peaks resulted from the functionalization of MWCNTs with vitamin B₁. The absorption bands at 1735 and 3464 cm⁻¹ could be attributed to the stretching vibration of C=O and O-H groups, respectively (Figure 4 curve (b)). For pure PEI, the bands at 1383 and 726 cm⁻¹ were related to the presence of the imide heterocycle in this polymer. The absorption bands at 1780 and 1726 cm⁻¹ corresponded to the carbonyl stretching vibrations of the imide and ester groups, respectively (Figure 4 curve (d)). The presence of CNTs in the polymer matrix demonstrated little changes in the FT-IR spectrum. It was probably attributed to low MWCNTs content, the weak vibration signal of MWCNTs and overlapping with the absorption peaks of pure PEI (Figure 4 curves (e-g)).

Figure 3. Schematic illustration of the possible interaction between the Tm-MWCNTs and the PEI matrix

Figure 4. FT-IR spectra of (a) MWCNTs-COOH, (b) Tm-MWCNTs, (c) thiamine hydrochloride, (d) pure PEI, (e) PEI/Tm-MWCNTs 5 wt%, (f) PEI/Tm-MWCNTs 10 wt%, (g) PEI/Tm-MWCNTs 15 wt%

Figure 5. XRD curves of (a) MWCNTs-COOH, (b) Tm-MWCNTs, (c) PEI, (d) PEI/Tm-MWCNTs 5 wt%, (e) PEI/Tm-MWCNTs 10 wt%, (f) PEI/Tm-MWCNTs 15 wt%

3.4. XRD studies

The XRD patterns of MWCNTs-COOH, Tm-MWCNTs, pure PEI, and nanocomposites with different loadings (5, 10, 15 wt%) are demonstrated in Figure 5. MWCNTs-COOH showed two peaks around $2\theta = 26$ and 43° , which related to the inter-layer spacing $d(002)$ and $d(100)$ reflections of the carbon atoms, respectively (Figure 5 curve (a)) [34]. The XRD pattern of Tm-MWCNTs was similar to MWCNTs-COOH. It confirmed that the cylinder wall structure and inter planner spacing of MWCNTs did not change (Figure 5 curve (b)). For the neat PEI, a broad peak centering at $2\theta = 18^\circ$ suggested that the PEI was in amorphous nature (Figure 5 curve (c)). For the nanocomposites, both characteristic peaks of the MWCNTs and the broad amorphous peak of PEI were observed. The peak intensity of Tm-MWCNTs was enhanced by the increasing of the loading level of Tm-MWCNTs in the nanocomposites (Figure 5 curves (d–f)).

3.5. Surface morphology studies

The morphological characterization of MWCNTs-COOH and Tm-MWCNTs was obtained using FE-SEM and the results are shown in Figure 6. The change of morphology after functionalization was

evidenced. The diameter of the Tm-MWCNTs became a little bigger than that of MWCNTs-COOH. This could be due to the absorption of vitamin B₁ on the surface of MWCNTs during the functionalization. The FE-SEM images of the fracture surfaces of pure PEI and nanocomposites are presented in Figure 7. It could be seen that the pure PEI had nanostructured morphology with a relatively spherical and smooth surface compared to the fracture surfaces of the nanocomposites (Figure 7a, 7b). For the nanocomposites, the distribution of bright dots and lines with protruding out of the polymer matrix was seen. These dots and lines represented the ends of the functionalized MWCNTs. It is clear that the Tm-MWCNTs were well dispersed in the PEI matrix and the increase of CNTs content did not lead to the formation of noticeable aggregation. The histograms of CNTs diameter distribution for the nanocomposites 10 and 15 wt%, showed mean CNTs diameter sizes of 30.98 and 34.50 nm, respectively (Figure 7). The effect of functionalization on the structure of the MWCNTs was studied by TEM (Figure 8). The MWCNTs-COOH were observed in the form of bundle and showed smooth surface with obvious aggregation (Figure 8e). After the attachment of vitamin B₁ onto the surface of MWCNTs, the debundling

Figure 6. The FE-SEM images of the fracture surfaces of Tm-MWCNTs (a, b) and MWCNTs-COOH (c, d)

of aggregates was observed and the diameter of MWCNTs was slightly increased. Moreover, the increased roughness of modified CNTs surface was apparent, which could be attributed to the functionalization (Figure 8a–8d).

The TEM images of nanocomposites containing 10 wt% Tm-MWCNTs are shown in Figure 9. The presence of isolated and well distributed nanotubes was clearly observed. The Tm-MWCNTs were embedded in the polymer matrix and the polymer layer wrapped around them. The result indicated a good compatibility and strong interfacial adhesion between modified CNTs and the polymer matrix.

3.6. Thermal properties

Figure 10 shows the TGA curve of MWCNTs-COOH, Tm-MWCNTs, pure PEI and the nanocomposites with different contents of Tm-MWCNTs. The thermal analysis data of the samples are summarized in Tables 1 and 2. Table 1 demonstrates ther-

Table 2. Thermal stability of CNTs samples obtained from TGA thermograms

Sample	T ₅ [°C] ^a	Char yield [%]
MWCNTs-COOH	550	90
Tm-MWCNTs	227	42

^aTemperature at which 5% weight loss was recorded by TGA at the heating rate of 20 °C/min under a nitrogen atmosphere.

Table 1. Thermal properties of the PEI and nanocomposites

Sample	T ₅ [°C] ^a	T ₁₀ [°C] ^b	Char yield [%] ^c	LOI ^d
Pure PEI	387	410	20	25.5
PEI/Tm-MWCNTs 5 wt%	388	414	30	29.5
PEI/Tm-MWCNTs 10 wt%	399	435	36	31.9
PEI/Tm-MWCNTs 15 wt%	417	459	38	32.7

^aTemperature at which 5% weight loss was recorded by TGA at heating rate of 20 °C/min under a nitrogen atmosphere.

^bTemperature at which 10% weight loss was recorded by TGA at heating rate of 20 °C/min under a nitrogen atmosphere.

^cWeight percentage of material left undecomposed after TGA analysis at a temperature of 800 °C under a nitrogen atmosphere.

^dLimiting oxygen index (LOI) evaluating at char yield at 800 °C.

Figure 7. FE-SEM photographs of pure PEI (a, b), PEI/Tm-MWCNTs (5 wt%) (c, d), PEI/Tm-MWCNTs (10 wt%) (e, f), PEI/Tm-MWCNTs (15 wt%) (g, h) and size distribution histograms of PEI/Tm-MWCNTs (10, 15 wt%) (e, g)

mal stabilities of the PEI and nanocomposites based on 5 and 10% weight loss (T_5 , T_{10}), residue at 800 °C (char yield) and limiting oxygen index (LOI). Pure PEI did not show substantial weight loss until 387 °C and this value was gradually increased with raising the concentration of Tm-MWCNTs in the nanocomposites, showing that an improvement was achieved due to the presence of Tm-MWCNTs as reinforcement. This could be ascribed to the excellent thermal stability of CNTs and their effective interactions with the PEI matrix.

The extent of surface functionalization can be evaluated by the percentage of weight loss in the TGA curves. The MWCNTs-COOH exhibited approximately a minor weight loss of 10 wt% and the functionalized MWCNTs showed 58 wt%, when the temperature was up to 800 °C. The comparative analysis proved the existence of vitamin B₁ grafted on the surface of MWCNTs. The relative content of vitamin B₁ was determined about 48 wt% (Table 2). LOI could be used to evaluate the flame-retardancy of materials and theoretically predicted in accor-

Figure 8. TEM images of Tm-MWCNTs at different magnifications (a–d) and MWCNTs-COOH (e)

Figure 9. TEM micrographs of PEI/Tm-MWCNTs nanocomposites (10 wt%)

Figure 10. TGA curves of (a) MWCNTs-COOH, (b) Tm-MWCNTs, (c) pure PEI, (d) PEI/Tm-MWCNTs 5 wt%, (e) PEI/Tm-MWCNTs 10 wt%, (f) PEI/Tm-MWCNTs 15 wt%

dance with Van Krevelen and Hoftzyer equation [35]. Materials with an LOI above 28% will demonstrate self-extinguishing behavior. A self-extinguishing material is one that would stop burning after the elimination of the fire or ignition source. The LOI for the pure PEI was obtained 25.5%, while for those of the nanocomposites were in the range of 29.5–32.7%. Therefore, all nanocomposites can be classified as self-extinguishing materials.

$$\text{LOI} = 17,5 + 0,4\text{CR}, \text{ where CR} = \text{Char yield})$$

4. Conclusions

In this study, the surface of MWCNTs-COOH was functionalized with vitamin B₁ as a biological and

environmental-friendly molecule under ultrasonic irradiation. The chemical functionalization of MWCNTs could improve their compatibility with PEI, leading to better interaction of the polymer chains with Tm-MWCNTs and efficient load transfer from the polymer matrix to the CNTs. The grafting was confirmed by FT-IR spectroscopy, TGA, and electron microscopic techniques. A biodegradable and optically active PEI was synthesized by a direct polycondensation of L-phenylalanine based diacid and 4,4'-thiobis(2-tert-butyl-5-methylphenol) and used as a continuous medium to prepare PEI/Tm-MWCNTs composites. The obtained nanocomposites were studied in the terms of chemical structure, morphology and thermal stability by FT-IR, XRD, TGA, TEM and FE-SEM techniques. Based on TGA data, the comparative extent of grafted vitamin B₁ onto MWCNTs surface was estimated to be around 48 wt%. The incorporation of Tm-MWCNTs into the PEI matrix exhibited obvious improvements in the thermal properties as a result of homogenous and efficient dispersion of CNTs throughout the polymer matrix. Electron microscopic studies revealed that the Tm-MWCNTs were well dispersed and embedded in the PEI matrix, showing good compatibility of Tm-MWCNTs with the polymer matrix.

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