

# Chemical surface coating of MWCNTs with riboflavin and its application for the production of poly(ester-imide)/MWCNTs composites containing 4,4'-thiobis(2-tert-butyl-5-methylphenol) linkages: Thermal and morphological properties

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**ABSTRACT:** In this work, carboxylated multi-walled carbon nanotubes (MWCNTs) were functionalized with riboflavin as a biological molecule under microwave irradiation. Solution blending method was used to incorporate different modified MWCNTs content (5, 10, and 15 wt %) into a chiral and biodegradable poly(ester-imide) (PEI) to fabricate PEI-based nanocomposites. The products were characterized for assessing the spectroscopic, thermal, and morphological properties by Fourier-transform infrared spectroscopy, thermogravimetric analysis (TGA), X-ray diffraction, transmission electron microscopy (TEM), and field-emission scanning electron microscopy (FESEM). Optically active PEI was prepared by step-growth polymerization of amino-acid-based diacid and aromatic diol. Functionalized MWCNTs were well dispersed in the PEI matrix and their distribution was homogeneous. This was confirmed by morphology study of the fractured surfaces of nanocomposites by FESEM and TEM. The addition of functionalized MWCNTs improved the thermal stability of NCs compared to the pure PEI. It was found from TGA data that temperature at 10% weight loss was increased from 409°C for pure PEI to 417, 420, and 424°C for nanocomposites containing 5, 10, and 15% functionalized MWCNTs, respectively. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2016**, *133*, 42908.

**KEYWORDS:** biocompatibility; blends; coatings; graphene and fullerenes; nanotubes; polycondensation

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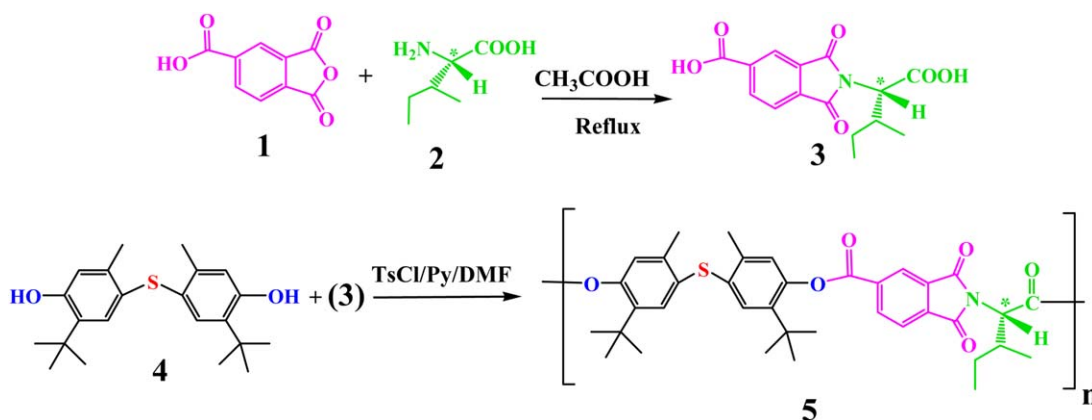
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## INTRODUCTION

Carbon nanotubes (CNT)s have been the research focus in both academia and industry due to their unique properties such as low density, high aspect ratio, high electrical, mechanical, and thermal properties.<sup>1–3</sup> They have received much attention for their many potential applications in nanoelectronic and photovoltaic devices, electromechanical actuators,<sup>4</sup> chemical sensors, biosensors, probe tips, and so on.<sup>5</sup> They can serve as a promising reinforcement phase incorporated into a polymer matrix. Extensive research work has been carried out on CNTs-reinforced polymer composites, due to their excellent electrical conductivity and improved mechanical strength at relatively low CNT content.<sup>6–11</sup>

CNTs have high aspect ratios, strong van der Waals forces, and  $\pi$ - $\pi$  stacking interactions between tubes, which cause them to

entangle and form bundles. Therefore, preparation of homogeneous nanocomposites (NC)s with CNTs, which determines the final properties of CNTs filled material, remains a technical challenge.<sup>12</sup> Mechanical methods (such as ultrasonication and high-shear mixing nanotubes) and chemical methods were among the generally used methods to overcome this problem.<sup>5</sup> Ultrasonic irradiation is broadly used to emulsify mixtures, dispersing nanoparticles, and produce NCs and nanoforms of chemical compounds.<sup>13</sup> This method can control the size distribution and morphology of the nanosized particles. Also, by using this method, nanotubes are separated from each other and its dispersivity is improved.<sup>14</sup> Chemical methods are aimed to modify the surface chemistry of the CNTs either covalently (functionalization) or noncovalently (adsorption). Covalent functionalization could be achieved by either direct covalent



**Scheme 1.** Synthetic route used to obtain the PEI. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

sidewall functionalization or indirect chemical modification with carboxylic groups on the surface of CNTs.<sup>15–20</sup> Surface functionalization of CNTs plays an important role to enhance the dispersion of CNTs into polymer matrix. The functionalization generates functional groups at the surfaces of the CNTs. These functional groups could react with prepolymers, polymers, and other chemicals, thereby improving the interfacial adhesion between the CNTs and the matrix.<sup>3</sup>

Poly(ester-imide)s (PEI)s inherit desirable characteristics from both polyesters and polyimides. This class of polymers shows high thermal stability, good mechanical properties, facile processing, and electrical insulation.<sup>21–23</sup> These properties have made them suitable for different applications in printed circuit boards, engineering thermoplastics, electronic devices, membranes, and adhesives.<sup>24–26</sup> These polymeric materials are able to incorporate with various nanofillers such as CNTs, leading to a new area of high-performance NCs.

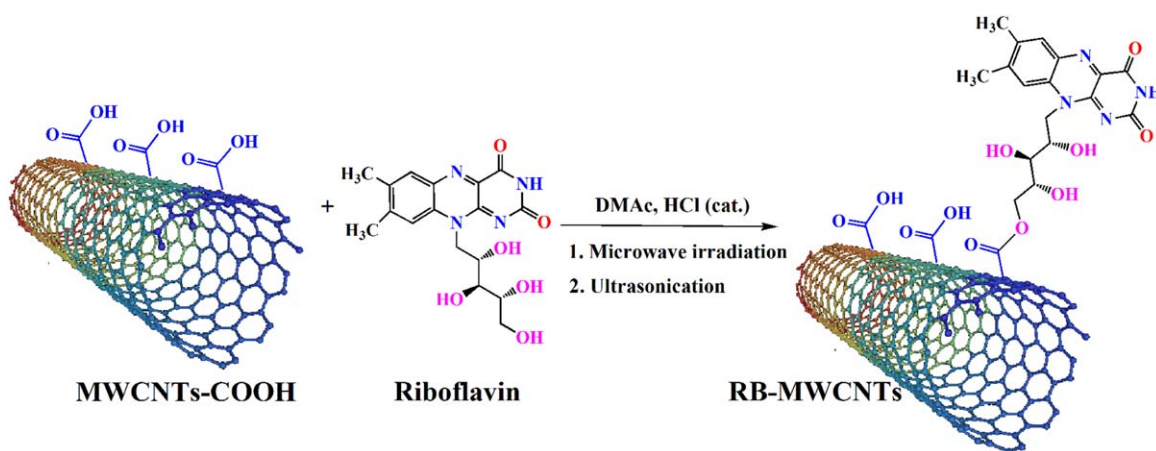
In this work, a procedure was presented for a surface modification of CNTs to reduce agglomeration and ensure better filler dispersion. Carboxylated MWCNTs (MWCNTs-COOH) were functionalized with riboflavin under microwave irradiation. MWCNTs reinforced NCs were prepared using synthesized PEI by a direct polycondensation and the different contents of func-

tionalized MWCNTs (5, 10, and 15 wt %) under ultrasonic irradiation. Microscopic and spectroscopic techniques were used to investigate the chemical structure, morphology, and thermal stability of the modified MWCNTs and the obtained NCs. According to thermogravimetric analysis (TGA) data, the obtained NCs showed better thermal stability than pristine polymer.

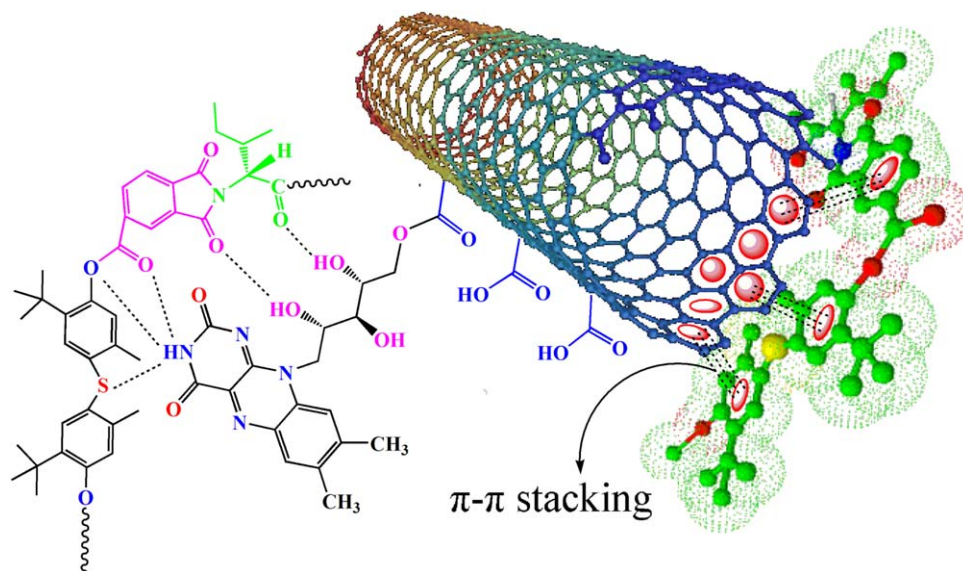
## EXPERIMENTAL

### Materials

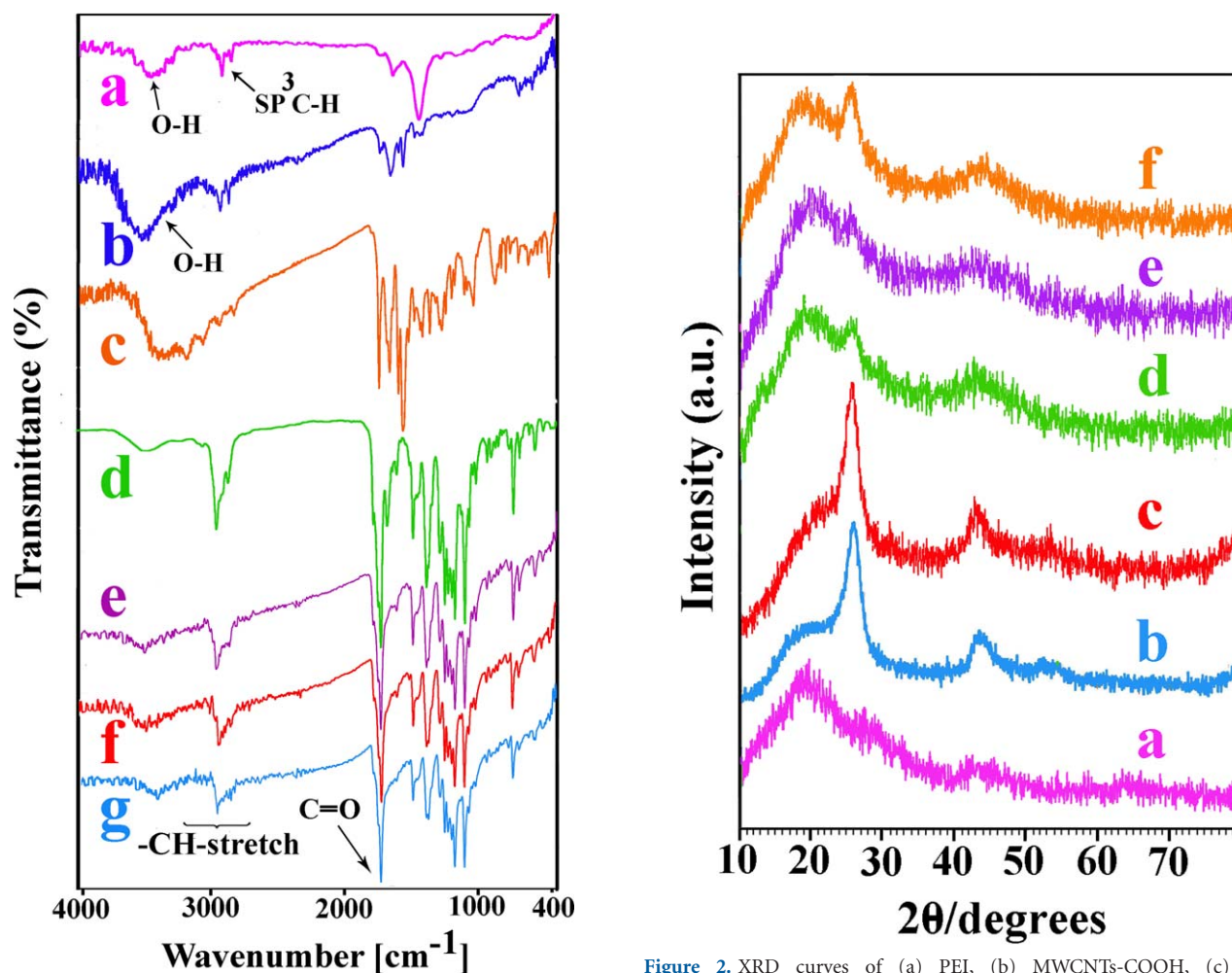
MWCNTs-COOH were obtained from Neutrino Co. (Iran) and prepared by a thermal chemical vapor deposition process. They had inner diameter of 5–10 nm, outer diameter of 10–20 nm, length  $\sim 30 \mu\text{m}$ , carboxyl content of 2.00 wt %, and the purity was above 95 wt %. Other chemicals and solvents were reagent-grade quality, achieved commercially from Fluka Chemical Co. (Buchs, Switzerland), Aldrich Chemical Co. (Milwaukee, WI), Riedel-deHaen AG (Seelze, Germany), and Merck Chemical Co. (Germany). Trimellitic anhydride (1) was purified by recrystallization from acetic anhydride followed by sublimation. *N,N*-dimethyl formamide (DMF) and *N,N*-dimethylacetamide (DMAc) were distilled over barium oxide under the reduced pressure. Riboflavin (vitamin B2), L-isoleucine, and 4,4'-thiobis(2-tert-butyl-5-methylphenol) (TTMP) were used as received without further purification.



**Scheme 2.** Chemical attachment of vitamin B2 to MWCNTs-COOH. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



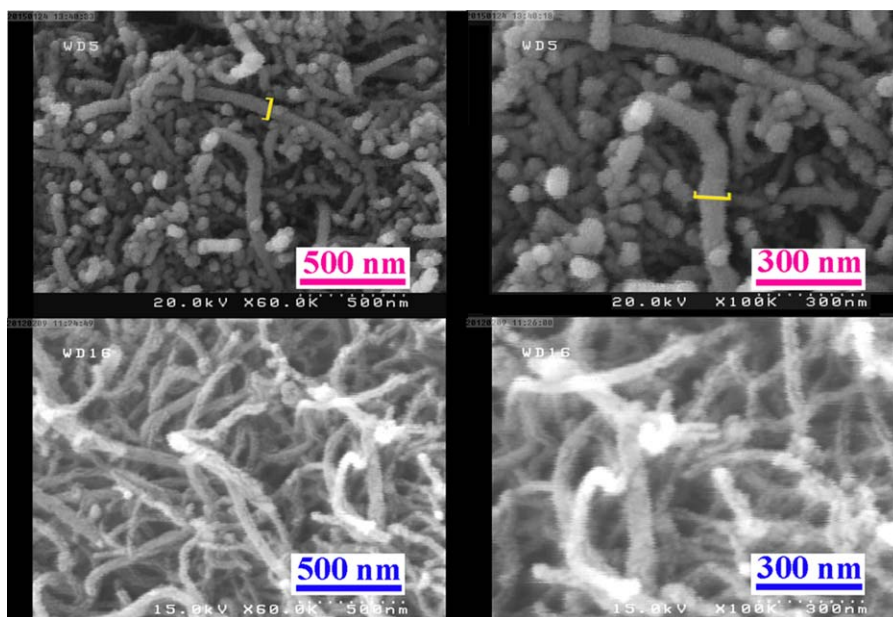
**Scheme 3.** Schematic illustration of the possible interactions between the RB-MWCNTs and the PEI matrix. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]



**Figure 1.** FTIR spectra of (a) MWCNTs-COOH, (b) RB-MWCNTs, (c) riboflavin, (d) pure PEI, (e) PEI/RB-MWCNTs 5 wt %, (f) PEI/RB-MWCNTs 10 wt %, and (g) PEI/RB-MWCNTs 15 wt %. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

**Figure 2.** XRD curves of (a) PEI, (b) MWCNTs-COOH, (c) RB-MWCNTs, (d) PEI/RB-MWCNTs 5 wt %, (e) PEI/RB-MWCNTs 10 wt %, and (f) PEI/RB-MWCNTs 15 wt %. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]





**Figure 3.** The FESEM images of the fracture surfaces of RB-MWCNTs (up) and MWCNTs-COOH (down). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Characterization

TGA data were taken on an STA503 instrument (Bahr-Thermoanalyse GmbH, Hüllhorst, Germany) in an argon atmosphere at a rate of 20°C/min. The reaction was carried out on MISONIX ultrasonic liquid processors, XL-2000 SERIES (Raleigh, NC, USA). Ultrasound was a wave of frequency  $2.25 \times 10^4$  Hz and power of 100 W. Transmission electron microscopy (TEM) photographs were taken by a Philips CM 120 operating at 100 kV (Germany). Field-emission scanning electron microscopy (FESEM) images were obtained at 15 kV using a HITACHI S-4160 instrument (Tokyo, Japan). X-ray diffraction (XRD) patterns of the samples were recorded using a Philips X'PERT MPD with a copper target at 40 kV and 35 mA and Cu K $\alpha$   $\lambda = 1.54 \text{ \AA}$  in the range of 10–80° at the speed of 0.05°/min. FTIR 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).

### Monomer Synthesis

*N*-Trimellitylimido-L-isoleucine (3) was prepared according to the reported procedure<sup>27</sup> with the following procedure (Scheme 1): 0.10 g ( $5.20 \times 10^{-4}$  mol) of trimellitic anhydride (1) and 0.11 g ( $5.72 \times 10^{-4}$  mol) of L-isoleucine (2) were dissolved in 6 mL of acetic acid. The solution was stirred at room temperature for 2 h and refluxed for 8 h. The mixture was poured into 20 mL of a 10% HCl solution. A white precipitate was formed, filtered off, and dried in vacuum at 80°C for 4 h.

### Polymerization Procedure

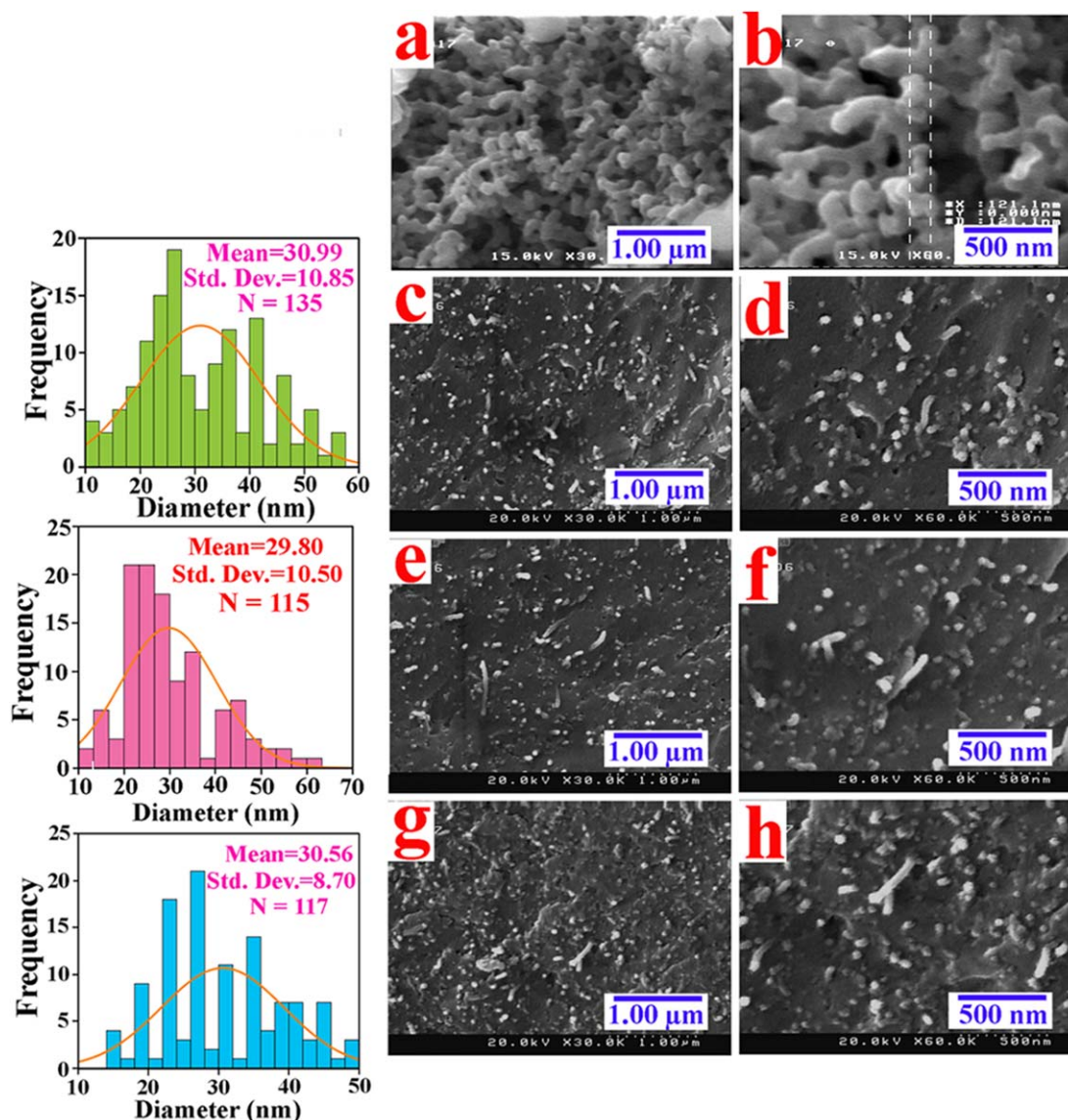
The chiral and biodegradable PEI (5) was prepared by step-growth polymerization of an equimolar mixture of aromatic diol (4) and chiral diacid (3) using TsCl/Py/DMF as a condens-

ing agent, according to our published article (Scheme 1).<sup>28</sup> Py (0.20 mL;  $2.50 \times 10^{-3}$  mol) solution of TsCl (0.31 g;  $1.63 \times 10^{-3}$  mol) after 30 min stirring at room temperature, was treated with 0.09 mL DMF ( $1.22 \times 10^{-3}$  mol) for 30 min and the resulting solution was added dropwise to a solution of diacid 4 (0.10 g;  $3.27 \times 10^{-4}$  mol) in Py (0.20 mL). The mixture was kept at room temperature for 30 min and TTMP (5) (0.11 g;  $3.27 \times 10^{-4}$  mol) was added. The total solution was stirred at 120°C for 6 h and the viscous liquid was precipitated in 30 mL of methanol to yield 0.152 g (76%) of the PEI.

### Riboflavin Functionalized MWCNTs (RB-MWCNT)s

Vitamin B2 was used for surface functionalization of CNTs under microwave irradiation. Vitamin B2 is a biological molecule with great importance in life sciences. It can be used in iron metabolism, nerve conduction, cancer prevention, and antiatherosclerosis.<sup>29</sup> CNTs functionalized with biological molecules demonstrate great potential for application in nanotechnology and bioengineering. The carboxylic acid groups on the surface of MWCNTs could be reacted with the primary hydroxyl group of vitamin B2 by a condensation reaction under microwave irradiation. Vitamin B2 could be attached onto CNTs through the  $\pi$ - $\pi$  interactions between the nanotube sidewalls and isoalloxazine ring of riboflavin molecules. The RB-MWCNTs were prepared by the following procedure:

Seventy-five milligrams of riboflavin was dissolved in 25 mL of DMAc at 70°C. Then the MWCNTs-COOH (50 mg) and 0.10 mL of conc. HCl were added to the solution and stirred at 80°C for 2 h. Subsequently, the suspension was heated in a domestic microwave chamber up to 120°C for 15 min with the output power of 700 W. Then, the mixture was cooled to room temperature and ultrasonicated for 1 h. The resulting suspension was centrifuged and washed thoroughly with DMAc and water to eliminate any unreacted reactants. Finally, the black



**Figure 4.** FESEM photographs of (a and b) pure PEI, (c and d) PEI/RB-MWCNTs (5 wt %), (e and f) PEI/RB-MWCNTs (10 wt %), (g and h) PEI/RB-MWCNTs (15 wt %), and (c, e, g) size distribution histograms of PEI/RB-MWCNTs (5, 10, and 15 wt %). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

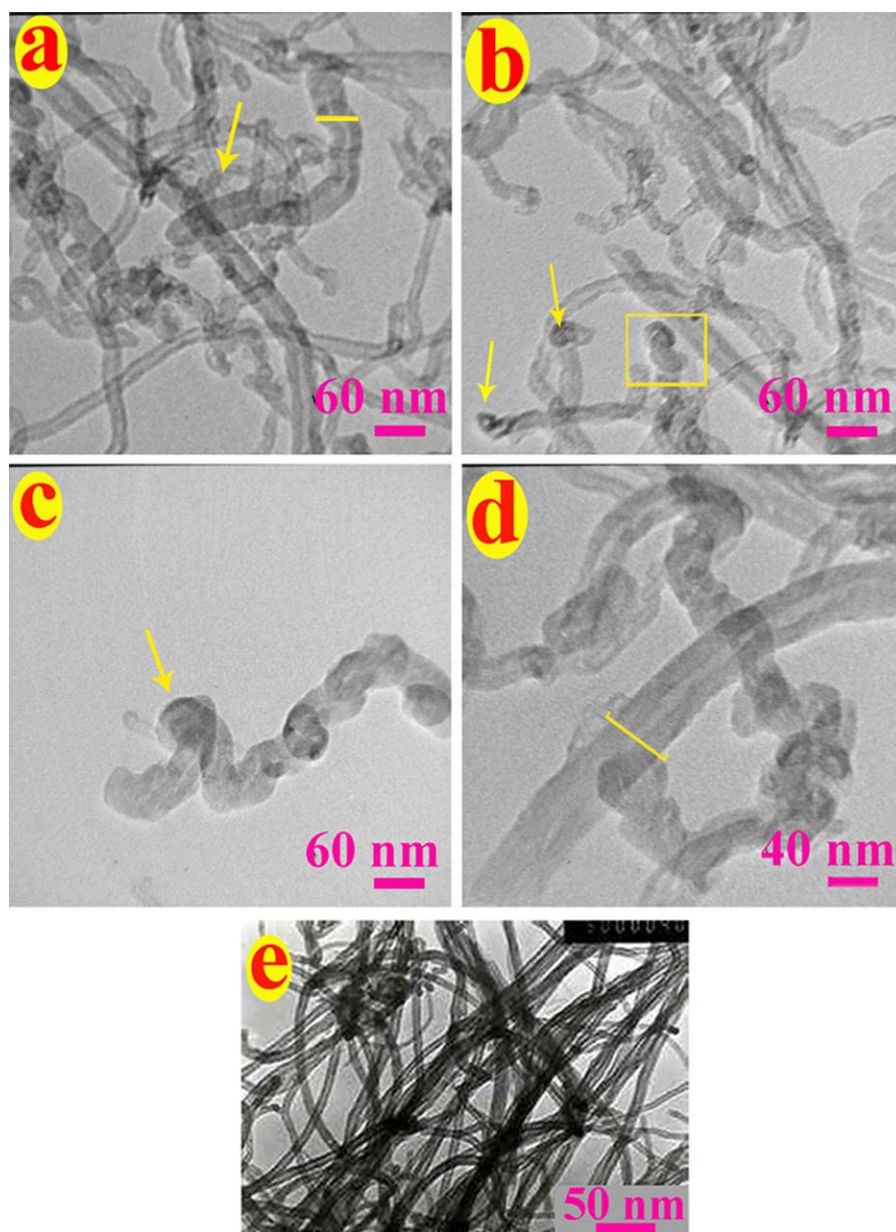
solid was dried at 50°C for 48 h. The detailed reaction scheme is depicted in Scheme 2.

#### Fabrication of the PEI/RB-MWCNTs NCs

The different weight fractions of RB-MWCNTs (5, 10, and 15 wt %) were dispersed in DMAc solvent by stirring for 1 day at 30–40°C. The PEI was added into this solution and sonicated for 1 h using an ultrasonic probe. Thereafter, the obtained suspension were poured into glass Petri dishes and dried first at 40–50°C for 1 day and then in vacuum at 120°C for 6 h to remove the remaining solvent.

For preparation of PEI/RB-MWCNTs, various amounts of modified MWCNTs was used to evaluate the effect of the different ratio of modified MWCNTs on morphology and thermal

properties of the obtained NCs. CNTs modification and ultrasonication were used as two useful methods to prevent nanotube aggregation, which help to better dispersion and stabilization of CNTs in the polymer matrix. The introduced vitamin B2 is expected to interact with different polar groups such as carbonyl, nitrogen, and sulfur into the backbone of polymer through van der Waals, hydrogen bonding, electrical, and hydrophobic interaction. Since the obtained PEI had aromatic structures, it is possible the interaction of delocalized  $\pi$ -bonds on the CNTs wall with  $\pi$ -bonds of polymer molecules of the matrix through  $\pi$ -stacking, leading to improve the interfacial interaction between MWCNTs and PEI matrix and efficient MWCNTs dispersion. Possible interactions between polymer chains and RB-MWCNTs are illustrated in Scheme 3.



**Figure 5.** TEM images of (a–d) RB-MWCNTs at different magnifications and (e) MWCNTs-COOH. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

## RESULTS AND DISCUSSION

### FTIR Spectroscopy

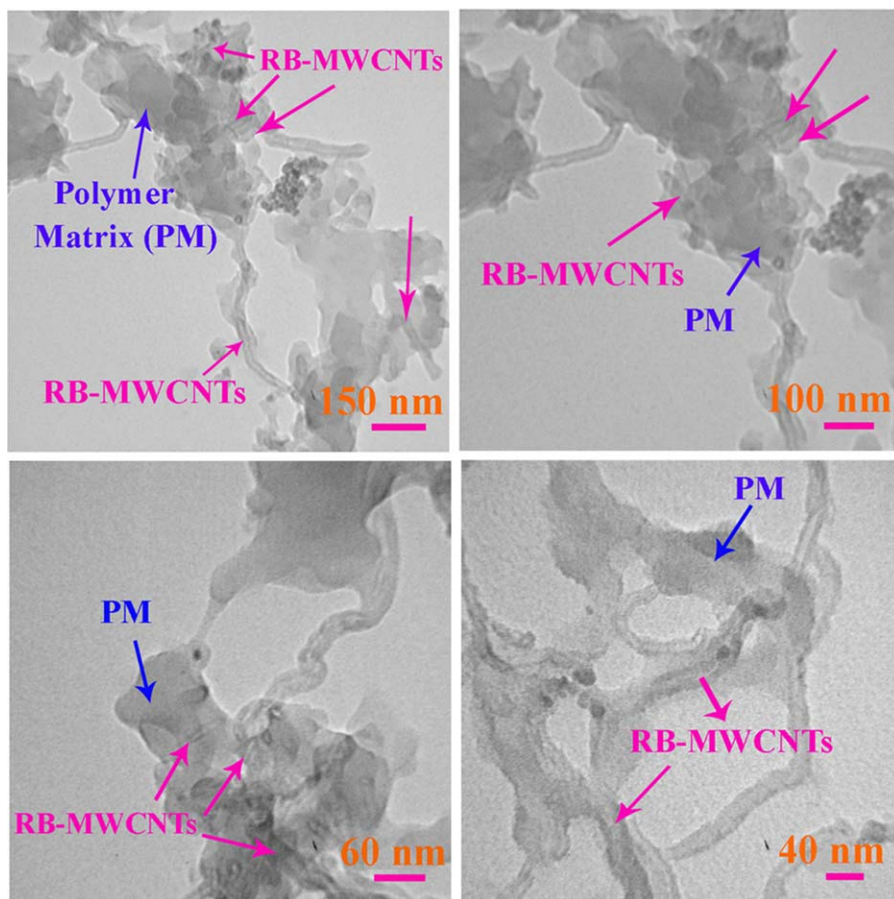
Figure 1 presents the FTIR spectra of MWCNTs-COOH, RB-MWCNTs, riboflavin, PEI, and NCs with 5, 10, and 15 wt % of RB-MWCNTs. An absorption peak at  $3454\text{ cm}^{-1}$  was observed for the O–H stretching mode of the carboxylic acid groups and the characteristic peaks at  $2852$  and  $2922\text{ cm}^{-1}$  could be assigned to C–H stretching vibrations of MWCNTs-COOH defects.<sup>30</sup> The peaks at  $1629$  and  $1431\text{ cm}^{-1}$  corresponded to the stretching of the CNT backbone<sup>31</sup> [Figure 1(a)]. For RB-MWCNTs, the broad absorption band in the range of  $3324$ – $3589\text{ cm}^{-1}$  were attributed to the stretching vibration of O–H bonds of riboflavin and carboxylic acid groups on the surface of MWCNTs. The peaks at  $2856$  and  $2931\text{ cm}^{-1}$  could be assigned to the aliphatic  $\text{sp}^3$  C–H stretching

vibrations. The carbonyl absorption bands of the isoalloxazine ring of riboflavin and ester groups could be overlapped and appeared at  $1727\text{ cm}^{-1}$  [Figure 1(b)]. For pure PEI, the bands at  $1383$  and  $726\text{ cm}^{-1}$  were attributed to the presence of the imide heterocycle in this polymer. Two absorption bands appeared at  $1780$  and  $1726\text{ cm}^{-1}$  corresponding to the carbonyl stretching vibrations of the imide and ester groups, respectively [Figure 1(d)]. The FTIR spectrum of NCs demonstrated very little changes compared to the pure PEI. This could be attributed to low MWCNTs content, the weak vibration signal of MWCNTs, and overlapping with the absorption peaks of pure PEI [Figure 1(e–g)].

### X-ray Diffraction Data

The XRD spectra for pure PEI, MWCNTs-COOH, RB-MWCNTs, and NCs with different loadings (5, 10, and 15 wt





**Figure 6.** TEM micrographs of PEI/RB-MWCNTs NCs (10 wt %). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

%) are shown in Figure 2. The X-ray patterns of the pure PEI showed a broad peak at  $2\theta = 18^\circ$ , indicating that the PEI was in amorphous nature [Figure 2(a)]. The pattern for the MWCNTs-COOH revealed two peaks around  $2\theta = 26^\circ$  and  $43^\circ$ , corresponding to the interlayer spacing  $d(002)$  and  $d(100)$  reflections of the carbon atoms, respectively [Figure 2(b)].<sup>32</sup> No significant difference was observed for X-ray pattern of the RB-MWCNTs compared to the MWCNTs-COOH. The presence of riboflavin did not seem to affect the structure of MWCNTs [Figure 2(c)]. The XRD spectrum of the NCs showed both broad amorphous peak of PEI and the characteristic peaks related to the MWCNTs [Figure 2(d–f)].

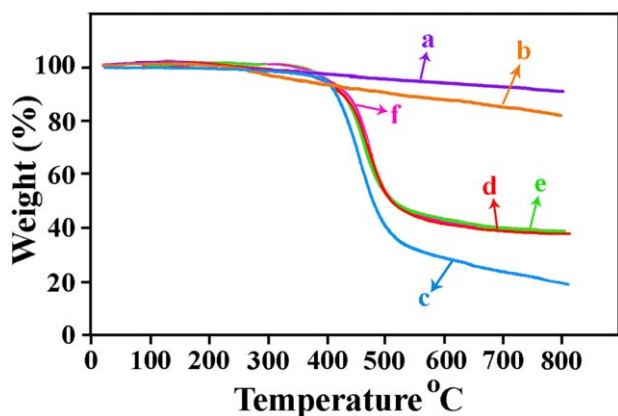
### Morphological Properties

Figure 3 presents the surface morphology of MWCNTs-COOH and RB-MWCNTs. It is easy to observe that after functionalization, the diameter of the RB-MWCNTs became a little bigger than that of MWCNTs-COOH, indicating that a thin layer of riboflavin was grafted on the side of MWCNTs. The FESEM images of fracture surfaces of pure PEI and NCs were also examined to characterize the morphology and dispersity of RB-MWCNTs in the composites, as displayed in Figure 4. Pure PEI showed different morphology compared to the NCs with a cylindrical-like structure [Figure 4(a,b)]. For the NCs, the bright dots and lines represented the ends of RB-MWCNTs pulled out

on the fracture surface. It could be seen that the RB-MWCNTs were well dispersed and partly strongly embedded in the matrix and partly demonstrate the tendency to pull out of matrix. It could be seen that the increase of CNTs amount did not lead to formation of noticeable aggregation [Figure 4(c–h)]. Diameter distribution histograms, plotted for the NCs 5, 10, and 15 wt %, showed mean CNT diameter sizes of 30.99, 29.80, and 30.56 nm, respectively (Figure 4).

Further evidence for the functionalized MWCNTs was obtained by TEM analysis (Figure 5). TEM images showed that MWCNTs-COOH were bundled together, and tubes are less isolated and distinct. After functionalization with riboflavin, RB-MWCNTs were debundled and tubes were distinct and form cyclic nanotubes. Furthermore, increased roughness of the functionalized CNTs surface was evident. This surface roughness may imply the partial damage of graphitic carbon, which could have resulted from the functionalization processes.

Figure 6 shows the TEM images of the NCs containing 10 wt % RB-MWCNTs. It was observed that RB-MWCNTs were dispersed separately and embedded to the PEI matrix. This finding indicated that the functionalized CNTs have a good compatibility with the polymer, as a result of interfacial interaction between functional groups formed on the surfaces of the MWCNTs and PEI matrix.



**Figure 7.** TGA curves of (a) MWCNTs-COOH, (b) RB-MWCNTs, (c) pure PEI, (d) PEI/RB-MWCNTs 5 wt %, (e) PEI/RB-MWCNTs 10 wt %, and (f) PEI/RB-MWCNTs 15 wt %. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

### Thermogravimetric Analysis

TGA curve of MWCNTs-COOH, RB-MWCNTs, neat PEI, and the NCs with various contents of RB-MWCNTs are shown in Figure 7. The samples were heated to 800°C at a heating rate of 20°C/min under argon atmosphere. Tables I and II summarize the thermal analysis data, containing the temperature of 5% and 10% weight loss ( $T_5$  and  $T_{10}$ ) and weight residue at 800°C (char yield).

As shown in Figure 7, the weight loss of MWCNTs-COOH is only 10 wt % at 800°C, which could be attributed to the small amount of amorphous carbon contained in the original material together with decomposition of organic groups like acidic sites. Based on TGA data, the relative content of riboflavin coated on the surface of MWCNTs was estimated as the difference in residual weight between carboxylated MWCNTs and RB-MWCNTs at 800°C to be 9 wt % (Table II). By looking at the data listed in Table I, pure PEI showed negligible weight loss below 399°C and this value gradually increased when more RB-MWCNTs were incorporated in the NCs, indicating a greater stability of the polymer in the presence of RB-MWCNTs. It could be attributed to good dispersion of RB-MWCNTs and high heat transfer of CNTs, preventing the accumulation of heat

**Table I.** Thermal Properties of the PEI and NCs

CNTs content (wt %)	$T_5$ (°C) <sup>a</sup>	$T_{10}$ (°C) <sup>b</sup>	Char yield (%) <sup>c</sup>	LOI <sup>d</sup>
0	399	409	19	25.1
5	400	417	37	32.3
10	405	420	39	33.1
15	406	424	39	33.1

<sup>a</sup> Temperature at which 5% weight loss was recorded by TGA at heating rate of 20°C/min under an argon atmosphere.

<sup>b</sup> Temperature at which 10% weight loss was recorded by TGA at heating rate of 20°C/min under an argon atmosphere.

<sup>c</sup> Weight percentage of material left undecomposed after TGA analysis at a temperature of 800°C under an argon atmosphere.

<sup>d</sup> Limiting oxygen index (LOI) evaluating at char yield at 800°C.

**Table II.** Thermal Stability of CNT Samples Obtained from TGA Thermograms

Sample	$T_5$ (°C) <sup>a</sup>	Char yield (%)
MWCNTs-COOH	550	90
RB-MWCNTs	345	81

<sup>a</sup> Temperature at which 5% weight loss was recorded by TGA at the heating rate of 20°C/min under an argon atmosphere.

at certain points for degradation.<sup>33</sup> According to TGA data, 10% RB-MWCNTs loading is a preferred content for the preparation of NCs.

Limiting oxygen index (LOI) can be used to estimate the flammability tendency of materials and calculated based on the Van Krevelen and Hoftyzer equation.<sup>34</sup> A material with LOI above 28% would be considered “self-extinguishing”. LOI represents the minimum concentration of oxygen that will support combustion and is evaluated by passing a mixture of nitrogen and oxygen over burning samples, and decreasing the oxygen level until the minimum oxygen level that maintains the burning is achieved.<sup>35</sup>

$$LOI = (17.5 + 0.4CR) \quad (\text{where } CR = \text{char yield})$$

### CONCLUSIONS

In this study, the sonication and microwave assisted process were used for the functionalization of MWCNTs with riboflavin as a biosafe and environmental-friendly molecule. The grafting was confirmed by FTIR spectroscopy, TGA, as well as electron microscopic methods. Functionalized MWCNTs were effectively dispersed in chiral and biodegradable PEI as a continuous medium to prepare PEI/RB-MWCNTs composites. Optically active PEI was prepared by a direct polycondensation of L-isoleucine based diacid and 4,4'-thiobis(2-tert-butyl-5-methylphenol). Polymers that are produced from naturally occurring building blocks such as amino acids are favorable materials for pharmaceutical and biomedical purposes since their degradation products are nontoxic and can be metabolized properly by living tissues. Combining these materials with biomolecules functionalized MWCNTs could produce materials which could be expected to have biodegradability and biocompatibility properties. The effect of incorporating RB-MWCNTs on structural, morphological, and thermal properties of the PEI-based NCs were studied by XRD, FT-IR, TGA, TEM, and FESEM. It was found that the functionalized MWCNTs have a substantial effect on the morphology and thermal stability of the resulting products. The modified MWCNTs improved the interfacial bonding and made the dispersion of MWCNTs homogeneous in the matrix, giving the composites present better properties. The comparative extent of grafted riboflavin onto MWCNTs surface was evaluated by the percentage of weight loss in the TGA curves. It was about as ~9 wt %. The homogenous and well-dispersed morphologies were observed by TEM and FESEM analysis. The RB-MWCNTs were decorated with a layer of polymer and did not show significant nanotube agglomeration.



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