

## Novel Method of Dispersion of Multiwalled Carbon Nanotubes in a Flexible Epoxy Matrix

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**ABSTRACT:** We describe a simple and novel method for dispersing multiwalled carbon nanotubes (MWCNTs) in a flexible epoxy matrix. The MWCNTs were modified with half-neutralized dicarboxylic acids having different numbers of carbon atoms. The modified MWCNTs were prereacted with epoxy in the presence of triphenylphosphine. The dispersion of the MWCNTs and the enhancement in the tensile properties were found to be better for composites prepared with a solvent. Among the half-neutralized dicarboxylic acids used, half-neutralized adipic acid (HNAA) exhibited the best performance. Scanning electron microscopy and transmission electron microscopy studies clearly indicated an improvement in the level of dispersion of the MWCNTs with the addition of the modifier. The good dispersion of the MWCNTs and the resulting improvement in their properties were attributed to the cation- $\pi$  interactions (the cation of HNAA and the  $\pi$ -electron clouds of the MWCNTs) between the HNAA and MWCNTs and the chemical bonding of -COOH groups of HNAA and the epoxy resin. The cation- $\pi$  interaction and chemical bonding was assessed with Fourier transform infrared spectroscopy and Raman spectroscopy. This approach did not destroy the  $\pi$ -electron clouds of the MWCNTs in contrast to a chemical functionalization strategy. © 2013 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 130: 2610–2618, 2013

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### INTRODUCTION

In recent years, polymer/carbon nanotube (CNTs) nanocomposites have drawn considerable attention because of the extraordinary properties of CNTs.<sup>1</sup> Various polymer matrices have been used to prepared polymer/CNT nanocomposites for different applications.<sup>2–8</sup> However, the effective reinforcement of the polymer matrix is hindered because of the agglomeration of CNTs. Therefore, it is important to obtain a uniform dispersion of multiwalled carbon nanotubes (MWCNTs) within the polymer matrix and adhesion.<sup>9,10</sup>

To achieve enhancements in the properties of composites,<sup>11,12</sup> CNTs can be treated with two widely used strategies: (1) covalent functionalization with acid treatment and (2) noncovalent functionalization with a surfactant. Tasis and coworkers<sup>13,14</sup> covered various aspects of the covalent and noncovalent functionalization of CNTs. The noncovalent functionalization of CNTs with surfactants is a one of the best choices for researchers, because there is the possibility of preserving the structural integrity of the nanotubes. The use of surfactants, including non-ionic surfactants and ionic surfactants, has been reported in previous studies; they triggered debundling without disturbing

the  $\pi$ -electron clouds of the CNTs.<sup>15–17</sup> Recently, ionic modification through cation- $\pi$  or  $\pi$ - $\pi$  interactions have been realized as one of the best ways to disperse CNTs.<sup>13,14</sup> The cation- $\pi$  or  $\pi$ - $\pi$  interactions between the modifier and CNTs reduces the van der Waal's forces by electrostatic attraction and steric repulsive forces. The stronger interactions between the cations of the modifier and the  $\pi$ -electron clouds of the CNTs promote the dispersion of nanotubes in the polymer matrix.<sup>13,14</sup>

Among various polymer matrices, the unique characteristics of epoxy resins make them widely used in high-performance composites, structural adhesives, electronics, and many other industrial applications.<sup>18</sup> With CNTs, many research reports have been devoted to the preparation of reinforced epoxy composites.<sup>19–21</sup> However, the majority of reports on epoxy/CNT composites have been based on high-glass-transition-temperature ( $T_g$ ) epoxy systems because they can be used for high-performance applications. The effects of MWCNTs on the rubbery epoxy (low  $T_g$ ) matrix have been reported to be less than those on a glassy epoxy matrix. Yang et al.<sup>22</sup> comparatively studied the effects of different nanofillers, including MWCNTs, on glassy epoxy and rubbery epoxy matrices. They found that the rubbery matrix was reinforced more effectively by the fillers than the

glassy matrix, but typically, the rubbery epoxy was not used for structural composites. Liu et al.<sup>23</sup> also studied the reinforcement of CNTs in rubbery and glassy epoxy resins. They found a much better dispersion of nanotube dispersion in the rubbery epoxy resin than in glassy epoxy. Similarly, the reinforcements of CNTs in epoxy composites with different matrix stiffnesses was studied extensively by Lijie and Jinbo.<sup>24</sup> They concluded that in the soft and ductile composite, the CNTs showed a significant reinforcement because of the possible accelerated curing process and the better interfacial adjoining. The interfacial interaction was poor in the case of the stiff composite because of the complete crosslinking of the polymer molecules surrounding the CNTs. Loos et al.<sup>25</sup> reported the effects of the matrix stiffness on the tensile and thermal properties of CNT/epoxy composites. All of these studies on the rubbery epoxy matrix concluded that the reinforcing effect in the flexible matrix was more prominent than that observed in the glassy one.

Ratna et al.<sup>26</sup> reported rubbery epoxies that had potential applications in vibration damping. The poor mechanical properties are a major problem with these epoxies, and this restricts their application. In this study, we used a reinforcing strategy with MWCNTs to enhance the performance of these rubbery epoxies. The MWCNTs were modified noncovalently with half-neutralized dicarboxylic acid, which contains a cation ( $\text{Na}^+$ ) that was expected to interact with the  $\pi$ -electron clouds of the MWCNTs via cation- $\pi$  interaction, and free  $-\text{COOH}$  groups could form chemical bonds with the epoxy resin. To the best of our knowledge, there has been no report on the use of half-neutralized dicarboxylic acid as a modifier (with the ability to interact with nanotubes and form chemical bonds with the epoxy resin) for the rubbery epoxies. The effects of half-neutralized dicarboxylic acid modified MWCNTs on the mechanical, dynamic mechanical properties, and we discuss the morphology of the epoxy matrix in this article.

## EXPERIMENTAL

### Materials

The epoxy resin, diglycidyl ether of bisphenol A (LY556), was purchased from Vantico and had an equivalent weight per epoxide group of  $195 \pm 5$  g/mol. Jeffamine [poly(ether amine)], with a molecular weight of 900, was used as a hardener (Sigma Aldrich, India). The MWCNTs (Baytube 150P) were procured from Bayer Material Science AG (Leverkusen, Germany). Adipic acid, succinic acid, and sebacic acid were purchased from Merck (India). Sodium hydroxide, acetone (99.9%), and tetrahydrofuran (THF) were supplied by Merck (India).

### Preparation of the Modified MWCNTs

The preparation of half-neutralized dicarboxylic acids having different numbers of carbon atoms was performed in distilled water with a 1:1 molar ratio of dicarboxylic acid to sodium hydroxide. The half-neutralized dicarboxylic acids used were designated as half-neutralized succinic acid (HNSCA), half-neutralized adipic acid (HNAA), and half-neutralized sebacic acid (HNSA). The modification of the MWCNTs was carried out by the mixture of the MWCNTs and half-neutralized dicarboxylic acid in a 1:1 w/w ratio. Half-neutralized dicarboxylic acid was dissolved in 250 mL of distilled water in a 500-mL

beaker, and then, the MWCNTs were added to it. The mixture was sonicated for 15 min with probe sonication (Bandelin Ultrasonic homogenizer, SONOPULS HD-3200, Germany, working frequency = 20 kHz) with the beaker kept in cold water. The water was removed with a Rota evaporator, and the modified MWCNTs were dried in a vacuum oven at  $100^\circ\text{C}$  for 48 h.

### Preparation of the Nanocomposites

A typical procedure for the 0.5 wt % modified MWCNTs composites prepared with acetone is described as follows. An amount of 0.125 g of MWCNTs was added to 5–10 mL of acetone in 100-mL beaker and sonicated with probe sonication for 1 h at room temperature. An amount of 25 g of epoxy resin was added to this, and the mixture was sonicated for 20 min with the beaker kept in cold water. The acetone was removed completely by the application of a vacuum. About 1 mg (0.8 wt % with respect to the MWCNTs) of triphenylphosphine (TPP) was added to the reaction mixture. The mixture was stirred and heated at  $100^\circ\text{C}$  for 3 h until all of the carboxylic acid groups were completely reacted. Then, 19 g of curing agent (Jeffamine 900) was added to the mixture, and it was mixed uniformly for 15 min, degassed for 10 min, and allowed to cure in a Teflon mold at  $80^\circ\text{C}$  for 6 h.

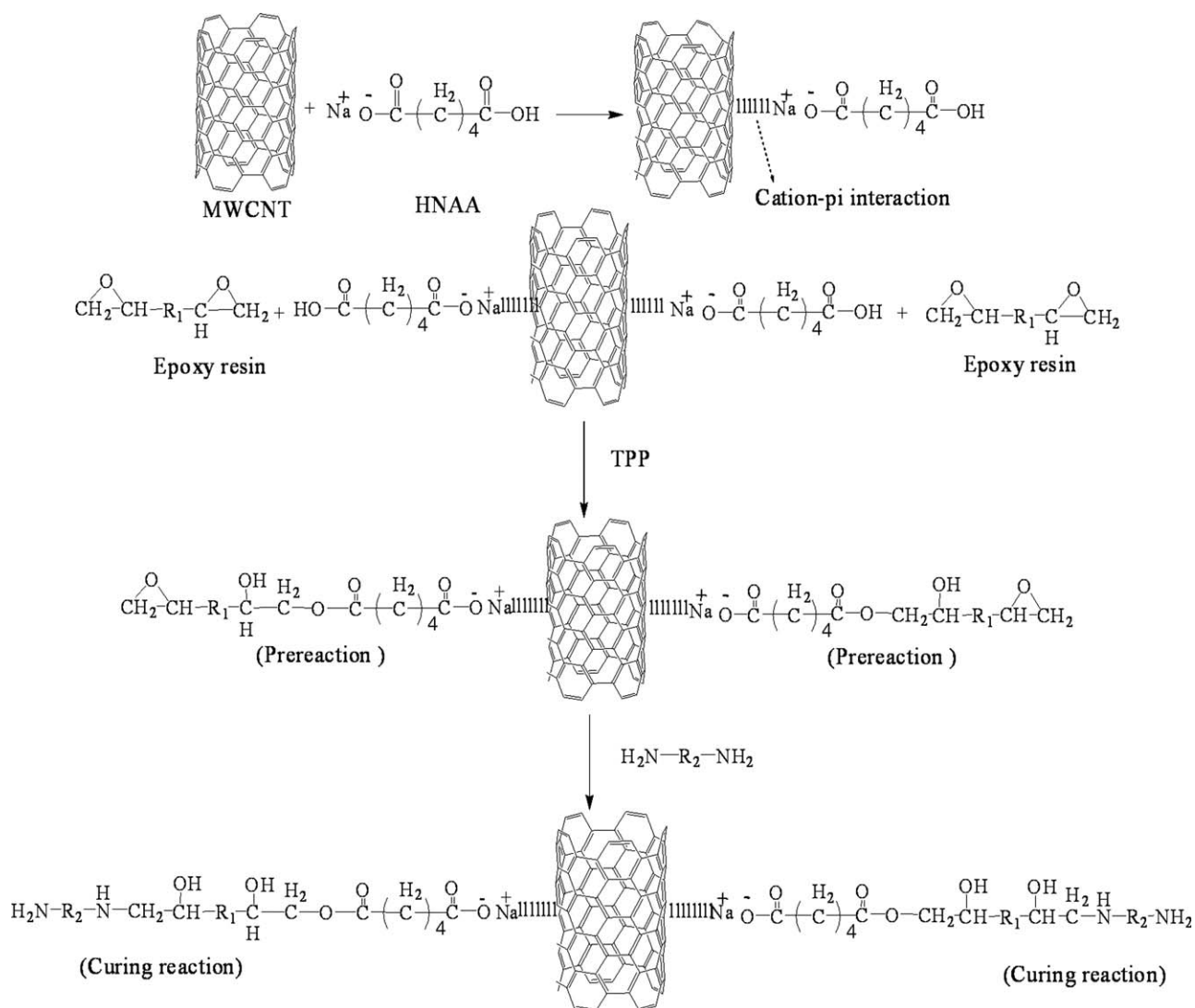
The composites prepared with acetone were designated as Epoxy (EP)/MWCNT (0.5 wt %), EP/MWCNT (0.5 wt %)/HNSCA, EP/MWCNT (0.5 wt %)/HNSA, and EP/MWCNT (0.1, 0.25, 0.5, 0.75, 1, 1.5, and 2 wt %)/HNAA. For comparison, the composites with 0.5 wt % MWCNTs and the HNSA-modified MWCNTs were made without acetone with the same procedure. The composite with only 0.5 wt % HNAA was also prepared with acetone to compare the properties of composites without MWCNTs and were designated as EP/HNAA (0.5 wt %).

### Characterization

The tensile strength, tensile modulus, and percentage elongation at break of the neat epoxy and nanocomposites sample were measured with a Hounsfield 50 KS Instron universal testing machine (United Kingdom) according to ASTM D 638. The crosshead speed was 20 mm/min, and the gauge length was 50 mm. All of the tests were performed at  $27 \pm 2^\circ\text{C}$ , and the results are expressed in megapascals. The quoted results are the average of the values obtained from four dumbbells.

Fourier transform infrared (FTIR) spectra of the MWCNTs, HNAA-modified MWCNTs, and their composite samples were taken in attenuated total reflection mode by a Nicolet 510 FTIR spectrometer (Germany) over a scanning range from 800 to  $4000\text{ cm}^{-1}$  with a nominal resolution of  $2\text{ cm}^{-1}$ . For each spectrum, 64 runs were collected and averaged. The Raman spectra of the unmodified MWCNTs, HNAA-modified MWCNTs, and EP/MWCNT/SAHA composite samples were recorded with a Renishaw 2000 UK system with an argon-ion laser exciting wavelength of 514 nm over a scanning range of  $500\text{--}2000\text{ cm}^{-1}$ .

A high-resolution scanning electron microscope Field Gun Emission Scanning Electron Microscopy (FEG-SEM, Zeiss Supra 40 VP, Germany) was used to study the fractured surface morphology of the EP/MWCNT composite samples. The



**Figure 1.** Representation of the cation- $\pi$  interactions of HNAA with MWCNTs, chemical bonding between the HNAA and epoxy resin, and formation of the epoxy network.

composite samples were quenched in liquid nitrogen and cryogenically fractured to obtain the cross sections, which were sputter-coated with carbon to prevent charging before the scanning electron microscopy (SEM) observation. High-resolution transmission electron microscopy (TEM) analysis of the EP/MWCNT composite samples was conducted on a JEOL (JEM-2100, Japan) electron microscope at 200 kV. Ultrathin sections of the composite films were prepared with a thickness of 130–150 nm for TEM imaging with a Leica ultracut microtome (Leica Mikrosysteme, GmbH, A-1170, Austria) with liquid nitrogen.

The thermal behavior of the neat epoxy and the EP/MWCNT composites was studied with DSC (TA Instruments Q100 series). About 6–10 mg of sample was placed in an aluminum pan, heated from  $-80$  to  $100^\circ\text{C}$  at a heating rate  $5^\circ\text{C}/\text{min}$ , and cooled to room temperature. The reference was an empty aluminum pan.

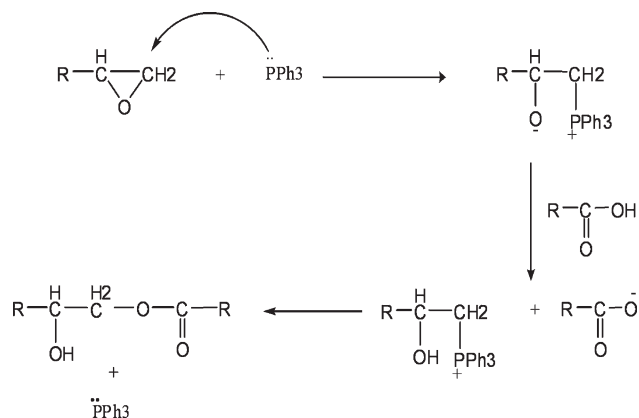
Dynamic mechanical analysis of the neat epoxy and EP/MWCNT composite samples was carried out with a dynamic

mechanical thermal analyzer (MK IV, Rheometric Scientific). The test specimen was cooled to  $-80^\circ\text{C}$ , allowed to stabilize, and then heated at a rate of  $3^\circ\text{C}/\text{min}$  to  $100^\circ\text{C}$ . Liquid nitrogen was used for the subambient region. The dynamic modulus and loss modulus were obtained in dual-cantilever bending mode for a sample size of  $30 \times 10 \times 2 \text{ mm}^3$  with a fixed frequency of 1 Hz.

## RESULTS AND DISCUSSION

### Pre-reaction of the Modified MWCNTs with the Epoxy Matrix

To take full advantage of the extraordinary properties of the MWCNTs, a good dispersion and interfacial interaction with the polymer matrix are absolutely necessary. In the absence of sufficient interfacial adhesion between the nanotubes and the polymer, the tubes will simply be pulled out and will not contribute toward the enhancement in the mechanical properties of the composites. To resolve both of these issues (good dispersion and interfacial adhesion), modifiers are designed in such a way



**Figure 2.** Mechanism of the TPP-catalyzed prereaction of  $\text{—COOH}$  of the half-neutralized dicarboxylic acid with epoxy groups of the epoxy resin.

that they contain a cation that can interact with the  $\pi$ -electron clouds of the MWCNTs and the  $\text{—COOH}$  group of the modifier can form chemical bonds with the epoxy resin. The chemical bonding between the modifier and epoxy resin makes nanotubes more effective for load transfer, and this is expected to improve the mechanical properties of the composites. Because the epoxy-amine reaction is faster than the epoxy-carboxylic acid reaction, before mixing with the hardener; the epoxy resin was prereacted with the free carboxylic groups of the modifier in the presence of TPP as a catalyst until no carboxyl groups remained. This reaction makes nanotubes become an integral part of crosslinking through covalent bonding between the modifier and epoxy resin. Figure 1 illustrates the cation- $\pi$  interaction between HNAA with the MWCNTs, the chemical bonding of the carboxylic acid with the epoxy resin, and the curing reaction of the epoxy resin with the hardener. The mechanism of the TPP-catalyzed prereaction of  $\text{—COOH}$  of the half-neutralized dicarboxylic acid with the epoxy group of the epoxy resin is shown in Figure 2.

#### Effect of the Processing Method on the Tensile Properties

The tensile properties of the EP/(0.5 wt %) unmodified MWCNT and HNSA-modified MWCNT composites prepared with acetone and without acetone are presented in Table I. The composites prepared with acetone showed better tensile strength and tensile modulus values than the composite prepared without acetone. This was attributed to the fact that the addition of

solvent reduced the viscosity of the matrix and favored the dispersion of the MWCNTs; this led to the enhanced tensile properties. The EP/MWCNT (0.5 wt %)/HNSA composite prepared with acetone showed around a 41% improvement in the tensile strength and a 120% improvement in the tensile modulus compared to the neat epoxy. On the other hand, the same composite prepared without acetone showed only a 29% improvement in the tensile strength and a 32% improvement in the tensile modulus. This clearly indicated that the use of acetone was very much effective in improving the tensile strength and tensile modulus of the EP/MWCNT composites. Hence, all of the composites were prepared with acetone and are discussed in the subsequent section.

#### Effect of the Nature of the Modifier on the Tensile Properties

A series of EP/MWCNT composites were made with 0.5 wt % unmodified MWCNTs and HNSCA-, HNAA-, and HNSA-modified MWCNTs with acetone. The effect of the number of carbon atoms and the polarity of the three different modifiers (HNSCA, HNAA, and HNSA) on the tensile properties of the related composites were studied, and the results are summarized in Table I. All of the composites containing modified MWCNTs showed improvements in the tensile strength and tensile modulus. This was attributed to the increase in the level of dispersion of the MWCNTs and the chemical bonding with the epoxy matrix due to the addition of the modifier.

Among all of the modified MWCNTs, the composite containing HNAA-modified MWCNTs exhibited the best performance. The tensile strengths of the composites containing HNSCA- and HNSA-modified MWCNTs were found to be 0.74 and 0.86 MPa, and tensile moduli for the same composites were found to be 1.22 and 1.34 MPa, respectively. The tensile strength and tensile modulus values for the HNAA-modified MWCNT composite were found to be 1.04 and 1.76 MPa, respectively. The best performance of the HNAA-modified MWCNTs was a result of a combined effect of polarity matching and dicarboxylate formation. For polarity matching with epoxy resin, higher numbers of carbon atoms are required. To achieve both good dispersion and chemical bonding, the formation of salt with one carboxylate and one carboxylic acid group was most desirable. Because the cation associated with the carboxylate ion could interact with the  $\pi$ -electron clouds of the MWCNTs, the dispersion of MWCNTs improved, and the carboxylic acid group

**Table I.** Tensile Properties of the Neat Epoxy and EP/MWCNT Composite Containing 0.5 wt % Unmodified MWCNTs and HNSA, HNAA, and HNSCA-Modified MWCNTs with a 1:1 Ratio of the Modifier to the MWCNTs

Sample	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
Neat epoxy	0.61 ± 0.02	0.61 ± 0.03	121 ± 10
EP/MWCNT (0.5 wt %)	0.72 ± 0.02	0.87 ± 0.03	94 ± 4
EP/MWCNT (0.5 wt %) without acetone	0.71 ± 0.03	0.75 ± 0.02	113 ± 5
EP/MWCNT (0.5 wt %)/HNSA	0.86 ± 0.04	1.34 ± 0.2	87 ± 5
EP/MWCNT (0.5 wt %)/HNSA without acetone	0.79 ± 0.02	0.80 ± 0.04	112 ± 7
EP/MWCNT (0.5 wt %)/HNAA	1.04 ± 0.1	1.76 ± 0.3	66 ± 3
EP/MWCNT (0.5 wt %)/HNSCA	0.74 ± 0.04	1.22 ± 0.1	74 ± 6

**Table II.** Tensile Properties of the Neat Epoxy and the EP/HNAA (0.5 wt %) and EP/MWCNT/HNAA (1:1) Composites with Various Concentrations (wt %) of MWCNTs

Sample	Tensile strength (MPa)	Tensile modulus (MPa)	Elongation at break (%)
Neat epoxy (0%)	0.61 ± 0.02	0.61 ± 0.03	121 ± 10
EP/HNAA (0.5 wt %)	0.52 ± 0.04	0.74 ± 0.02	87 ± 9
EP/MWCNT (0.1 wt %)/HNAA	0.72 ± 0.01	0.95 ± 0.01	86 ± 4
EP/MWCNT (0.25 wt %)/HNAA	0.79 ± 0.04	1.11 ± 0.04	92 ± 6
EP/MWCNT (0.5 wt %)/HNAA	1.04 ± 0.1	1.76 ± 0.3	66 ± 3
EP/MWCNT (0.75 wt %)/HNAA	0.87 ± 0.05	1.38 ± 0.1	77 ± 4
EP/MWCNT (1 wt %)/HNAA	0.83 ± 0.01	1.48 ± 0.06	62 ± 2
EP/MWCNT (1.5 wt %)/HNAA	0.82 ± 0.03	1.83 ± 0.03	56 ± 7
EP/MWCNT (2 wt %)/HNAA	0.80 ± 0.02	1.63 ± 0.02	61 ± 4

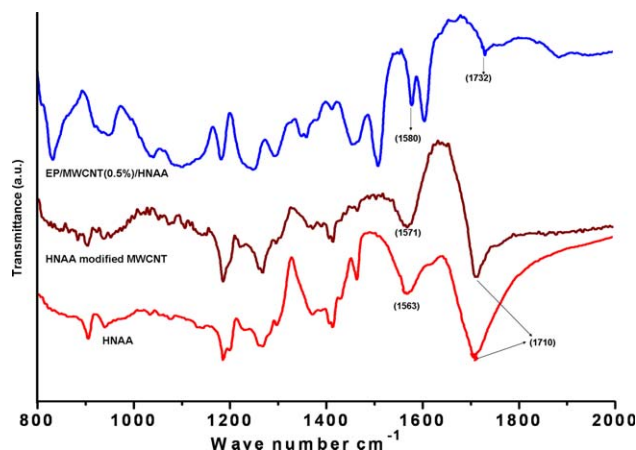
formed chemical bonds with the epoxy resin, which improved the interfacial bonding. A similar observation was reported for Poly (ethylene oxide) (PEO)/MWCNT composites, where a carboxylate ion interacted with the  $\pi$ -electron cloud of the MWCNTs, and free carboxylic acid groups could form H bonds with PEO; this improved the interfacial adhesion.<sup>27</sup> From these results, the HNAA-modified MWCNTs were used for further characterization of the composites with various concentrations of MWCNTs.

The tensile properties of the EP/MWCNT/HNAA composites prepared with various concentrations of HNAA-modified MWCNTs are presented in Table II. The tensile strength of the composites increased up to 0.5 wt % MWCNTs and thereafter decreased. Variations in the tensile modulus of all of composites were clearly evident from Table II. The percentage elongation at break was found to decrease significantly because of the incorporation of MWCNTs. The decrease in the elongation at break was more prominent in the case of the modified MWCNT composites. This was attributed to the good dispersion of modified MWCNTs in the epoxy matrix, which reduced the mobility of the matrix around the nanotubes. Composites with only 0.5 wt % HNAA were also prepared to compare the effects of HNAA on the tensile properties of the epoxy matrix. There was no

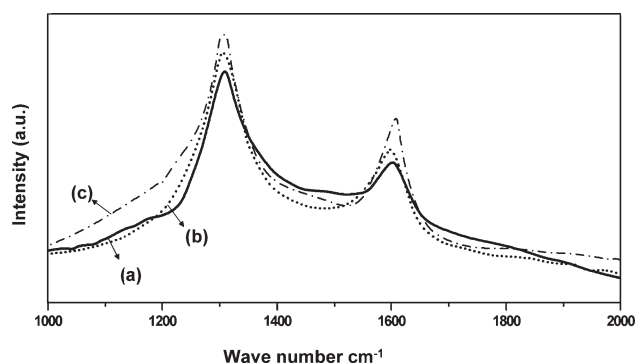
improvement in the tensile strength and moderate improvement in the tensile modulus, as evident from Table II. This implied that the improvements in the tensile strength and tensile modulus were the results of well-dispersed MWCNTs.

#### Interaction Between the Epoxy, HNAA, and the MWCNTs

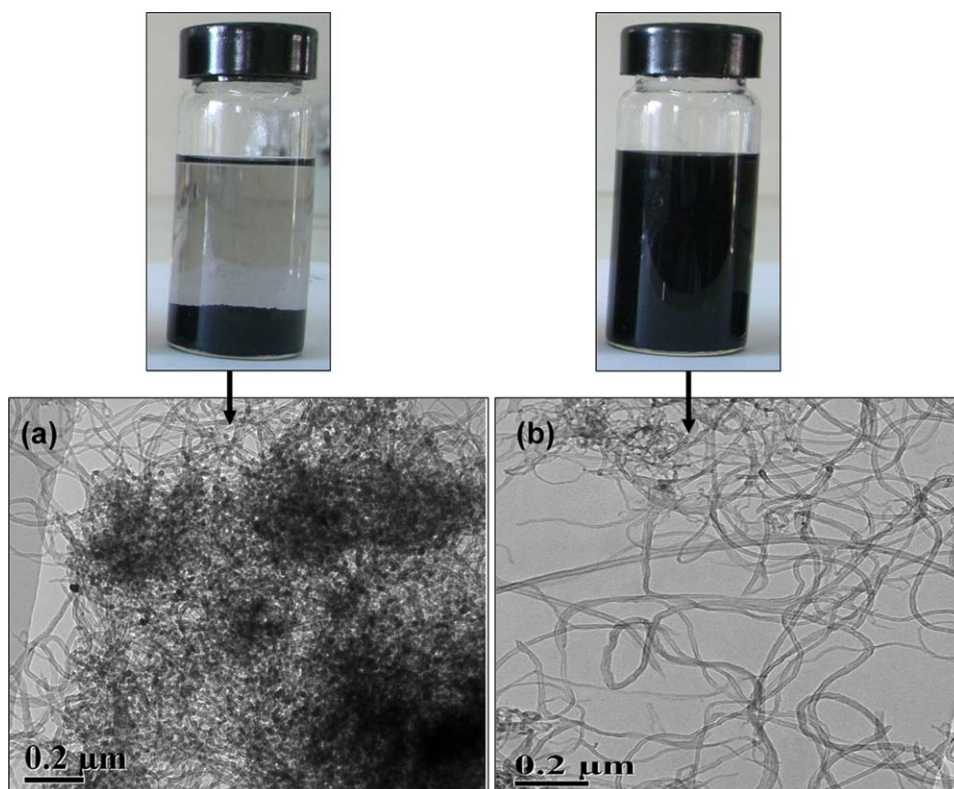
To substantiate the cation- $\pi$  interaction and chemical bonding, FTIR and Raman analyses were carried out. Figure 3 shows the FTIR spectra of the HNAA, HNAA-modified MWCNTs (1:1), and EP/MWCNT (0.5 wt %)/HNAA. The peaks at 1710 and 1563  $\text{cm}^{-1}$  corresponded to the stretching of the C=O groups of carboxylic acid and carboxylate ions of HNAA. After the modification of the MWCNTs with HNAA, the carboxylate peak shifted toward a higher wave number, from 1563 to 1571  $\text{cm}^{-1}$ . This shift of carboxylate ion peaks was mainly due to the existence of cation- $\pi$  interactions between the HNAA and MWCNTs. The cation ( $\text{Na}^+$ ) associated with the carboxylate group of HNAA interacted with the  $\pi$ -electron clouds of the MWCNTs via cation- $\pi$  interactions.<sup>27,28</sup> In the EP/MWCNT (0.5 wt %)/HNAA composite, the stretching peak of the C=O group of carboxylate ions also shifted, from 1563 to 1580  $\text{cm}^{-1}$ . This provided further evidence for the existence of the cation- $\pi$  interaction between the MWCNTs and HNAA.<sup>27-32</sup> We also noted that the stretching of the C=O group of carboxylic acid shifted from 1710 to 1732  $\text{cm}^{-1}$  for the EP/MWCNT(0.5 wt %)/HNAA composite. This was attributed to the chemical



**Figure 3.** FTIR spectra of the HNAA, HNAA-modified MWCNTs, and EP/MWCNT (0.5 wt %)/HNAA. [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://www.wileyonlinelibrary.com).]



**Figure 4.** Raman spectra of the (a) MWCNTs, (b) HNAA-modified MWCNTs, and (c) EP/MWCNT (0.5 wt %)/HNAA.

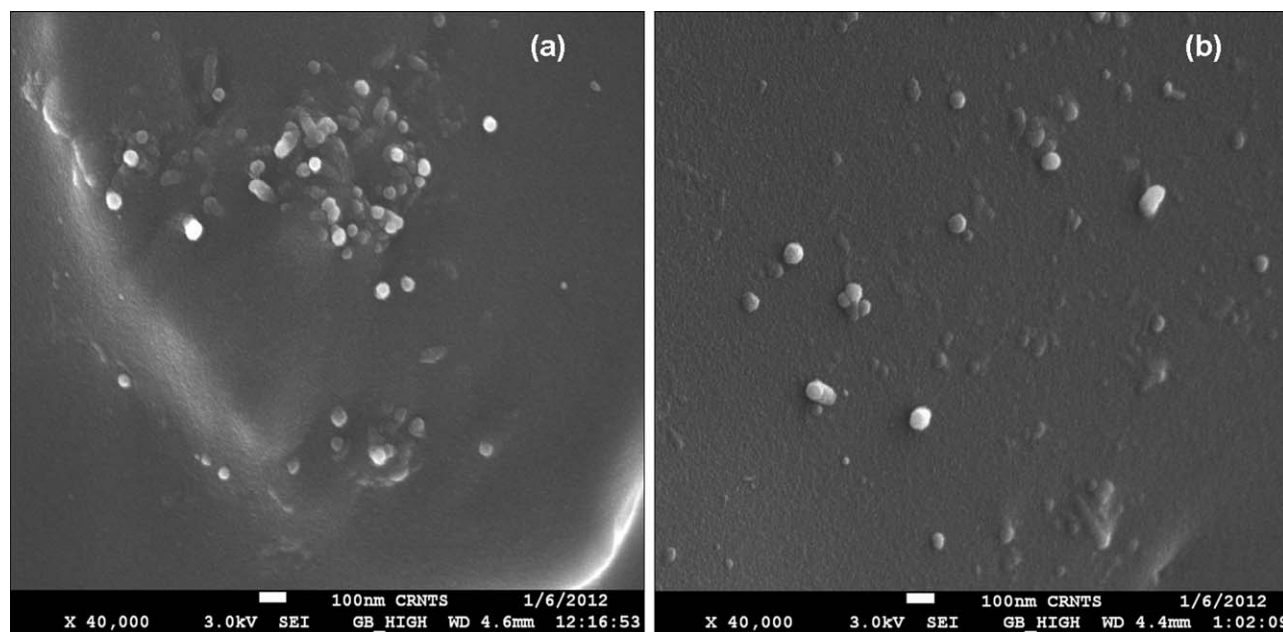


**Figure 5.** TEM images of the (a) unmodified MWCNTs and (b) HNAA-modified MWCNTs (1:1). [Color figure can be viewed in the online issue, which is available at [wileyonlinelibrary.com](http://wileyonlinelibrary.com).]

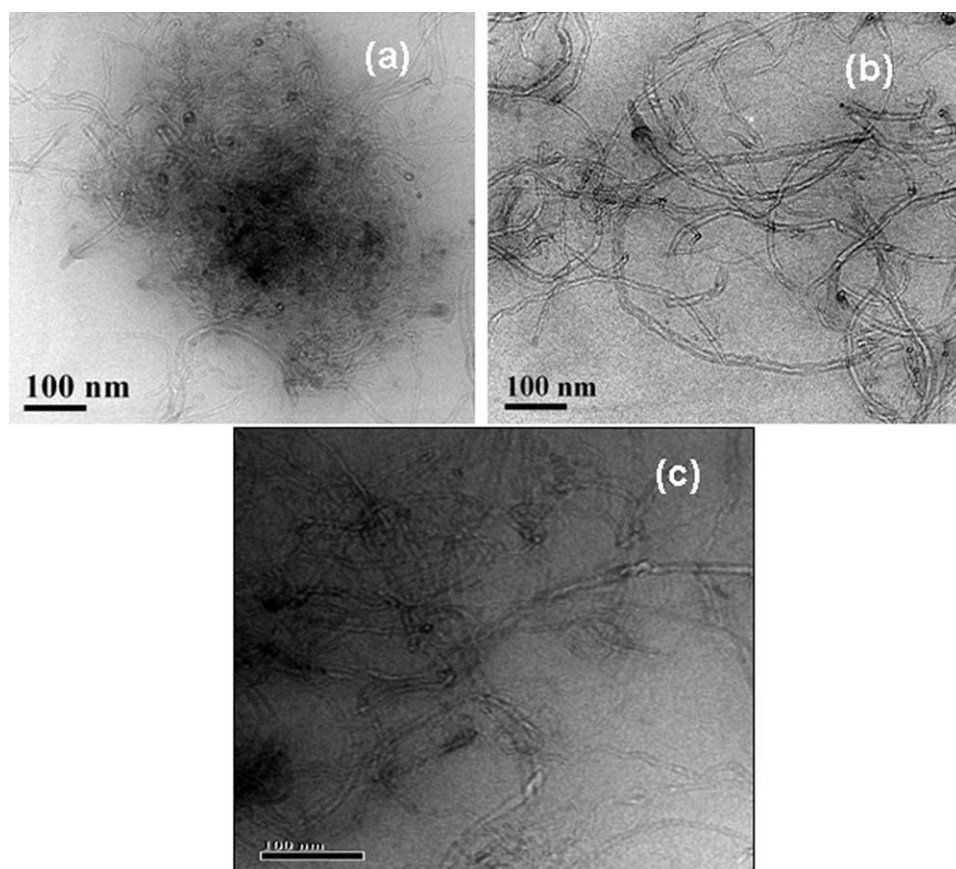
bonding between the carboxyl groups of HNAA and the epoxy resin.

Raman spectrum of MWCNT exhibits two characteristics band namely, G and D band indicating usual MWCNT structure and the density defects. Figure 4 represents the Raman spectra of

the MWCNTs, HNAA-modified MWCNTs, and EP/MWCNT (0.5 wt %)/HNAA. There was no discernible change in the peak position of the G and D band of the MWCNTs after mixture with HNAA. This implied that the modification of the MWCNTs did not generate any defect in the MWCNTs. We also



**Figure 6.** SEM images of the cryogenically fractured composite samples: (a) EP/MWCNT (0.5 wt %) and (b) EP/MWCNT (0.5 wt %)/HNAA.



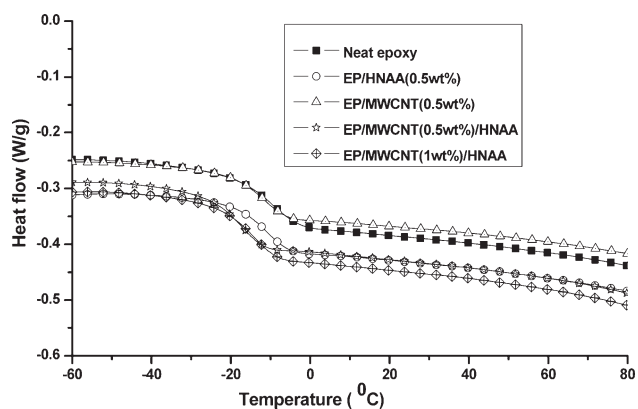
**Figure 7.** TEM images of the epoxy/MWCNT composites: (a) EP/MWCNT (0.5 wt %), (b) EP/MWCNT (0.5 wt %)/HNAA, and (c) EP/MWCNT (1 wt %)/HNAA.

noted that both the G and D band intensities of the HNAA-modified MWCNTs and EP/MWCNT (0.5 wt %)/HNAA were higher compared to those of the unmodified MWCNTs. This indicated the existence of cation- $\pi$  interactions and the debundling of the MWCNT aggregates.<sup>27–32</sup>

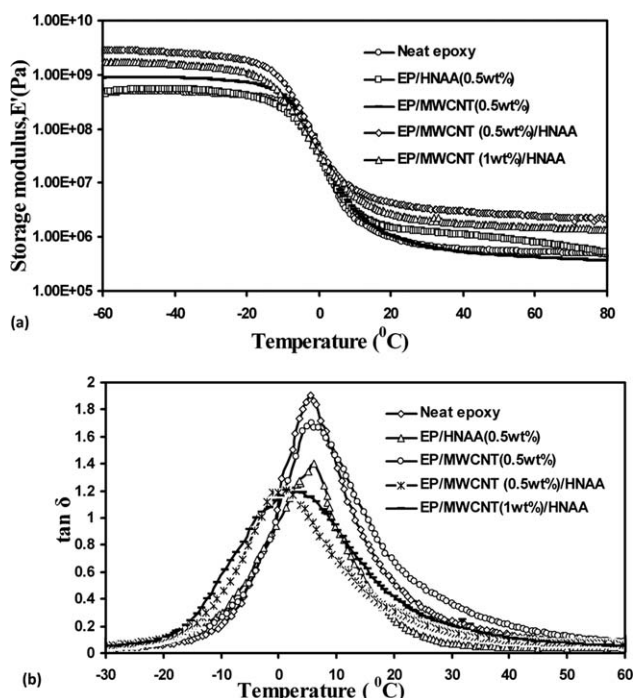
To support the previous observation, the powder sample of unmodified MWCNTs and HNAA-modified MWCNTs were assessed by TEM. The TEM photographs of the unmodified MWCNTs and HNAA-modified MWCNT samples are presented in Figure 5. The unmodified MWCNTs showed many black spots and crowded MWCNT bundles throughout the image because of agglomeration. However, in the case of the HNAA-modified MWCNTs, the nanotubes were well dispersed and had less entanglement [Figure 5(b)]. Furthermore, the suspension stability of the unmodified MWCNTs and HNAA-modified MWCNTs was studied with THF because the polar nature of THF provides good compatibility with the -COOH groups of HNAA. The photographs of the sonicated sample vials are shown in Figure 5. We saw that the suspension of the HNAA-modified MWCNTs was stable even after 1 month of storage at room temperature. This clearly indicated that the dispersion of the MWCNTs was due to addition of the modifier, which interacted with the MWCNTs via cation- $\pi$  interaction.

#### Microscopic Analysis of the EP/MWCNT Composites

SEM and TEM analyses were conducted on EP/MWCNT (0.5 wt %) and EP/MWCNT (0.5 wt %)/HNAA composite samples to study the dispersion of the MWCNTs in the epoxy matrix. The composite samples were cryogenically fractured and subjected to SEM analysis. The microphotographs are shown in Figure 6. The EP/MWCNT (0.5 wt %) composite [Figure 6(a)]



**Figure 8.** DSC plots for the neat epoxy, EP/HNAA (0.5 wt %), EP/MWCNT (0.5 wt %), EP/MWCNT (0.5 wt %)/HNAA, and EP/MWCNT (1 wt %)/HNAA composites.



**Figure 9.** (a) Storage modulus versus temperature and (b)  $\tan \delta$  versus temperature plots for the neat epoxy, EP/HNAA (0.5 wt %), EP/MWCNT (0.5 wt %), EP/MWCNT (0.5 wt %)/HNAA, and EP/MWCNT (1 wt %)/HNAA.

clearly demonstrated the presence of agglomerated nanotubes. However, the EP/MWCNT (0.5 wt %)/HNAA composite showed uniformly dispersed nanotubes, and some nanotubes were pulled out from the matrix, as also shown in Figure 6(b).

Figure 7 shows the TEM microphotographs of the EP/MWCNT (0.5 wt %), EP/MWCNT (0.5 wt %)/HNAA, and EP/MWCNT (1 wt %)/HNAA composites. The EP/MWCNT (0.5 wt %) composite showed agglomerated MWCNTs because of the high degree of entanglement [Figure 7(a)]. On the other hand, the EP/MWCNT (0.5 wt %)/HNAA composite showed well-dispersed MWCNTs [Figure 7(b)]. This indicated that the cation- $\pi$  interaction between HNAA and the MWCNTs helped to break the agglomeration of the MWCNTs. Furthermore, at higher concentrations (1 wt %) of MWCNTs, it was difficult to prevent the agglomeration, as shown in Figure 7(c). This explains why the tensile properties decreased beyond 0.75 wt % of the HNAA-modified MWCNTs, as discussed earlier.

### Thermal Analysis

The neat epoxy and EP/MWCNT composite samples were subjected to DSC analysis. The DSC plot of the neat epoxy and MWCNT composites are shown in Figure 8. The absence of any exothermic peak above  $T_g$  indicated the completion of the curing reaction, as evident from Figure 8. The  $T_g$  values of the composites were found to be decreased to lower temperature because of the addition of the modified MWCNTs compared to neat epoxy.

Figure 9(a,b) shows the storage modulus versus temperature and the  $\tan \delta$  versus temperature plots of the neat epoxy and

EP/HNAA (0.5 wt %), EP/MWCNT (0.5 wt %), EP/MWCNT (0.5 wt %)/HNAA, and EP/MWCNT (1 wt %)/HNAA composites. We observed that the EP/MWCNT (0.5 wt %) composite showed a moderate improvement in the storage modulus in the glassy region, whereas in the rubbery region, it behaved like neat epoxy [Figure 9(a)]. We could explain this by considering the fact that the inert surface of the unmodified MWCNTs could not form any kind of bonding (poor interfacial adhesion) with the epoxy matrix. A significant improvement in the storage modulus of the EP/MWCNT (0.5 wt %)/HNAA and EP/MWCNT (1 wt %)/HNAA composite samples was observed. There was no improvement in the storage modulus when the same composite was made with the modifier [EP/HNAA (0.5 wt %)]. This implied that the reinforcing effect was exclusively the outcome of only well-dispersed MWCNTs and chemical bonding (Figure 1).

From Figure 9(b), we observed that the peak height of  $\tan \delta$  was significantly reduced because of the addition of HNAA-modified MWCNTs; this indicated an increase in the rigidity and stiffness of the matrix. The reduction in the height of the damping peak was associated with a strong interaction between the HNAA-modified MWCNTs with the epoxy matrix and chemical bonding. The  $\tan \delta$  after the addition of the HNAA-modified MWCNTs was still greater than 1, which was sufficient for vibration damping applications. We noted that the composite containing unmodified MWCNTs showed no change in  $T_g$ , whereas the shift in  $T_g$  to lower temperature for the EP/MWCNT (0.5 wt %)/HNAA and EP/MWCNT (1 wt %)/HNAA composites was evident in Figure 9(b). This could be explained by considering the fact that the pre-reaction of the carboxyl groups of HNAA with epoxy resin formed strong interfacial bonds, and this led to a nonstoichiometric balance between the epoxy resin and curing agent and thus led to the inhibition of the crosslinking reaction to a certain extent between them and a decrease in  $T_g$  of the composites due to the addition of the MWCNTs. Similarly, a decrease in  $T_g$  after the addition of MWCNTs has also been reported in the literature.<sup>33–36</sup>

### CONCLUSIONS

A process involving cation- $\pi$  interaction and chemical bonding (between MWCNTs and epoxy) was successfully used to prepare flexible epoxy/MWCNT composites. Among various modifiers investigated, adipic acid salts (HNAA) modified MWCNTs were found to be most effective in the improvement of the tensile strength and tensile modulus. The addition of 0.5 wt % HNAA-modified MWCNTs showed 70 and 190% improvements in the tensile strength and tensile modulus, respectively. The good dispersion of MWCNTs (as confirmed by SEM and TEM analysis) and the enhancement in the properties of the composites were achieved due to cation- $\pi$  interactions between the HNAA and MWCNTs and chemical bonding of the HNAA with the epoxy matrix. The cation- $\pi$  interaction broke the agglomerates of the MWCNTs, and chemical bonding improved the interfacial adhesion of the nanotubes with the epoxy matrix. The proposed interaction between the HNAA and MWCNTs was explained by FTIR and Raman spectroscopy. This approach did not disturb the  $\pi$ -electron clouds of the CNTs in contrast to chemical functionalization.



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