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Poly(ethylene oxide)-Multiwall Carbon Nanotube Composites: Effect of Dicarboxylic Acid Salt-Based Modifiers

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ABSTRACT: An investigation was carried out to improve the dispersion of multiwall carbon nanotubes (MWCNTs) in the poly(ethylene oxide) (PEO) matrix using a half-neutralized sodium salt of dicarboxylic acid with various number of carbon atoms. The effects of nature of various modifiers on mechanical properties of PEO were investigated. Among various dicarboxylic acid salts, half neutralized adipic acid (HNAA) is found to be highly effective in achieving the improvement in mechanical and dynamic mechanical properties due to improved dispersion of MWCNT in the PEO matrix. The physical interaction of HNAA with MWCNT (cation–π interaction) has been established using Fourier transform infrared and Raman spectroscopic analyses. Scanning electron microscope and transmission electron microscope (TEM) studies clearly indicate the improvement in the level of dispersion of MWCNT due to the addition of HNAA. Crystallization behavior of the PEO/MWCNT composites made with unmodified and modified MWCNT were studied by differential scanning colorimetry. Our approach is a noncovalent one and does not destroy the π-electron clouds of MWCNT as opposed to chemical functionalization techniques and particularly attractive because of possibility of preserving the structural integrity of nanotubes as well as improved phase adhesion with polymer matrix. © 2012 Wiley Periodicals, Inc. J. Appl. Polym. Sci. 000: 000–000, 2012

KEYWORDS: nanocomposites; poly(ethylene oxide); multiwall carbon nanotubes; modification of MWCNT; organic salt

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INTRODUCTION

In recent years, the use of nanofiller has increased tremendously and the dramatic growth is showing every sign to continue in the future.[1–3] Among the various available nanofillers carbon nanotubes (CNTs) have been viewed as the most promising material in the area of polymer nanocomposites.[4] CNTs offer superior properties such as exceptionally high aspect ratio (>300), elastic modulus (>1 TPa), high thermal, and electrical conductivity which develop enormous interest in the scientific community. However, the realization of an effective nanoreinforcement of polymer/multiwall carbon nanotube (MWCNT) composites depends on the degree of dispersion of MWCNT.[5–11] Homogeneous dispersion of MWCNT is hindered by agglomerate formed due to strong Van der Waal forces. Therefore, the interfacial interaction between nanotubes and polymer, improved nanotube/matrix wetting and adhesion are the critical issues in respect of processing and applications of nanocomposites.[12–14]

Several studies have been conducted to overcome the problem of poor dispersion such as ultrasonication, high sear mixing, polymer chain wrapping, surface oxidation (covalent functionalization) by acid treatments, and use of surfactant.[15–21] Surface oxidation of MWCNT (covalent functionalization) by acid is an effective way to improve the dispersion of CNT by generating polar groups (e.g., COOH).[22] These polar groups can be further used to tailor the surface using covalent grafting method.[23–25] The disadvantage of this method is that it destroys the π-electron clouds of CNTs to a certain extent and reduces the inherent conductivity of CNTs. Dispersion of CNTs can also be improved by the use of surfactant which triggers the debundling of CNT by physical interactions without destroying the π-electron clouds of CNT (ionic or nonionic type). This is purely noncovalent approach and particularly attractive because of the possibility of preserving the structural integrity of nanotubes as well as improved adhesion with the polymer matrix. Neutral surfactants have been reported to promote dispersion through the Van der Waals interactions within the nanotube.[26–30] Ionic surfactants are expected to perform better for dispersion of CNTs in an aqueous solution of a high molecular weight polymer due to the stronger interactions (referred to "cation–π interaction" or π–π interaction) between cations and with extended delocalized π-electron clouds of the CNTs. Although there are various reports on the use of such modifier for dispersion of CNTs in melt blending,[31,32] Interestingly, reports are scanty[33] on the direct use of such modifier for water soluble polymers.

In this study, we have selected a water soluble polymer for example, poly(ethylene oxide) (PEO) for the aforementioned studies. PEO is a promising material showing application such as phase change materials[34,35] solid polymer electrolytes[36,37] for use in battery, supercapacitor, fuel cell applications, and crystallizable switching segment for shape memory polymer (SMP) systems.[38] The common problem of PEO for all the applications is linked with poor mechanical properties of PEO. Recently, MWCNT is found to be most promising materials for improving mechanical properties of the PEO-based electrolytes and SMP system.

Several reports are addressed to synthesis of PEO/MWCNT composites using acid treated and grafting technique.[22,39] However, as discussed earlier, due to the acid treatment and chemical functionalization, the outer shells of CNTs were damaged to some extent causing a reduction in the inherent conductivity of the CNT.[40] Very recently, Ratna et al.[33] investigated ionic modifier for the aqueous polymer matrix and studied the effect of full- and half-neutralized sodium salt of suberic acid for dispersion of MWCNT in aqueous solution of PEO. It was reported HNSA is more effective in improvement of dispersion of MWCNT in PEO matrix due to its ability to interact with both the MWCNT and PEO.

In this study, we have used dicarboxylic acid salts having different number of carbon atoms to improve the dispersion of MWCNT and their effect on the tensile and other properties were investigated. In general, compared to other thermoplastic polymer less numbers of reports are available on tensile property of PEO/MWCNT-based composites because they are not used for high strength application. Therefore, reinforcement of PEO using nanofillers is needed to improve its tensile property for the development of high performance of PEO-based composites. In this article, we studied the effect of nature of modifier on tensile property, crystallization behavior, thermomechanical properties, and morphology of PEO/MWCNT composites. The modifier is designed in such a way that the cation of modifier is expected to interact with π-electron cloud of MWCNT (cation–π interaction) and H-bonding interaction between the carboxyl group and PEO matrix.

EXPERIMENTAL

Materials

The matrix PEO with weight average molecular weight of 600,000 g/mole was purchased from Sigma-Aldrich India Ltd. MWCNT (Baytube® 150P) was procured from Bayer Material Science AG (Leverkusen, Germany). Distilled water was used as a solvent. Adipic acid, succinic acid, sebacic acid, and sodium hydroxide were purchased from Merck, India Ltd. and used as received.

Preparation of PEO/MWCNT Nanocomposites

Preparation of three different half-neutralized sodium salt of dicarboxylic acids having different number of carbon atoms were performed in distilled water with 1 : 1 mole ratio of dicarboxylic acid to sodium hydroxide. The modifier designated as half-neutralized succinic acid (HNSCA), half-neutralized adipic acid (HNAA), half-neutralized sebacic acid (HNSA), respectively. Modification of MWCNT with half-neutralized sodium salt of dicarboxylic acid was done in distilled water by sonication method. Nanocomposites films were made by dispersing MWCNT in 10 wt % aqueous solution of PEO. Ten gram of PEO (10%) dissolved in 100 mL of distilled water and allowed for overnight. The modifier and MWCNT were mixed in 50 mL of distilled water in 100-mL beaker and mixture was sonicated for 15 min using a probe sonication, keeping the beaker immersed in cold water. An aqueous solution of modified MWCNT was added into 10% aqueous solution of PEO and again sonicated for 15 min using a probe sonication. Finally, aqueous solution of modified MWCNT and PEO was poured into suitable molds and kept in air ventilated oven at 65°C for 3 days for complete removal of water. Composites were prepared using various concentration of MWCNT are designated as PEO/MWCNT (0.5 wt %), PEO/HNAA (0.5 wt %), PEO/MWCNT (0.5 wt %)/HNSA, PEO/MWCNT (0.5 wt %)/HNSCA, and PEO/MWCNT (0.25 wt %, 0.5 wt %, 0.75 wt %, 1 wt %, 1.5 wt %)/HNAA.

Characterization

Tensile tests were performed on dumb-bell shaped type V samples according to ASTM D-638. The tensile strength, modulus, and % elongation at break were measured using Universal Testing Machine (Hounsfield 50 KS). Tensile tests of PEO and modified-MWCNT composites samples were performed on dumb-bell shaped type V samples according to ASTM D-638. The dumb-bell shaped samples ($50 \times 4 \times 2$ mm^3) die were cut by suitable mold.

Fourier transform infrared (FTIR) spectra of modified MWCNT and its composites samples with attenuated total reflection mode were taken by a Nicolet 510 FTIR spectrometer, Germany, over a scanning range 600–4000 cm^{-1} with a nominal resolution of 2 cm^{-1}. For each spectrum, 64 runs were collected and averaged. Raman spectroscopic analysis of MWCNT, modified-MWCNT and composites samples were performed over a scanning range of 500–2000 cm^{-1} with incident laser exciting wavelength of 514 nm.

A scanning electron microscope (FEG-SEM) (Zeissa Supra 40 VP) was used to study the morphology of the MWCNT and their composites samples. The composite samples were quenched in liquid nitrogen and cryogenically fractured to obtain the cross-sections, which were sputter coated with carbon to avoid the charging before the SEM observation.

High-resolution transmission electron microscope analysis of composites samples was conducted on a JEOL, JEM-2100 electron microscope at 200 KV. Ultrathin sections were prepared with thickness of 80–100 nm for TEM imaging using Leica ultracut microtome (Leica Mikrosysteme, GmbH, A-1170) of composites film using liquid nitrogen.

Thermal behavior of PEO and PEO/MWCNT composites was studied with differential scanning colorimetry (DSC; TA instruments Q100 series). About 6–10 mg of sample was placed in an aluminum pan and heated from room temperature to 100°C and cooled to 0°C with heating and cooling rate at 5°C/min.

Table I. Tensile Properties of PEO Containing 0.5 wt % Unmodified MWCNT and Three Different Modified MWCNT Having Different Dicarboxylic Acid Salts

Samples	Tensile strength (MPa)	Modulus (MPa)	Elongation at break (%)
PEO	11.0	117	376
PEO/MWCNT (0.5 wt %)(100 : 1 : 0)	10.7	132	364
PEO/MWCNT (0.5 wt %)/HNSCA(100 : 1 : 1)	12.4	198	675
PEO/MWCNT(0.5 wt %)/HNAA (100 : 1 : 1)	16.6	196	888
PEO/MWCNT(0.5 wt %)/HNSA(100 : 1 : 1)	13.4	154	476

The reference was an empty aluminum pan. Melting point (T_m), crystallization temperature (T_c), and enthalpy of crystallization (ΔH_c) were calculated as the maximum position of the endothermic peak and the area of crystallization curve under DSC thermogram.

Dynamic mechanical analysis (DMA) of PEO and PEO/MWCNT composites samples was performed using a dynamic mechanical thermal analyzer (MK IV, Rheometric Scientific); the test specimen was cooled to −100°C, allowed to stabilize and then heated at a rate of 3°C/min to 30°C. Liquid nitrogen was used for subambient region. Dynamic modulus and loss modulus were obtained by a dual cantilever mode for the sample of size 30 × 10 × 2 mm^3 using a fixed frequency of 1 Hz.

RESULT AND DISSCUSION

Effect of Nature of Modifier on Tensile Property

Table I compares the tensile properties of PEO/MWCNT composites (0.5 wt %) modified with dicarboxylic acid salts having different number of carbon atoms. The ratio of MWCNT to modifier (by weight) was maintained as 1 : 1. It was observed that all composites containing modified MWCNT show higher tensile properties compared to the pure PEO and it is interesting to note that an improvement in the tensile property is achieved in all respects. This can be attributed to the increase in the level of dispersion of MWCNT due to addition of modifier and good interfacial adhesion with PEO as a result of modification. The good dispersion of MWCNT is believed to originate from the cation–π interaction (cation of the modifier with π-electron clouds of MWCNT) between the modifiers with MWCNT and H-bonding of carboxylic acid of modifier with PEO which is presented in Figure 1 for the adipic acid salts. Conversely, the unmodified-MWCNT composite does not shows significant reinforcing effect due to poor dispersion as a result of agglomeration. The presence of agglomerated nanotubes reduces the crystallinity of the PEO and leading to decrease in inherent strength of PEO. As shown in Table I, the adipic acid salt exhibits the best tensile property compared to the other acid salts with higher and lower number of carbon atoms. This can be explained by considering two factors namely polarity matching and the formation of salts with one carboxylate ions. For polarity matching with PEO, higher numbers of carbon atoms are required. However, with increase in number of carbon atoms of acid, the probability of formation of salt with one carboxylate ion decreases. Note that the acid salt is prepared using half equivalent of sodium hydroxide. So, there is always a possibility of formation of dicarboxylate. The formation of dicarboxylate is more for acids with higher number of carbon atoms. For achieving both debundling and interfacial adhesion, the formation of salt with one carboxylate and one carboxylic

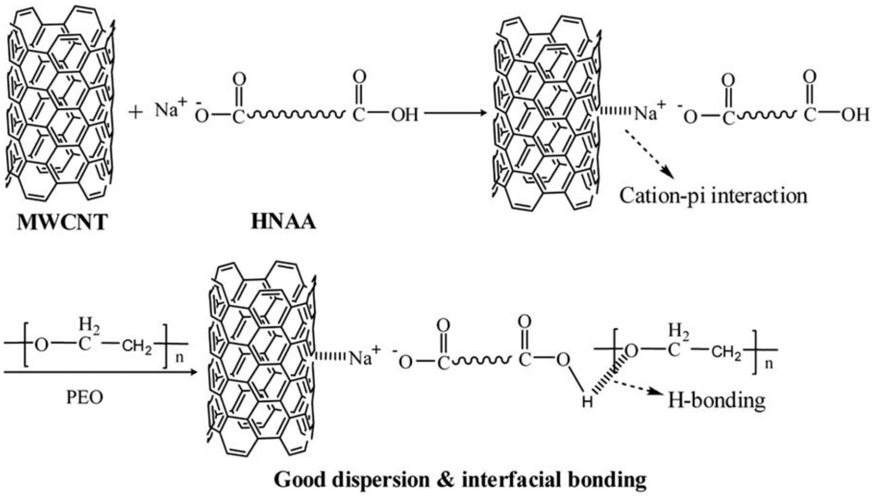

Figure 1. The cation–π interaction (cation of the modifier with π-electron clouds of MWCNT) between the modifier (HNAA) with MWCNT and H-bonding of carboxylic acid of HNAA with PEO.

Table II. Tensile Properties of PEO Containing 0.5 wt % of HNAA Modified MWCNT with Different Mole Ratio of MWCNT to HNAA

Samples	Ratio	Tensile strength (MPa)	Modulus (MPa)	Elongation at break (%)
PEO	–	11.0	117	376
PEO/MWCNT(0.5 wt %)/HNAA	100 : 1 : 0.5	15.5	164	784
PEO/MWCNT(0.5 wt %)/HNAA	100 : 1 : 1	16.6	196	888
PEO/MWCNT(0.5 wt %)/HNAA	100 : 1 : 1.5	13.6	116	554
PEO/MWCNT(0.5 wt %)/HNAA	100 : 1 : 2	13.2	172	422

acid group is most desirable as shown in Figure 1. The best performance of adipic acid salts (HNAA) compared to other acid salts is a result of a combined effect of polarity matching and dicarboxylate formation. Hence, from the above results, the adipic acid salt (HNAA) is used for further characterization and discussion.

To find out optimum concentration of modifier (HNAA) required for the good dispersion, a series of composites with 0.5 wt % MWCNT were made using different ratio of MWCNT to HNAA (referred as HNAA-modified MWCNT) and their tensile properties were evaluated. The results are summarized in Table II. In this case, the MWCNT to modifier HNAA ratio were maintained as 1 : 0.5, 1 : 1, 1 : 1.5, and 1 : 2. It was observed that among all concentration, the 1 : 1 ratio of MWCNT to HNAA exhibits the best performance. This shows around 50% improvement in the tensile strength, around 67% improvement in the tensile modulus and 136% improvement in elongation at break, respectively. This indicates that the 1 : 1 concentration of MWCNT to HNAA is the optimum concentration and can improve the tensile property of PEO composites.

Further, we made a series of composites using various concentrations (wt %) of the (1 : 1) HNAA-modified MWCNT to study the possible improvement in the tensile property without any agglomeration. One can see from Table III, the tensile properties (tensile strength, tensile modulus, and elongation at breaks) increases with increase in the concentration of MWCNT up to 0.75 wt % and thereafter decreases. Maximum value of tensile strength and tensile modulus is found to be 16.9 and 198 MPa (Figure 2). This improvement in the tensile property can be attributed to uniform distribution of nanotubes and the strong interaction between PEO and modifier. The decrease in tensile property beyond the 0.75 wt % of MWCNT is due to the agglomerated MWCNT as evident from microscopic studies which will be discussed in subsequent section.

Table III. Tensile Properties of PEO/MWCNT/HNAA (1 : 1) Composites Having Different Concentration (wt %) of MWCNT

Samples	Tensile strength (MPa)	Modulus (MPa)	Elongation at break (%)
PEO	11.0	117	376
PEO/HNAA (0.5 wt %)	11.7	114	279
PEO/MWCNT(0.25 wt %)/HNAA	09.0	129	516
PEO/MWCNT(0.5 wt %)/HNAA	16.6	196	888
PEO/MWCNT(0.75 wt %)/HNAA	16.9	144	815
PEO/MWCNT(1 wt %)/HNAA	12.1	141	786
PEO/MWCNT(1.5 wt %)/HNAA	11.8	111	786
PEO/MWCNT(2 wt %)/HNAA	10.2	88	602

Interaction Between HNAA, MWCNT, and PEO

The desired properties of a polymer/MWCNT composites depend on two factors; namely, the level of dispersion in the polymer matrix and the extent of interfacial interaction between the polymer and MWCNT. A good dispersion is absolutely necessary to realize the effectiveness of MWCNT. However, if there is not enough bonding between the nanotubes and the polymer matrix, the tubes will be simply pulled-out and will not contribute to enhance the mechanical properties of the polymer. In the present case, the modifier is designed in such a way that it can interact with MWCNT via cation–π interaction and with PEO by H-bonding as shown in Figure 1. The dispersibility of nanotubes was studied by preparing a suspension of MWCNT using tetrahydrofuran (THF) as a solvent. The successful incorporation of nanotubes depends on the ability of debundling which will lead to a homogeneous and stable suspension. We have studied the suspension stability of unmodified MWCNT and HNAA-modified MWCNT in the THF as a quantification of debundling. The modification of MWCNT with HNAA was performed in distilled water by sonication method and water was completely removed from the modified-MWCNT sample by keeping in vacuum oven at 80°C for 48 h. A fixed amount

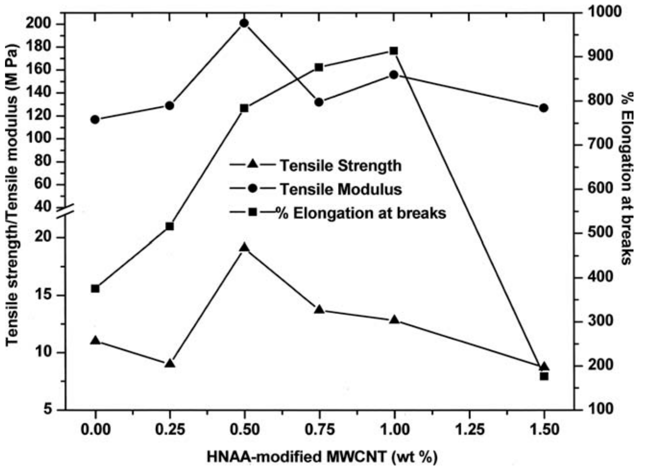

Figure 2. Effects of different wt % of HNAA-modified MWCNT on the tensile property of PEO matrix.

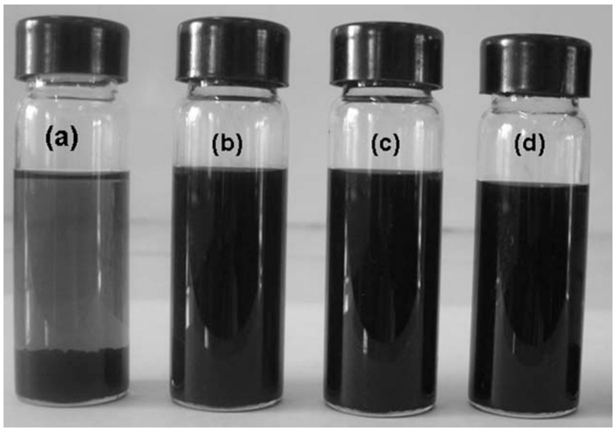

Figure 3. Photograph showing dispersion of MWCNT in THF (a) MWCNT, (b) HNAA-modified MWCNT (1 : 0.5), (c) HNAA-modified MWCNT (1 : 1), and (d) HNAA-modified MWCNT (1 : 2).

(5 mg) of fully dried unmodified MWCNTs and HNAA-modified MWCNT were added to a sample vials containing THF and each sample vial was sonicated for 5 min. The photographs of the sonicated sample vials are shown in Figure 3(a–d). It was observed that the HNAA-modified MWCNTs reveal the homogeneous and stable suspension [Figure 3(b–d)] of MWCNT even after 1 month of storage at room temperature. This can be explained by considering the polar carboxyl group of HNAA provides good compatibility with THF and cation–π interaction between HNAA and MWCNT. Conversely, the unmodified MWCNTs [Figure 3(a)] are settled at the bottom due to agglomeration. Further, we support this observation by TEM analysis of unmodified MWCNT and (1 : 1) HNAA-modified MWCNT. It can be seen from Figure 4(a) that, the nanotubes are highly agglomerated and bundled in unmodified MWCNT, whereas well-separated individual nanotubes can be seen in the case of HNAA-modified MWCNT [Figure 4(b)] sample. This is due to the existence of interaction between the cation of HNAA and π-electron clouds of MWCNT which promote the MWCNT to disentangle. The HNAA interact with the nanotubes through its ionic group by means of "cation–π interaction" as evidenced by FTIR and Raman spectroscopic analyses discussed below.

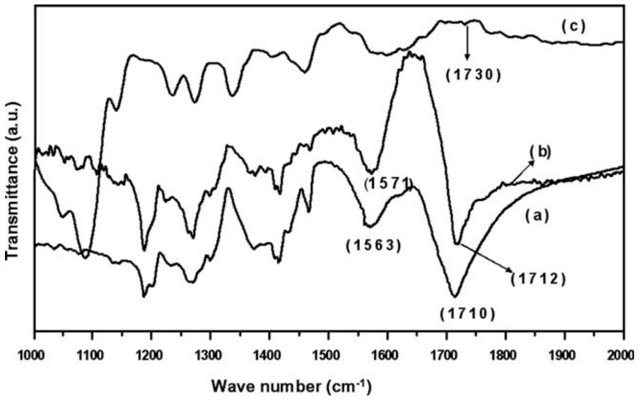

Figure 5. FTIR spectra of (a) HNAA, (b) HNAA-modified MWCNT, and (c) PEO/MWCNT (0.5 wt %)/HNAA composites.

Figure 5 shows the FTIR spectra of HNAA, HNAA-modified MWCNT, and PEO/MWCNT (0.5 wt %)/HNAA. HNAA shows stretching of C=O group of carboxylate ion and carboxylic acid peaks at 1563 and 1710 cm^{-1}, respectively. The C=O group of carboxylate exhibits a peak at a lower wave number compared to the same of carboxylic acid because the negative (–ve) charge on oxygen atom of carboxylate ion undergoes dislocation and reduces the bond strength of C=O group and results reduction in the wavenumber.[41] When the HNAA is mixed with MWCNT, the carboxylate peak shifts toward a higher wavenumber, that is, from 1763 to 1571 cm^{-1}. This can be explained by considering the fact that the Na$^+$ (cation) of HNAA interacts with π-electron clouds of MWCNT via ionic interaction which reduces the effectiveness of the dislocation mentioned above [Figure1]. This discussion clearly supports the cation–π interaction between HNAA and MWCNT.[33,42,43] Conversely, we found no change in stretching of C=O group of carboxylic acid of HNAA when mixed with MWCNT. This indicates the absence of any interaction between carboxylic acid groups of HNAA with MWCNT. However, It is interesting to note that stretching of C=O group

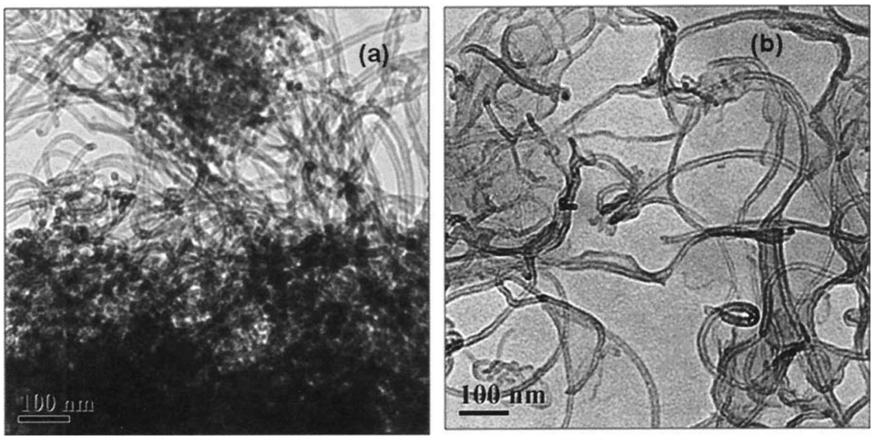

Figure 4. TEM images showing dispersion of MWCNT in THF (a) MWCNT and (b) (1 : 1) HNAA-modified MWCNT. The nanotubes were dispersed in acetone by sonication and cast onto the 300-mesh copper grid directly and inspected after complete removal of acetone.

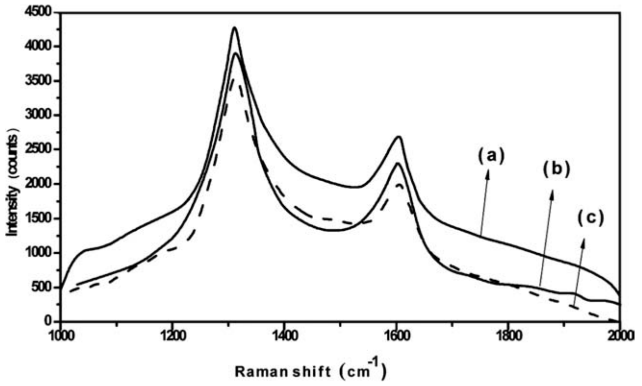

Figure 6. Raman spectrum of (a) PEO/MWCNT (0.5 wt %)/HNAA, (b) HNAA-modified MWCNT (1 : 1), and (c) unmodified MWCNT.

of carboxylic acid is shifted from 1710 to 1730 cm^{-1} for PEO/MWCNT/HNAA composite. This can be attributed to the H-bonding interaction between the carboxylic acid group of HNAA and ether group of PEO. The composites containing higher concentration of MWCNT could not be analyzed by FTIR because strong IR absorption of the MWCNT.

The Raman spectroscopic technique is widely used to characterize the MWCNT and their composites. Raman spectra of unmodified MWCNT, HNAA-modified MWCNT, and PEO/MWCNT/HNAA composites are presented in Figure 6. In general, Raman spectrum of MWCNT exhibits two characteristic bands (G and D band) indicating the usual MWCNT structures and the density defects. The D band of MWCNT arises due to the disorder graphitic structure and corresponding G band is due to the tangential stretching of carbon–carbon bond.[44] Interestingly, there is no significant shift in the bands of modified MWCNT compared to unmodified MWCNT. This Raman spectral profile indicated that the interaction between the modifier and the MWCNT was only physical in nature without any chemical denaturalization of MWCNT.[45] However, it can also be noted that G-band and D-band peak intensities are slightly higher for HNAA-modified MWCNT and its composite compared to the unmodified MWCNT. The shift in peak to higher intensity of G-band and D-band on addition of modifier is a manifestation of existence of the cation–π interaction.[42,43] This observation confirms the existence of interaction between cation (Na$^+$ ion) of modifier and π electron clouds of MWCNT. The increase in peak intensity of G band is due to the debundling of MWCNT aggregates.[46]

Morphological Analysis of PEO/MWCNT Composites

The dispersion of CNTs in the PEO matrix was studied by SEM and TEM to substantiate the effectiveness of proposed interaction on dispersion of MWCNT. The SEM provides distinct difference in dispersion of unmodified and modified MWCNT and interfacial adhesion with matrix. The cryogenically fracture MWCNT composites were subjected to SEM analysis and photographs are shown in Figure 7(a,b). The composite containing unmodified MWCNT [Figure 7(a)] clearly demonstrate the presence of agglomerated nanotubes. Although homogenously dispersed bright dots which are broken end of nanotubes was observed in the case of HNAA-modified MWCNT composite [Figure 7(b)]. This result indicates the modification of MWCNT provides not only good dispersion but also strong interfacial interaction and good compatibility with PEO.

TEM images of PEO/MWCNT (0.5 wt %), PEO/MWCNT (0.5 wt %)/HNAA, and PEO/MWCNT (1 wt %)/HNAA are shown in Figure 8(a–c). The PEO/MWCNT composite shows agglomerated nanotubes throughout the image indicating poor dispersion as evident from Figure 8(a), whereas the PEO/MWCNT (0.5 wt %)/HNAA composite exhibits exfoliated nanotubes [Figure 8(b)]. This can be explained by considering the debundling of nanotubes due to the cation–π interactions and H-bonding interaction of PEO as described in Figure 1. The above mentioned morphological features clearly explained the higher mechanical properties of MWCNT composites discussed earlier. At higher concentration (wt %) of MWCNT, it is difficult to

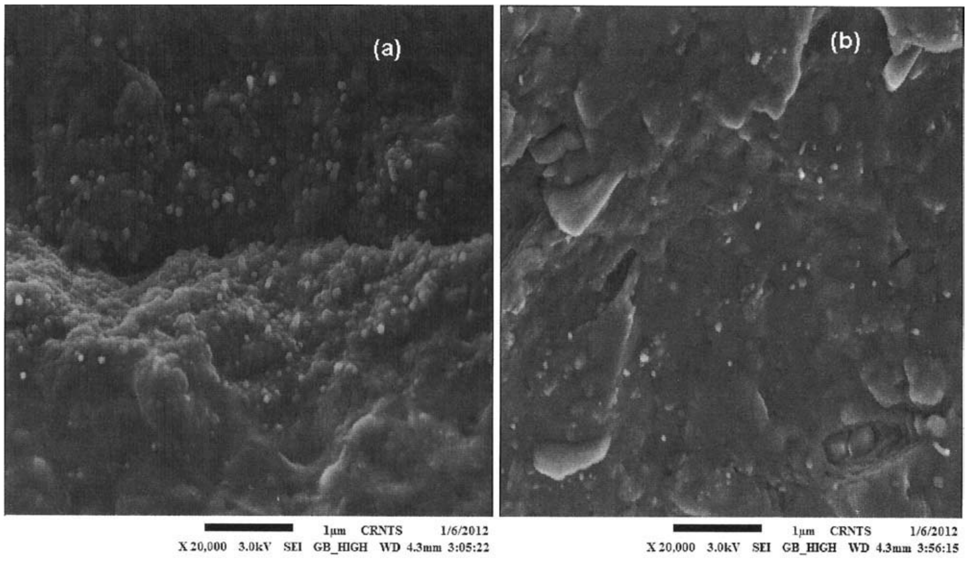

Figure 7. SEM photograph for fracture surface of (a) PEO/MWCNT (0.5wt %) and (b) PEO/MWCNT (0.5 wt %)/HNAA.

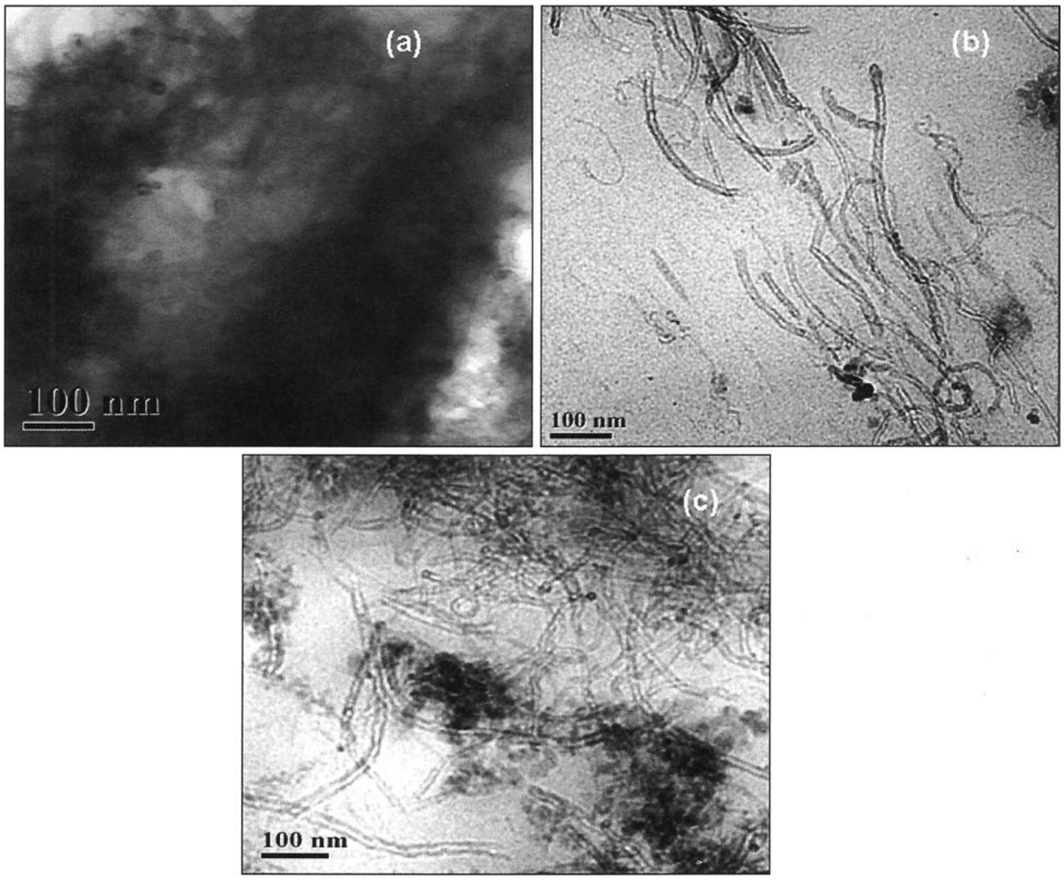

Figure 8. TEM photograph for PEO/MWCNT composites (a) PEO/MWCNT (0.5 wt %), (b) PEO/MWCNT (0.5 wt %)/HNAA, and (c) PEO/MWCNT (1 wt %)/HNAA.

prevent the agglomeration as shown in Figure 8(c). This explains why beyond 0.75 wt % of MWCNT, the tensile property of composites decreases as discussed earlier.

Thermal Analysis

DSC analysis is generally one of the most convenient methods for analyzing first-order transition like melting and crystallization. We studied the crystallization behavior of PEO/MWCNT composites using DSC and typical thermogram of composites displaying the crystallization peak are shown in Figure 9. Melting point (T_m), crystallization temperature (T_c), and heat of crystallization (ΔH_c) of all composites samples were listed in Table IV. From the crystallization plots, the heat of crystallization, ΔH_c is calculated from the formula given below:

$$\Delta H_c = \frac{(\Delta H_c)_{\text{total}} \times 100}{w \times y} \tag{1}$$

where $(\Delta H_c)_{\text{total}}$ is obtained from the peak area of DSC cooling curve, w is the weight of sample taken for DSC experiment, and y is the concentration of PEO in wt %.

As shown in Figure 9, the PEO/MWCNT composite exhibits lower the melting (T_m) and crystallization temperature (T_c) compared to the PEO. This can be attributed to these composite nanotubes are mostly in agglomerated form (as evidenced by TEM discussed earlier) and exert steric hindrance by blocking the crystalline growth fronts leading to a decrease in crystallization temperature.[47] Conversely, melting (T_m) and crystallization temperature slightly changed to higher temperature due to addition of modified MWCNT. This indicates that the modified MWCNT being dispersed well do not exert any steric hindrance to the crystallization process. It was also observed that all the

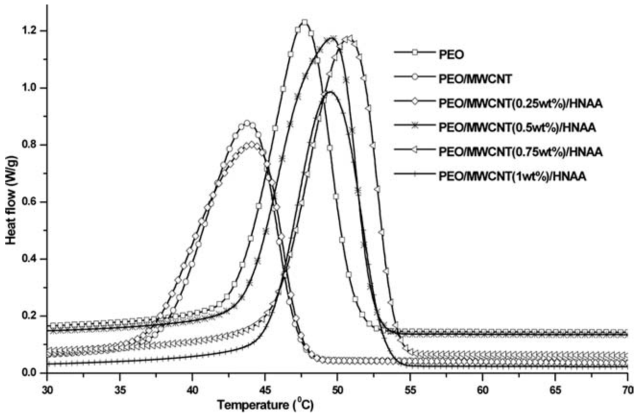

Figure 9. Crystallization peaks of PEO, PEO/MWCNT (0.5 wt %), PEO/MWCNT (0.25 wt %)/HNAA, PEO/MWCNT (0.5 wt %)/HNAA, PEO/MWCNT (0.75 wt %)/HNAA, and PEO/MWCNT (1 wt %)/HNAA.

Table IV. Crystallization Parameters and DSC Analysis of PEO/MWCNT/HNAA Composites

Sample	T_m (°C)	T_c (°C)	ΔH_c (J g^{-1})
PEO	67.3	47.7	129
PEO/MWCNT (0.5 wt %)	65.1	43.8	140
PEO/MWCNT(0.25 wt %)/HNAA	69.0	44.0	117
PEO/MWCNT(0.5 wt %)/HNAA	69.9	49.6	138
PEO/MWCNT(0.75 wt %)/HNAA	70.2	50.8	176
PEO/MWCNT (1 wt %)/HNAA	68.9	49.5	153
PEO/MWCNT(1.5 wt %)/HNAA	64.3	33.9	118

composites exhibit higher heat of crystallization compared to the pure PEO. This can be explained by considering the role of nanotubes as the nucleating agents leading to increase in the crystalanity.[33]

To study effect of modification of MWCNT on the dynamic mechanical properties, PEO and few selected nanocomposites samples were subjected to DMA analysis. Figures 10 and 11 represents storage modulus and loss moduli of PEO and its nanocomposites containing 0.5 wt % of unmodified and modified MWCNT. It was observed that the composite containing unmodified MWCNT shows lower storage modulus compared to pure PEO due to agglomerated MWCNT. This decrease in modulus is explained by considering the fact that the presence of agglomerated nanotubes reduces the crystallinity of PEO as indicated by DSC study. Significant improvement in storage modulus is achieved for HNAA-modified MWCNT composites compared to the pure PEO as evident from Figure 10. This dramatic increase in the dynamic storage modulus is believed to originate from the interaction of Na^+ cation of the HNAA with π-electron clouds of MWCNT. This type of interaction reduces strong Van der Waal interaction between nanotubes and promotes their debundling as evidenced by SEM and TEM analysis discussed earlier. All the composites show higher loss modulus compared to pure PEO (Figure 11). This behavior is quite different from that observed for conventional fillers, which always reduces the loss modulus. The higher damping loss can be explained by considering the phenomenon similar to "constrained layer damping" (CLD) concept.[48] The nanotubes uniformly dispersed in polymer matrix can be considered to form a large number of nano CLDs where the nanotube acts as constraining layers and PEO form the viscoelastic layer. The strong interaction between the PEO and MWCNT resulted in a higher loss because the shearing action between the nanotubes and PEO chains leading to a higher loss modulus.[33]

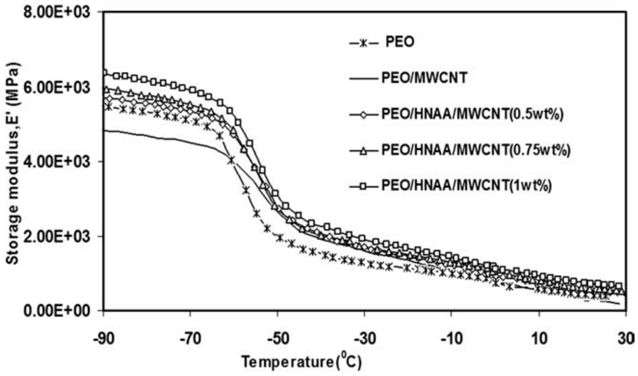

Figure 10. Storage modulus versus temperature plots for PEO, PEO/MWCNT, PEO/MWCNT (0.5 wt %)/HNAA, PEO/MWCNT (0.75 wt %)/HNAA, and PEO/MWCNT (1 wt %)/HNAA.

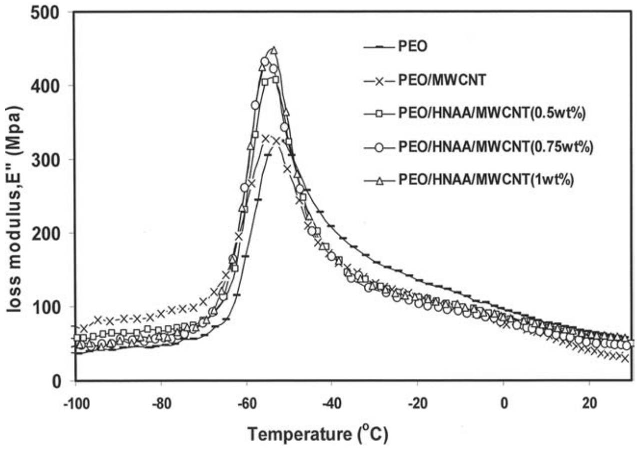

Figure 11. Loss moduli versus temperature plots for PEO, PEO/MWCNT, PEO/MWCNT (0.5 wt %)/HNAA, PEO/MWCNT (0.75 wt %)/HNAA, and PEO/MWCNT (1 wt %)/HNAA.

CONCLUSIONS

The PEO/MWCNT composites were successfully synthesized using dicarboxylic acid salts having different number of carbon atoms by aqueous dispersion method. The MWCNT composite containing adipic acid salt (HNAA) exhibited the best tensile property compared to other acid salts. The improvements in the tensile property of PEO/MWCNT composites was achieved in all respects, that is, addition of 0.5 wt % of HNAA-modified MWCNT improved the tensile strength around 50%, tensile modulus around 67%, and elongation at break by 136%, respectively. Addition of modifier (HNAA) significantly improved the dispersion of MWCNT in PEO matrix as evidenced from SEM and TEM analysis. This is reflected in the increase storage modulus and change in crystallization behavior. FTIR and Raman spectroscopic analysis show the evidence of existence of cation–π interaction between modifier and MWCNT. The improved dispersion achieved using the modifier was explained in terms of cation–π interaction (HNAA and MWCNT) and H-bonding interaction (between HNAA and PEO). This is a purely noncovalent approach and does not destroy the π-electron clouds of MWCNT opposed to chemical functionalization techniques and particularly attractive because of possibility of preserving the structural integrity of nanotubes as well as improved phase adhesion with polymer matrix.

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