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Influence of Surface Modified MWCNTs on the Mechanical, Electrical and Thermal Properties of Polyimide Nanocomposites

B. P. Singh · Deepankar Singh · R. B. Mathur ·
T. L. Dhami

Abstract Polyamic acid, the precursor of polyimide, was used for the preparation of polyimide/multiwalled carbon nanotubes (MWCNTs) nanocomposite films by solvent casting technique. In order to enhance the chemical compatibility between polyimide matrix and MWCNTs, the latter was surface modified by incorporating acidic and amide groups by chemical treatment with nitric acid and octadecylamine ($C_{18}H_{39}N$), respectively. While the amide-MWCNT/polyimide composite shows higher mechanical properties at low loadings (<3 wt%), the acid-MWCNT/ polyimide composites perform better at higher loadings (5 wt%). The tensile strength (TS) and the Young's modulus (YM) values of the acid-MWCNT/polyimide composites at 5 wt% MWCNT loadings was 151 and 3360 MPa, respectively, an improvement of 54% in TS and 35% in YM over the neat polyimide film (TS = 98 MPa; YM = 2492 MPa). These MWCNT-reinforced composites show remarkable improvement in terms of thermal stability as compared to that for pure polyimide film. The electrical conductivity of 5 wt% acid modified MWCNTs/polyimide nanocomposites improved to 0.94 S cm^{-1} (6.67 × 10^{-18} S cm^{-1} for pure polyimide) the maximum achieved so far for MWCNT-polyimide composites.

Keywords Multiwalled carbon nanotubes · Polyimide · Nanocomposites · Electrical properties · Mechanical properties

B. P. Singh · R. B. Mathur (✉) · T. L. Dhami
Carbon Technology Unit, Engineering Materials Division,
National Physical Laboratory, New Delhi 110012, India
e-mail: rbmathur@mail.nplindia.ernet.in

D. Singh
Central Institute for Plastics Engineering and Technology,
Chennai 600 032, India

Introduction

After their discovery in 1991 by Iijima [1], carbon nanotubes (CNTs) have attracted considerable interest because of their unique as well as superior physical, electrical, magnetic, chemical stability, thermal conductivity and mechanical properties [2]. Due to their exceptionally high aspect ratio and mechanical properties, incorporation of small amounts of CNTs into a polymer matrix is expected to enhance the properties of the resulting nanocomposites more than any existing material. The most critical issue of CNTs/polymer nanocomposites is the adhesion/compatibility between the nanotubes and polymer which ultimately controls the interface between the CNTs and the polymer matrix. Unfortunately pure CNTs are insoluble in any organic solvents and they tend to form agglomerates because of strong Van der Wall forces which results in negative effects on the properties of the resulting nanocomposites. As such achieving a high degree of dispersion of CNTs in any polymer matrix is quite a challenging task. Chemical functionalization is the simplest and widely accepted method to improve the compatibility between CNTs and polymer in which CNTs are treated with strong acids like nitric acid and sulphuric acid or combination of both. The functionalized CNTs contain carboxylic and hydroxyl functional groups and are soluble in most of the organic solvents [3].

Polyimide is a high performance specialty class of polymers of aromatic nature with chemical structure –R(CO)N–, which comes under the family of ladder polymers, due to their flexibility, high strength, superior thermal stability and dielectric properties. As a result it is used in applications ranging from adhesives, thermal resistant coatings, high performance composites, fibres, foams, membranes, mouldings and films [4]. It can be used

up to 500 °C for short duration and prolonged use between 200 and 350 °C without much deterioration in mechanical and other properties. Polyimides are produced by the condensation reaction of an aromatic dianhydride and aromatic diamine to form an oligomer of amic acid known as polyamic acid which act as a precursor for polyimide and can be further cyclized (imidization) by thermal means to produce polyimide. Out of the many types of aromatic polyimides produced worldwide, the largest market and most preferred polyimide for various applications is based on the pyromellatic dianhydride (PMDA) and 4,4′-oxydi-aniline (ODA) [4].

In recent times considerable effort has been devoted in the field of preparation and study of CNTs/polyimide nanocomposites from various angles ranging from highly conductive to super strong CNTs/polyimide nanocomposites. Addressing the problem of poor dispersion of CNTs in the polyimide matrix, Park et al. [5] used in situ polymerization technique to disperse unmodified single wall carbon nanotubes (SWCNTs) in polyimide. Ouanies et al. [6] studied the electrical properties of SWCNTs doped polyimide nanocomposites. Zhu et al. [7] described a method for achieving enhanced dispersion of multiwalled carbon nanotubes (MWCNTs) in the polyimide matrix by the acid treatment of MWCNTs. However, they reported a slight decrease in the thermal properties of the nanocomposites due to acid modification. Mo et al. [3] employed in situ technique to disperse functionalized MWCNTs in polyimide matrix and reported a maximum achievable strength of 165.5 MPa at 7 wt% loading of functionalized MWCNTs. Yuen et al. concluded that by using amino functionalized MWCNTs the electrical properties of the MWCNTs/polyimide nanocomposites are enhanced considerably; unfortunately, it resulted in decreased tensile strength (TS) due to a possibility of reaction between the amino functionalized MWCNTs with polyamic acid [8]. Hu et al. also studied amino functionalized MWCNTs/polyimide nanocomposites using in situ polymerization method to disperse MWCNTs in the polyimide matrix [9].

Looking at the above scenario, it seems that it is difficult to achieve significant improvement in both the electrical as well as mechanical properties of the CNT/polyimide

composites simultaneously. A new type of amino functional groups was therefore grafted on the MWCNTs by treating them with octadecylamine ($C_{18}H_{39}N$). The grafted functional group consists of a secondary amide attached to the MWCNTs along with a long alkyl chain. The long alkyl chain helped in preventing agglomeration and bundling of MWCNTs due to repulsive force between the alkyl chain, producing a stable and homogeneous dispersion of MWCNTs. We report here that these amino functionalized MWCNTs reinforced polyimide nanocomposites not only exhibit improved mechanical properties, but also the electrical properties much superior to the one reported so far.

Experimental

Materials

MWCNTs were synthesized using toluene as a carbon source and ferrocene as catalyst precursor on a CVD set-up established in the laboratory [10]. The MWCNTs produced inside the reactor 40–70 nm in diameter and 50–100 μm long. These were 90% pure with <10 wt.% of catalyst Fe. Polyamic acid (ABRON-S 10) based on pyromellitic dianhydride (PMDA) and 4,4-oxydianiline (ODA) was procured from M/s ABR organics Ltd., India (Fig. 1). It was obtained as a 10% solution in DMAc (*N,N*-dimethyl-acetamide), with a solid content of 10–12%. It is a precursor form of polyimide (PI) polymer and was kept at 0 °C during this work. Octadecylamine ($C_{18}H_{39}N$) AR grade was supplied by M/s Across Organics Co., USA with a purity of 90%.

Acid Modification of MWCNTs

Two grams of MWCNTs were treated with 65% (v/v) HNO_3 for 48 h in a refluxing apparatus [11] with constant stirring to convert the MWCNTs to acid functionalized (MWCNTs-COOH). The treated material was washed several times with deionized water till washings were neutral to pH paper and dried at 100 °C for 12 h prior to use.

Fig. 1 Structure of PMDA/ODA-based polyamic acid
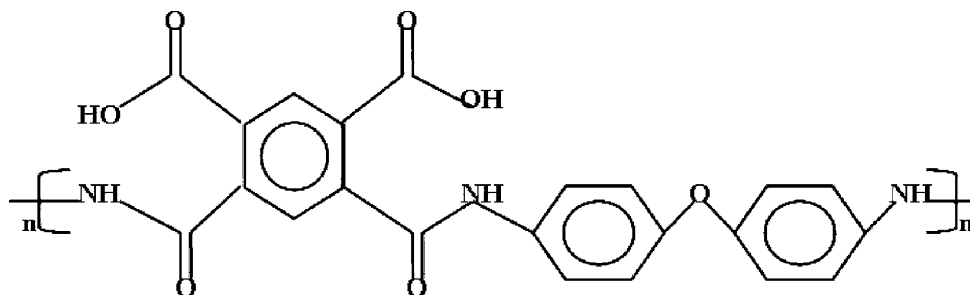
Amine Modification of Acid Modified

A 100 mL-flask was charged with 1 g of MWCNTs-COOH dispersed in 30 mL of anhydrous benzene (C_6H_6) to which 30 mL of thionyl chloride ($SOCl_2$) was subsequently added and stirred at 70 °C for 8 h. After the reaction, the whole reaction mixture was filtered and the solid residue (MWCNTs-COCl) was washed several times with anhydrous THF and dried at 50 °C overnight. Approximately 0.5 g of MWCNTs-COCl was suspended in THF and was stirred in excess of octadecylamine ($C_{18}H_{39}N$) for about 90 h to produce amine modified MWCNTs (MWCNTs-CO–NH–$C_{18}H_{37}$), the whole reaction mixture was maintained at a temperature of 100 °C. After functionalization reaction, MWCNTs were washed with ethanol to dissolve excess octadecylamine and subsequently with deionized water followed by drying under vacuum prior to use [12].

Nanocomposite Fabrication

Appropriate amount of acid or amine functionalized MWCNTs were separately mixed in 10 mL of DMAc by means of ultrasonication at room temperature to obtain a homogenous suspension of MWCNTs/DMAc. This suspension was poured into the polyamic acid and vigorously stirred with the help of a magnetic stirrer (80 rpm at 150 °C) for 40 min to obtain a highly viscous suspension of MWCNTs in polyamic acid. The viscous mass was casted on to a clean glass plate and dried in an air circulating oven at a temperature of 70 °C for 12 h to evaporate the solvent (DMAc) and to obtain a dried tack free film. Imidization (curing) of nanocomposites film was achieved by heating the nanocomposites film in an air circulating oven at 100, 150, 200, and 250 °C for 1 h at each respective temperature with a final heat treatment at 300 °C for 2 h. During imidization, the amide linkage converted in to imide linkage (cyclization) with the evolution of water molecules. The whole scheme of nanocomposites fabrication is illustrated in Fig. 2.

Characterization

Fourier Transform Infrared Spectroscopy

Functionalization of MWCNTs and conversion of polyamic acid to polyimide (imidization) was confirmed by the Fourier transform infrared spectra recorded on a Perkin Elmer spectrum BX FTIR spectrometer.

Scanning Electron Microscopy

The surface morphology of the as-produced, functionalized MWCNTs and the fractured surface of the nanocomposites was analysed on a Scanning Electron Microscope (Leo model: S-440).

Thermoxidative Stability

Thermal stability of the nanocomposites was examined by using a Thermo gravimetric analyser (Mettler Toledo TGA/SDTA 851^{e*}). The test was performed between 50 and 900 °C at a heating rate of 10 °C/min in air with a flow rate of 50 cc/min.

Mechanical Properties

The tensile strength (TS) and Young's modulus (YM) of the nanocomposites were measured on an Instron machine, Model 4411, at room temperature using ASTM-D882 test method. The test samples were cut into the strips of size 100 mm × 25 mm × 0.1 mm. The gauge length was kept as 50 mm, while the cross-head speed was maintained at 2 mm/min. The mechanical properties were evaluated using the built-in software in the machine. A minimum of five tests were performed for each composite sample and their average is reported.

Electrical Conductivity

The electrical conductivity of the composite films (100 mm × 25 mm × 0.1 mm) was measured by four-point contact method [13] using a Keithley 224 programmable current source for providing current, the voltage drop was measured by Keithley 197A auto ranging digital microvoltmeter. The values reported in text are averaged over five readings of voltage drops at different portions of the sample.

Result and Discussion

FTIR Studies

Figure 3 shows the FTIR spectra of acid and amino functionalized MWCNTs. In the acid functionalized MWCNTs, the peaks at 1634 and 1295 cm^{-1} correspond to C=O and C–O stretching, respectively. The two weak peaks at 2917 and 2847 cm^{-1} correspond to the –CH stretching mode. A broad peak corresponding to strong absorption at 3433 and 3150 cm^{-1} can be ascribed to –OH stretching vibration in –COOH group. In the amino functionalized MWCNTs, a strong and broad peak at 1631 cm^{-1} with a shoulder at 1707 cm^{-1} are ascribed to C=O stretching vibration due to the formation of amide linkage. The two strong peaks at 2918 and 2847 cm^{-1} with a third band appearing at

Fig. 2 Preparation scheme of polyimide/MWCNTs nanocomposites by the solvent casting method
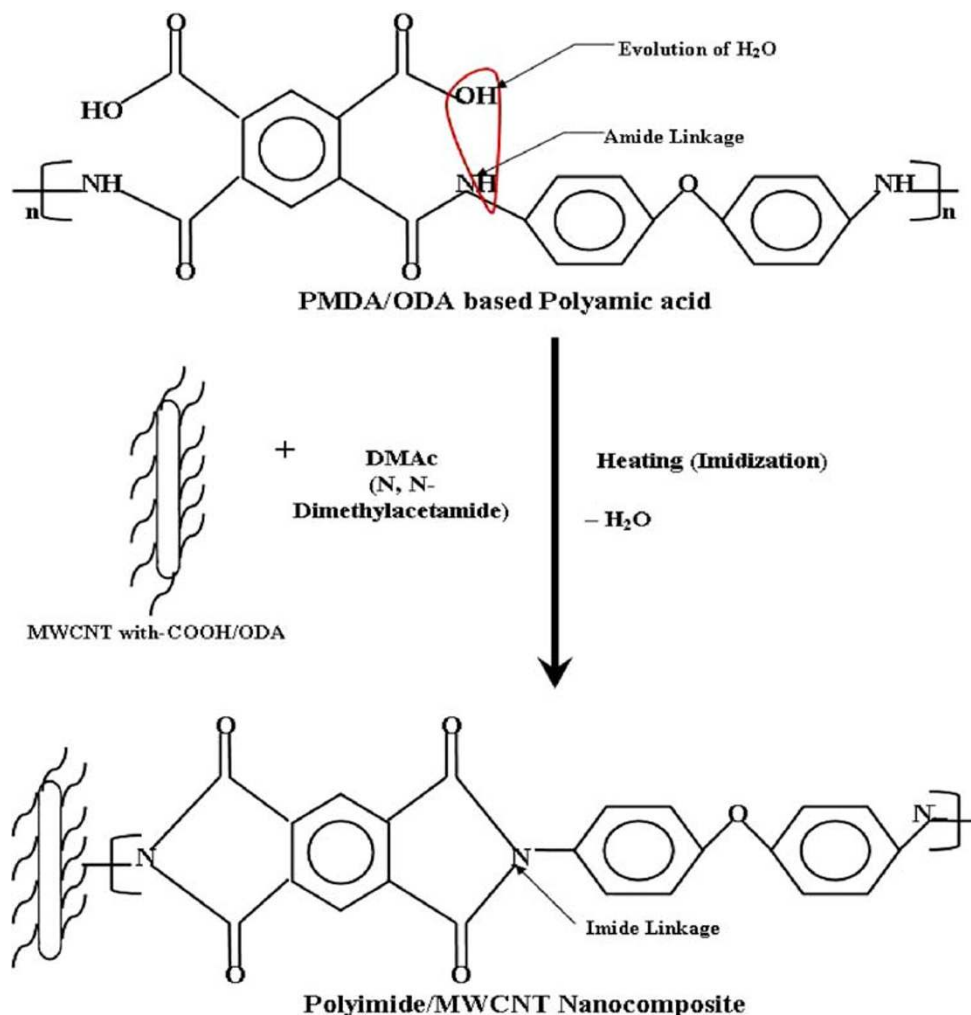
2954 cm^{-1} are ascribed to –CH stretching of the long alkyl chain of octadecylamine. Another peak at 1184 cm^{-1} corresponds to C–N stretching of amide group. Broad and strong peak with a shoulder at 3440, 3124 cm^{-1} should correspond to –NH stretching of the amine group.

For comparison, the FTIR spectra of the neat polyimide film is shown in Fig. 4a. A strong and broad peak at 1395 cm^{-1} and another at 3556 cm^{-1} are ascribed to the C–N stretching of imide ring. Characteristic strong peak due to C=O stretching appears at 1720 cm^{-1}, while asymmetric stretching of C=O as a weak peak at 1777 cm^{-1}. The peak at 725 cm^{-1} corresponds to bending vibration of C=O group. C–C stretching of the aromatic ring appears at 1515 cm^{-1}. The studies confirm the formation of polyimide and match well with the earlier reported data [14].

Figure 4b shows the FTIR spectrum of amide-MWCNTs reinforced polyimide composites. The spectrum matches closely with that of neat polyimide as shown in Fig. 4a. This is further confirmed by the absence of broad peak around the 3200 cm^{-1} due to –COOH functional groups which gets converted into polyimide. The IR spectra of both neat polyimide as well as MWCNT/polyimide composites also compare well with earlier reported data [14].

Surface Morphology of the MWCNTs

Figure 5(a–c) shows the SEM micrographs of the MWCNTs of the as-produced and the functionalized tubes. As seen from Fig. 5a, the raw MWCNTs are produced in the form of agglomerated bundles. These bundles are broken down into separate tubes due to violent refluxing during acid and amine functionalization (Fig. 5b, c). Treatment of MWCNTs with strong acids usually shortens the length of the MWCNTs, but in the present case we do not observe any such shortening of the tubes. A closer look at the micrographs reveal that the amino functionalized MWCNTs are relatively well dispersed as compared to raw and acid functionalized MWCNTs (Fig. 5a, c). This could be due to the repulsive forces generated between the long alkyl chain of the amino functional group.

Fig. 3 FTIR spectra of as such MWCNTs, acid modified MWCNTs and amine modified MWCNTs
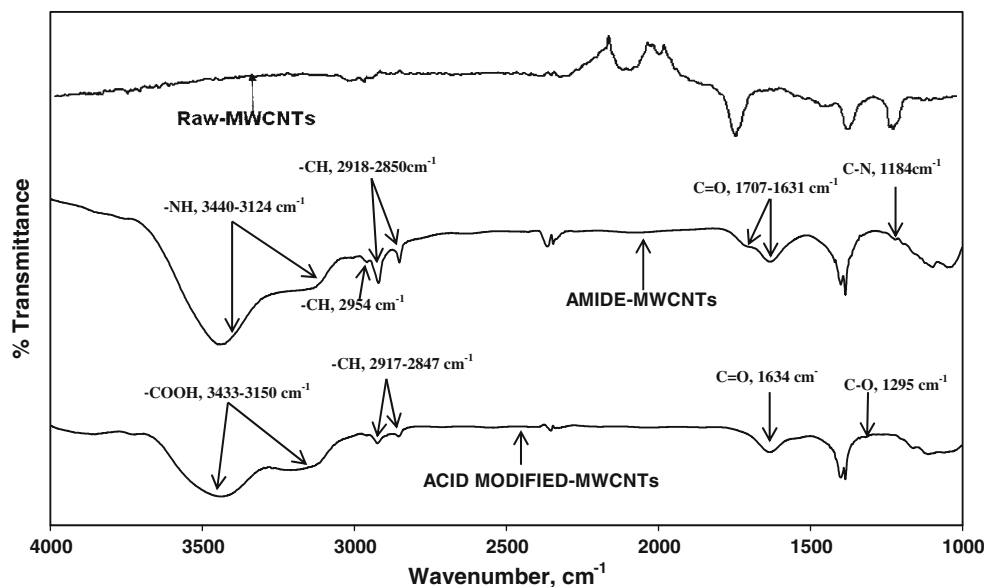
A typical microstructure of the fractured surface of the 2 wt% MWCNT acid-MWCNT/polyimide and amine-MWCNT/polyimide nanocomposite is shown in Figs. 6a and b, respectively. Though the MWCNTs show a high degree of dispersion throughout the polyimide matrix in both the cases; the amino functionalized MWCNTs are completely coated with the polymer (polyimide) and remain well embedded in the polyimide matrix, the acid modified tubes show very small amount of polymer coating. This feature clearly indicates better interfacial adhesion between the amino functionalized MWCNTs and matrix as compared to acid functionalized MWCNTs.

Thermoxidative Properties

Figure 7a clearly shows the onset of the degradation temperature of the raw, acid and amine modified MWCNTs. In the case of as produced MWCNTs, the weight loss starts at 475 °C, whereas in case of modified tubes the weight loss initiation temperatures shifts to around 300 °C for acid modified and 230 °C for amine modified tubes. The curves of the modified tubes show the weight loss in two steps, the initial one before 400 °C is due to decomposition of the functional groups, while the other one relates to the oxidation of the nanotubes. A weight loss of $\sim 17\%$ for acid-MWCNTs and $\sim 40\%$ for amide-MWCNTs is observed which quantitatively estimates these functional groups to 6 and 5 mmol/g, respectively. These values are quite high as compared to previous results from Reto et al. [12], Hu et al. [9] and Datsyuk et al. [15].

The weight loss behaviour of the respective composites with different weight fractions of functionalized MWCNTs are presented in Fig.7b and c. It is clear from the TGA curves that with increase in the acid-MWCNTs loading,

degradation temperature (T_d) also increases up to 3 wt% which is due to the synergistic of polyimide and MWCNTs wherein large volume of polyamic acid is converted into polyimide. However, when MWCNTs loading is increased to 5 wt% slight decrease in the T_d is observed. This can be attributed to the interference produced by the large number of acidic groups present on the MWCNTs which reduces the percentage conversion of polyamic acid to polyimide. In case of amide-MWCNTs/polyimide, nanocomposites increase in MWCNTs loading does not seem to show much increment in the T_d, which is explained by the fact that the amine group present onto the amine-MWCNTs inhibits the imidization process [7, 8]. Table 1 shows the numerical values of the T_d at different loadings. The table also provides degradation temperature corresponding to 5% wt loss (T_5) values of the composites, showing similar trend as T_d.

Mechanical Properties

The TS and YM of the nanocomposites with different MWCNT loadings are plotted in Figs. 8a and b, respectively. It is very much evident from the plots that there is a sharp rise in the mechanical properties at small loadings of functionalized MWCNTs. The increase is more gradual with higher loadings (>3 wt%). The difference in the TS values of the two composites is maximum at 1 wt% loading, wherein the amide-MWCNT/polyimide composite strength is 136 MPa as compared to only 110 MPa for acid-MWNT/polyimide composite. The difference in the TS values narrow down with higher loadings of the tubes so much so that at 5 wt% of MWCNTs, the TS of acid-MWCNT/polyimide composite becomes higher (151 MPa) relative to amide-MWCNTs/polyimide composites (126 MPa). This is very close to the value 165.5 MPa

Fig. 4 FTIR spectra of **a** neat polyimide and **b** 2 wt% amide-MWCNTs reinforced polyimide composite
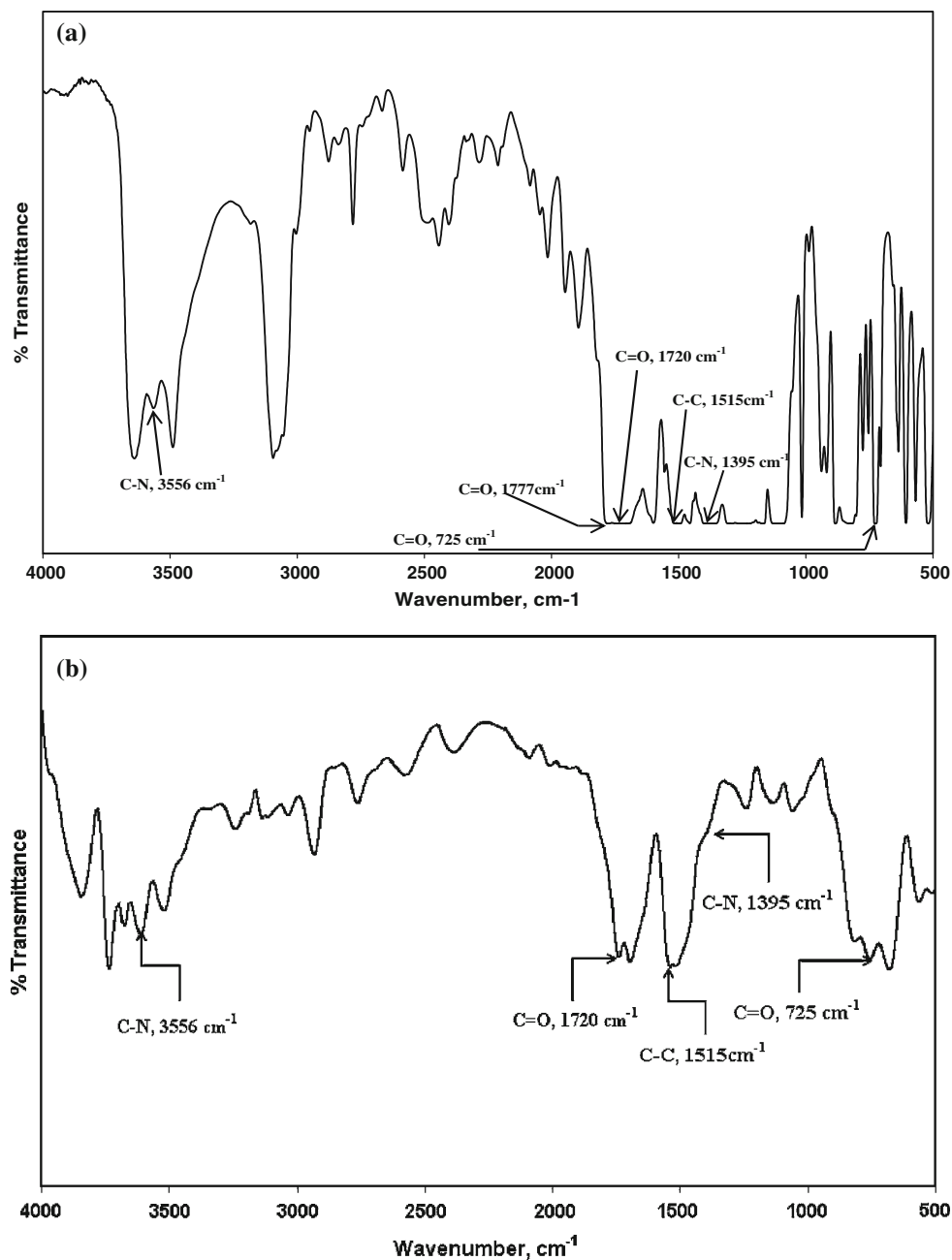
reported only by Mo et al. [3] with 7 wt% CNT loadings in polyimide. The fracture surfaces of the two composites are completely different. While in case of amine functionalized tubes a thick coating of the polymer matrix (Fig. 6b) is observed, in case of acid modified tubes such coating is either much thinner or even absent (Fig. 6a). Most of amine functionalized tubes remain embedded in the matrix, with few exceptions of MWCNT pull outs. Interestingly the pull out tubes show a telescopic failure (shown by arrows) and suggestive of sharing of load by the tubes before fracture due to strong MWCNT-polyimide bonding. There can be two reasons for lowering the strength at

higher loadings. Firstly, it can be traced to longer chains of amine groups present on the surface of the tubes. The longer alkyl chains provide more repulsion between the individual MWCNT, hence the available surface area for of the MWCNTs will be more as compared to acid-MWCNTs. The corresponding amount of polymer will not be sufficient to properly wet the large volume of MWCNTs surface, therefore creating voids in the composites. Secondly, the amine group present on the surface of MWCNTs may react with the polyamic acid and lower the imidization of polyamic acid to polyimide. The unreacted polyamic acid may be a cause of premature failure of the composites.
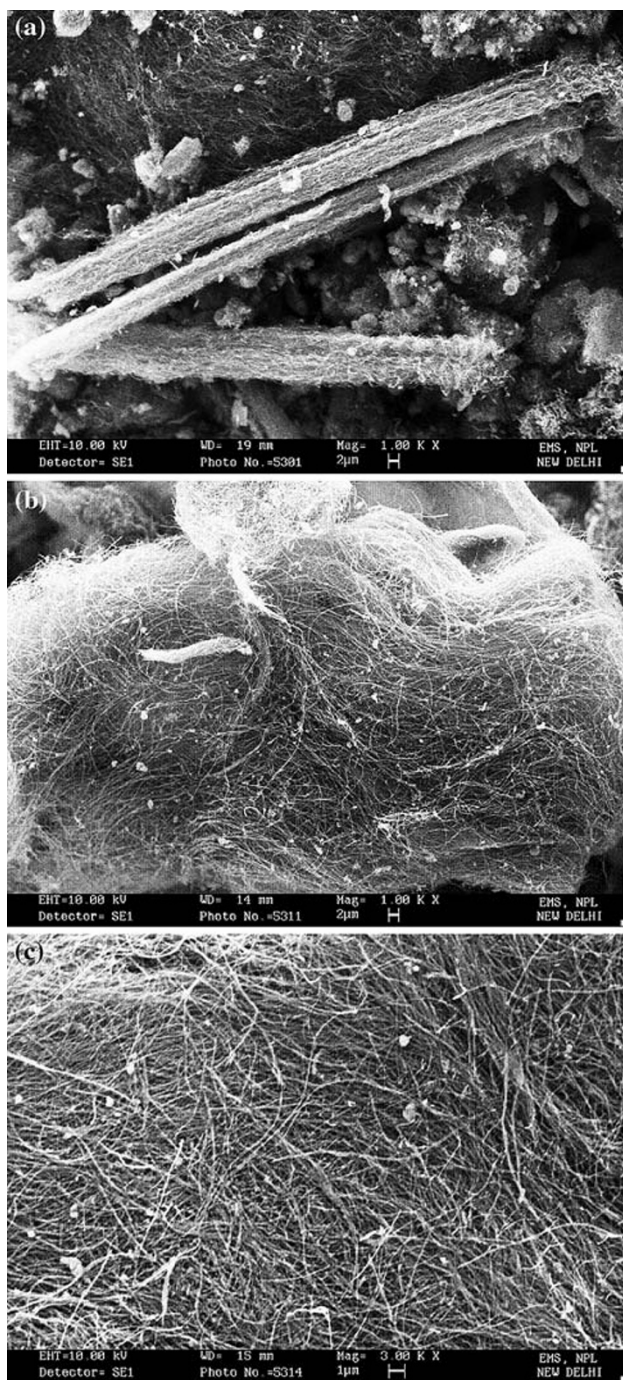
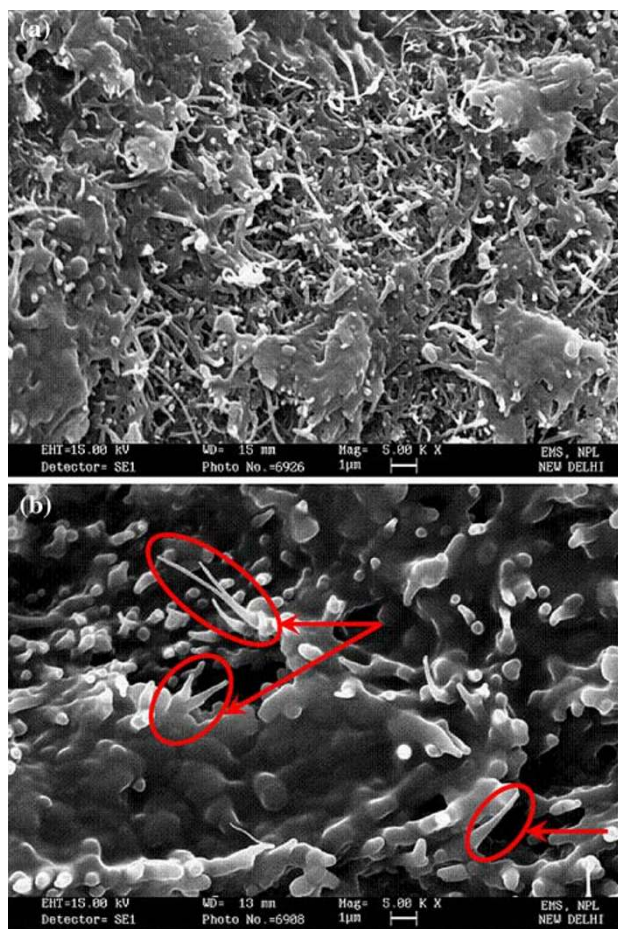Fig. 5 SEM images of **a** raw, **b** acid modified-MWCNTs and **c** amide-MWCNTs

Fig. 6 SEM fractographs of **a** 2 wt% acid modified-MWCNTs/ polyimide nanocomposites and **b** 2 wt% amide-MWCNTs/polyimide nanocomposites

As in the case of TS, the YM of the amide-MWCNTs/ polyimide is also higher (3.5 GPa) up to 3 wt% of MWCNT loadings as compared to only 2.75 GPa for acid-MWCNTs/polyimide nanocomposites. However, the value is much higher as compared to neat polyimide film (YM = 2.4 GPa). The study shows that the mechanical properties obtained with amide-MWCNTs/polyimide and that of acid-MWCNTs/polyimide composites are almost equivalent, the only difference being that these are achieved with only 3 wt% of MWCNT in case of former and with 5 wt% in case of the latter.

Electrical Properties

One unique property of the MWCNTs is their electrical conductivity because of their large aspect ratio and mobile π electrons. Addition of very small quantities of MWCNTs significantly increases the conductivity of the composite as observed in Fig. 9. As in the case of mechanical properties, there is a noticeable difference in the electrical conductivity of the two composites at 1 wt% loading. The conductivity is almost twice for amide-MWCNTs/polyamide as compared to acid-MWCNTs/ polyamide. The maximum value of the conductivities with 5 wt% acid-MWCNTs (0.938 S cm^{-1}) and 5 wt% amide-MWCNTs (1.032 S cm^{-1}) are much higher than the previously reported values in the literature by Yuen et al. (3.76×10^{-8} for acid modified at 6.98 wt%,
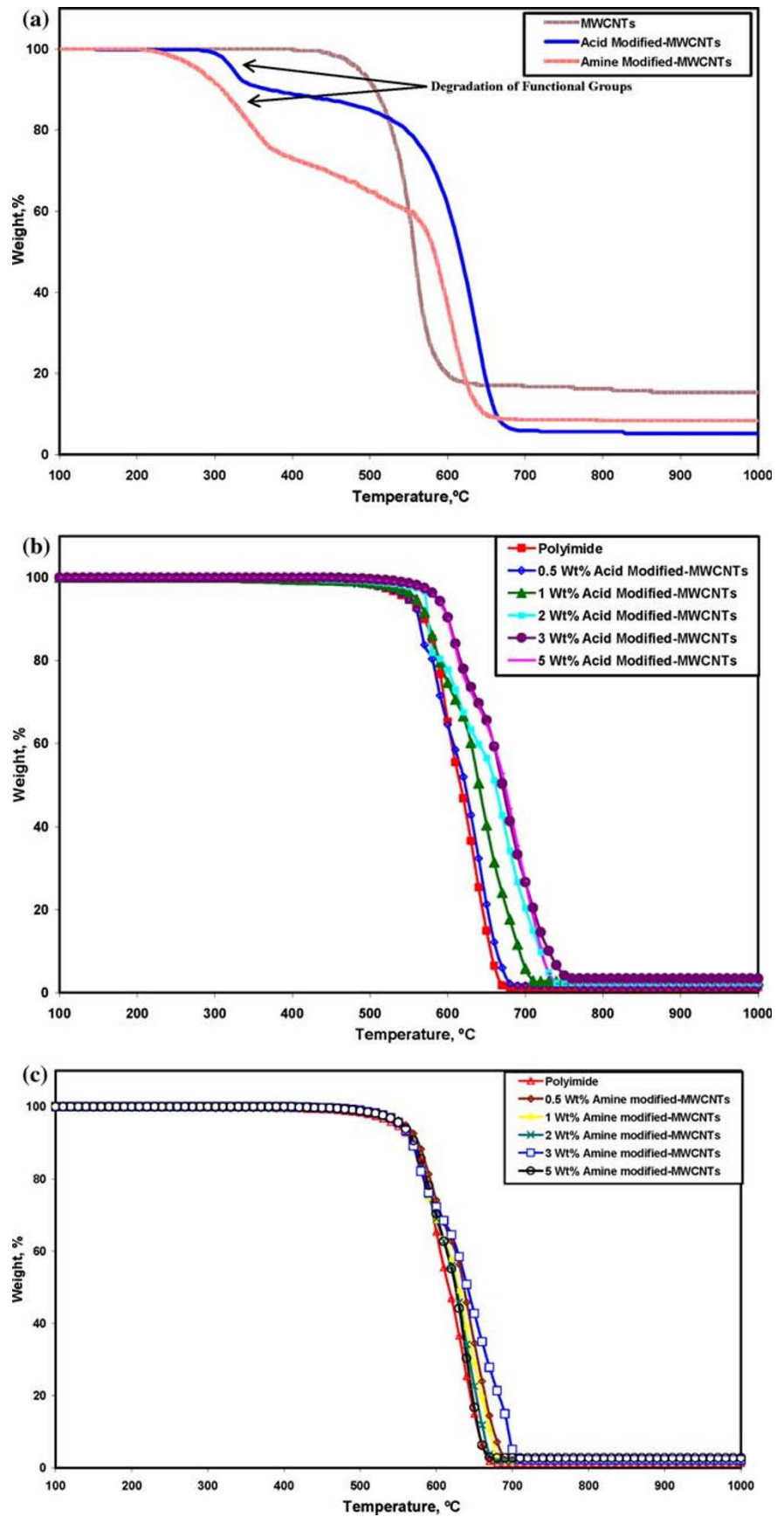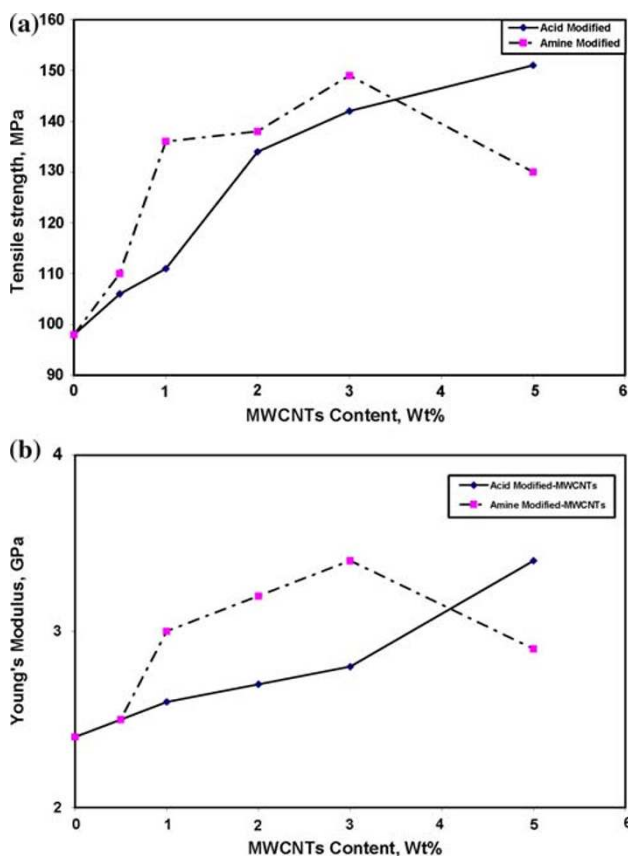
Table 1 Thermal degradation temperature (T_d) and T_5 of MWCNTs/polyimide nanocomposites

Temperature (°C)	Pure PI	Acid-MWCNTs/polyimide (MWCNTs wt%)					Amide-MWCNTs/polyimide (MWCNTs wt%)				
		0.5	1	2	3	5	0.5	1	2	3	5
*T_d	510	515	530	540	570	555	525	520	520	525	525
**T_5	540	545	555	565	585	580	553	550	550	550	550

* Temperature at which degradation starts

** Temperature at which 5 wt% of the material has degraded

Fig. 9 Effect of MWCNTs contents on the electrical conductivity of the MWCNTs/polyimide nanocomposites

Fig. 8 a Tensile strength and **b** Young's modulus of MWCNTs/polyimide nanocomposites at different MWCNTs loadings

5.78×10^{-8} S cm^{-1} for amine modified at 6.98 wt% [8]). The neat polymer film, however, behaves as a insulator as also measured by previous authors (6.53×10^{-18} S cm^{-1} [8]). A possible explanation for these observations is the high aspect ratio of the MWCNTs used in this study which ranges between 1000 and 3000. The authors in previous studies have used tubes with aspect ratio of almost 400 (diameter 40–60 nm, length 0.5–40 μm) which could be the reason for lower electrical conductivity of these composites. Moreover, in the present study the tubes remain intact and are not damaged during surface modification as observed in the SEM micrographs (Fig 5b, c).

Conclusion

Multiwalled carbon nanotubes were successfully functionalized with acid and amino groups. The functionalization resulted in uniform dispersion of the tube during imidization process which resulted in strong bonding and thick coating of the matrix. The fracture behaviour of amine functionalized MWCNT nanocomposites show a strong bonding of the tubes with the matrix which resulted in ~50% improvement in the TS and 35% improvement in the YM over the neat polyimide films. The electrical conductivity of the MWCNT reinforced polyimide composites was 0.938 S cm^{-1} (5 wt% acid-MWCNTs) and 1.032 S cm^{-1} (5 wt% amide-MWCNTs) is the highest achieved so far for polyimide composites. High electrical conductivity together with high strength and improved thermal stability makes these nanocomposites a promising candidate for high-temperature EMI shielding materials.

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