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Fast and clean functionalization of MWCNTs by DBD plasma and its influence on mechanical properties of C-epoxy composites

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Multiwalled carbon nanotubes (MWCNTs) were functionalized under helium/air plasma and the surface characteristics were compared with that of chemical functionalization. Changes in surface functional groups of MWCNTs due to plasma/chemical treatment were estimated by using temperature programmed decomposition (TPD), elemental analysis, Raman spectroscopy and BET surface area analysis. Raman spectroscopic studies highlighted that chemical functionalization increases the degree of disorder for MWCNTs when compared to plasma treatment. TPD also confirmed that air plasma treatment leads to the highest number of acidic groups on the surface that decomposes to evolve carbon dioxide. The modified MWCNTs were used as additional reinforcements to fabricate carbon fiber reinforced plastics (CFRPs). It has been observed that air plasma treated MWCNTs improved the tensile and flexural strength of C-epoxy composites significantly as compared to conventional chemical functionalization, whereas the best performance of air plasma treated MWCNTs is due to higher acid functional groups on the surface, which improves interface compatibility between the MWCNTs to the epoxy matrix.

1. Introduction

Multiwalled carbon nanotubes (MWCNTs) are known to posses good mechanical, thermal and electrical properties, which makes them attractive materials as reinforcements for carbon fiber reinforced plastics (CFRPs) for improving mechanical and electrical properties [1,2]. However, this application is limited by the inert nature of the carbonaceous surface of MWCNTs, which results in a strong tendency to agglomerate and poor wetting with the epoxy matrix systems. This leads to low levels of stress transfer between the matrix to the MWCNTs [3,4]. Therefore a surface modification is necessary to overcome these drawbacks and improve the function of MWCNTs [5]. Lack of surface compatibility of MWCNTs with the polymer matrix is generally overcome by using different functionalization methods which involve the generation of compatible surface functional groups on the MWCNTs [6]. There is a considerable success in improving the interface compatibility of MWCNTs with polymers by using chemical functionalization methods [7-9]. However, these chemical functionalization (HNO_3 treatment) methods would generate the toxic substances, damage the essential nanotube structure and generally too lengthy with possible problems of environmental pollution [10]. Only a few research groups have attempted alternate environmental friendly functionalization methods like ozone treatment and plasma treatment to generate active functional groups on MWCNTs surfaces [11-13]. In comparison with other plasma techniques, Dielectric barrier discharge (DBD) technique has advantages of simplification in experimental set-up and does not necessitates expensive vacuum equipment. Some research groups functionalized the carbon nanotubes by DBD plasma in the air and compared with those functionalized with HNO_3. It was found that the DBD plasma treatment induced less damage to the nanotubes and less pollution as compared to the modification in HNO_3 [14,15]. Plasma based functionalization is a viable alternative to conventional physico-chemical functionalization for carbon based materials in terms of time of processing, cost and environmental friendliness.

The objective of this study is to achieve an efficient MWCNT functionalization without significantly damaging the MWCNT structure, followed by characterization of MWCNTs and compare the reinforcement ability of plasma functionalized MWCNTs on tensile and flexural strength of the C-epoxy composites with pristine MWCNTs and conventional chemical functioned MWCNTs.

2.1. Experimental section

2.1.1. Raw materials:

Epoxy resin (commercial name LY556, Huntsman Advanced Materials (India) Pvt. Limited, Mumbai) made from Bisphenol A and epichlorohydrin along with diamine based curing agent (DETDA, commercial name HY 5200, Huntsman Advanced Materials (India) Pvt. Limited, Mumbai) were used as the matrix phase. Carbon fabric (PAN based T-300 grade fabric) was used as the main reinforcement. Multiwalled carbon nanotubes (CVD synthesized, procured from M/s Chemapal industries, Mumbai) were used as the nano reinforcement.

2.2. Fabrication of composites:

Initially 0.5 weight percentage (wt%) of MWCNTs was directly added into the epoxy resin. Dispersion of the MWCNTs was ensured by mechanical stirring at 2000 rpm for 2 h using a high speed mechanical stirrer followed by sonication at 50MHz frequency in a bath type sonicator for 90 minutes. Hardener in the ratio of 1: 4 to the resin weight was added to this mixture. This mixture was further sonicated for 30 min. Hereafter, this mixture is referred as MWCNT-epoxy-hardener system.

For the preparation of the MWCNT-C-epoxy composites, MWCNT-epoxy-hardener mixture was applied to the C-fabric. These fabric layers were stacked up and compacted by sandwiching between two flat steel plates to get required fiber-matrix ratio. Curing was carried out for 1h at 110ºC followed by curing at 160ºC for 2h. Post curing was carried out for 3h at 180ºC, which is nearer to the peak cure temperature of the composition under study [7]. Volume fraction (V_f) of the MWCNT-C-epoxy composites were controlled at 55% (±1%) by using the same number of layers and by controlling the thickness of the sample. V_f of the prepared MWCNT-C-epoxy composites were measured by following ASTM D3171. Thus five different MWCNT-C-epoxy composites corresponding to Raw, Helium and Air plasma treated (45 min and 90 min) and chemical functionalized MWCNTs were prepared. Flexural strength and tensile strength of the prepared composite laminates were determined as per ASTM D790 (three point bending test) and ASTM D638 respectively on the universal testing machine (United 50KN, USA). Typical sample dimensions for tensile and flexural strength are 200 mm x 10 mm x 2 mm and 60 mm x 10 mm x 2 mm respectively. Microstructure and fracture modes of the tested samples were analyzed by environmental scanning electron microscopy (ESEM-FEI, Quanta 400, USA).

2.3. Plasma treatment of MWCNTs: Plasma functionalization of MWCNTs was done in a homemade dielectric barrier discharge setup. Plasma reactor used for the plasma functionalization of MWCNTs was explained elsewhere [8]. Briefly schematic diagram of the plasma setup is given in Fig.1. The voltage is applied by AC high-voltage transformers (0−40 kV Jayanthi transformer) at a constant frequency of 50 Hz. Quartz reactor coated with silver paste acts as an outer electrode. The inner electrode is constructed with stainless steel and discharge gap is 3.5mm. The gas flow was regulated by a AALBORG mass flow controller (GFC-17).

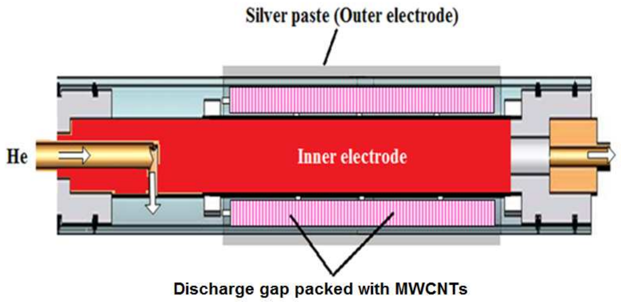

Fig.1. Schematic representation of dielectric barrier discharge reactor

Air was introduced into the DBD reactor at a flow rate 100 ml/min, through a teflon tube for the surface etching of the MWCNTs. Etching with Air plasma is carried out for 45 minutes. A separate batch of MWCNTs was etched for 90 minutes with air Plasma. Similarly MWCNTs were also etched with He plasma for two different durations namely 45minuntes and 90 minutes under the similar conditions. Thus, four different plasma etched MWCNT samples were generated.

2.4 Chemical functionalization of MWCNTs:

In a typical process, 2 g of multiwalled carbon nanotubes (MWCNTs) were dispersed in a mixture of concentrated nitric acid : concentrated sulphuric acid (total acid volume = 150 mL, 1:3 v/v HNO_3:H_2SO_4), and this solution was refluxed at 120 ^oC for 4 h. At the end of the reflux process, the solution was filtered, and a black precipitate was obtained, this precipitate was washed with deionized water, 5-6 times, to remove the excess acid. The precipitate was then dried in a hot-air oven for 12 h at 100 ^oC.

2.5. Characterization:

Brunauer-Emmett-Teller (BET) surface area was calculated by N_2 adsorption isotherms at 77K on Quantachrome Nova 2200e physisorption apparatus. Before analysis with N_2 adsorption, samples were degassed at 573K for 3h. Elemental analyzer (Euro Vector EA) was used to determine of the composition of C, H, N, S and O in the samples. Raman spectra of pristine HNO_3 treated and plasma treated MWCNTs were recorded on a Bruker senterra dispersive Raman microscope with laser excitation wavelength of 532 nm. Temperature Programmed Decomposition (TPD) was carried out in a fully automated Quantachrome gas sorption analyzer equipped with a thermal conductivity detector**.** Oxygen functional groups formed during the decomposition was quantified in a helium atmosphere (50 mL min−1, ramp 10 K min−1) in the temperature range 300 to 1,173 K [16, 17]. Before the TPD runs, the reactor was purged with He for 30 min. In a typical TPD run, 0.1 g of MWCNTs was placed in a quartz plug-flow reactor and the decomposition products were analyzed by a mass spectrometer (RGA PRISMA PLUS 200 AMU). The intensity of the following peaks with m/e 2, 4, 15, 18, 28, 30, 32, and 44 was monitored simultaneously.

3. Results and Discussion

3.1. Elemental analysis: Elemental analysis studies have shown that, air plasma treatment and HNO_3 treatment have added active functional groups on the surface of MWCNTs (Table.1). Increasing the oxygen content from 0.41 % for raw MWCNTs to 5.75 % for 90min air plasma treated MWCNTs and 5.12 % for HNO_3 treated MWCNTs, confirms introduction of active surface functional groups during plasma treatment and HNO_3 treatment.

3.2. BET surface area measurement: BET surface area of the raw MWCNTs, HNO_3 treated and plasma treated MWCNTs are given in Table. 1, which confirms increasing surface area due to HNO_3 treatment and plasma treatment. This could be due to surface etching as well as formation of active species on the surface [17]. This demonstrates that activation plays an important role in improving the surface properties of MWCNT samples.

3.3. Raman spectra

The information about the structural properties of MWCNTs could be obtained from the Raman spectroscopy. Figure 2 presented Raman spectra of the plasma treated MWCNTs, chemical functionalized MWCNTs along with pristine MWCNTs for comparison. Two distinct peaks around at 1350 cm^{-1} called D-band is associated with defects and disorder in MWCNTs (sp^3C), band at around 1580 cm^{-1} called G-band is assigned to the well ordered carbon (sp^2C), were observed for pristine, plasma treated and chemical functionalized MWCNTs [18,19].

The intensity ratio between the G-band (IG) and the D-band (ID) is sensitive to the chemical modification, and is an index of the defects of the MWCNTs [10]. For the pristine MWCNTs, the IG/ID was 2.9. In contrast, the IG/ID of the 90 min air plasma treated MWCNTs decreased to 1.0, and then 0.9 for chemical functionalized MWCNTs. The decreased IG/ID may be generation of various new defects due to the formation of new oxygen based functional groups identified by TPD on the surface of the MWCNTs (Fig.3 & Table.1).

Table.1. Physicochemical properties of plasma etched MWCNTs

Property	Raw CNT	45min Air plasma	90min Air plasma	45min He plasma	90min He plasma	Acid treated
BET Surface area (m^2/g)	215	236	248	222	229	251
Elemental analysis (Oxygen%)	0.41	4.74	5.75	0.36	0.31	5.12
CO $(mmol\ g^{-1})$	0.46	-	2.34	-	0.33	3.49
CO_2 $(mmol\ g^{-1})$	0.52	-	4.10	-	0.41	2.84
Total $(CO + CO_2)$ $(mmol\ g^{-1})$	0.98	-	6.44	-	0.74	5.33

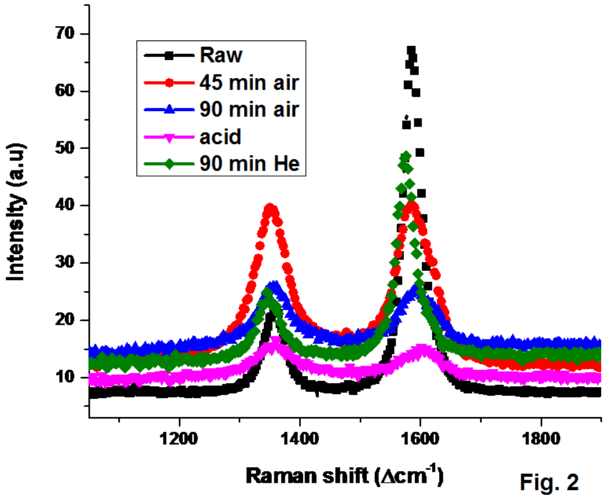

Fig. 2

Fig.2. Raman spectra of pristine, chemical functionalized and plasma treated MWCNTs.

3.4. Temperature Programmed Decomposition (TPD):

The presence of oxygen containing functional groups on MWCNTs changes the surface chemistry and influences the compatibility between the matrix and fiber. The quantities of the CO and CO_2 released during decomposition in the temperature range of 300 to 1,173 K are shown in Fig.3. The acidic functional groups decompose to liberate CO_2, whereas, the basic groups liberate CO. As seen in Fig.3a 90 min air plasma treated MWCNTs liberated higher amount of CO_2 when compared to unmodified and chemical functionalized MWCNTs. The low temperature, CO_2 evolution peak (<540 K) is mainly due to the carboxylic groups decomposition, whereas, the peak in the temperature range of 463 to 923 K is due to the decomposition of acid derivatives like lactone groups. Acid anhydride groups decompose with the simultaneous evolution of CO and CO_2 in the temperature range 650 to 950 K, whereas, CO evolution at temperature above 800 K may be due to the presence of phenols, ethers, carbonyls and quinones [16,20].

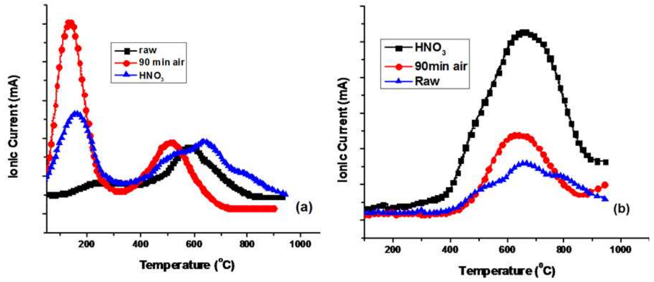

Fig.3. TPD profile of various MWCNTs samples before and after Air plasma treatment: (a) CO_2 evolution, (b) CO evolution

The CO_2 profile of air plasma and chemical functionalized MWCNTs showed, first maxima in the temperature range 323–573 K due to the decomposition of carboxylic groups, whereas, the second maxima was observed in the range of 673 –1023 K which could be due to decomposition of more stable anhydrides or lactone groups [20]. Air Plasma etched and chemical functionalized MWCNTs showed CO signal at above 673 K, indicating the existence of anhydride, ethers, carbonyls, phenols or quinones. On the other hand raw MWCNTs have shown the lower amount of CO_2 and CO (Fig.3a&3b). From these trends, it was confirmed that 90 min air plasma treatment has imparted more amount of oxygen containing surface functional groups on MWCNTs as compared to pristine, He plasma treated and chemical functionalized MWCNTs. Table 1 and Fig.3a confirms that 90 min air plasma treatment resulted higher amount of acid functional groups, than conventional HNO_3 treatment leads to more basic groups.

3.5. Mechanical properties of the C-epoxy composites:

3.5.1. Tensile Strength: 90 min air plasma treated MWCNTs reinforced C-epoxy composites have shown higher tensile strength as compared to the raw, He plasma treated and HNO_3 treated MWCNTs reinforced C-epoxy composites (Table.2). Reasons for this can be understood from the fracture modes of the raw MWCNT-C-epoxy and air plasma treated MWCNT-C-epoxy composites. It was observed that the fracture surfaces of the raw MWCNT-C-epoxy was smooth with complete inter filament debonding (Fig.4a). On the other hand, air plasma treated MWCNT-C-epoxy has shown strong interfilament bonding with significant matrix adhered to their surface (Fig.4b&4c). It can also be seen that, the matrix that is adheres to the surfaces of the C-fibers are rough indicating significant interface toughness due to the ability of air plasma treated MWCNTs (Fig.4d). Thus, for air plasma treated MWCNT-C-epoxy sample, higher interface toughness coupled with strong inter filament bonding ensured a uniform load distribution across all the carbon fibers [7]. The tensile strength of HNO_3 treated MWCNTs reinforced C-epoxy composites has slightly less than the 90 min air plasma treated MWCNTs reinforcement. This is due to the higher number of acidic groups on the MWCNTs surface for 90 min air plasma treatment compared to chemical functionalization. Hence, air plasma treated MWCNT-C-epoxy sample shows better tensile strength, which may be assigned due to the high amount of acid functional groups (Fig.3a).

Table.2. Mechanical properties of MWCNT-C-epoxy composites at 0.5wt% of CNTs.

Property	Blank	Raw CNT	45min Air plasma	90min Air plasma	45min He plasma	90min He plasma	HNO_3-CNT
Tensile strength(MPa)	862(20)	885(22)	954(24)	971(30)	915(23)	921(24)	959(28)
Flexural strength(MPa)	776(19)	789(20)	862(31)	883(25)	822(20)	819(22)	872(27)

*Values in the parentheses are standard deviations.

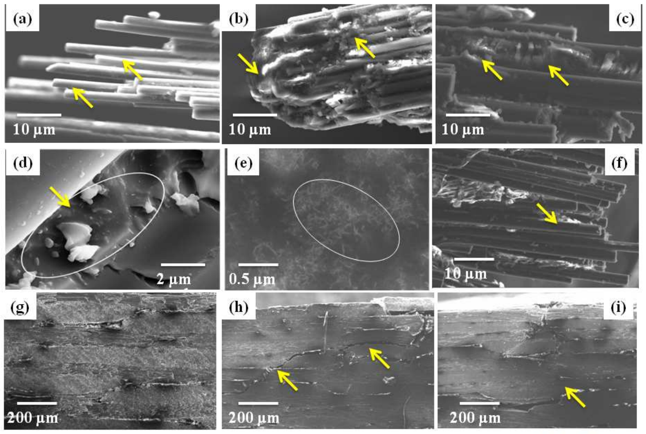

Fig. 4

Fig.4. SEM images of MWCNT-C- epoxy composites after failure under tensile load (a) Raw MWCNT-C-epoxy showing more fiber matrix debonding with smooth surfaces. (b&c) 45min Air plasma and 90 min air plasma treated MWCNT-C-epoxy showing strong interfacial bonding between C- fiber and matrix (d) magnified image of fig.4c also showing strong interfacial bonding between C- fiber and matrix (e) magnified image of Fig.4d. showing good dispersion of MWCNTs (0.5wt% MWCNTs on C-fabric) (f) 90 min He plasma etched CNT -C-epoxy composite showing poor improvement in the interfilament bonding, and SEM images of CNT-C- epoxy composites after failure under flexural load (g) Raw MWCNT-C-epoxy showing more inter layer shearing (h) 90min Air plasma etched CNT-C-epoxy showing crack propagation along the thickness (shown with arrows) with no interlayer shearing (i) 90 min He plasma etched CNT-C-epoxy showing poor crack propagation along the thickness of the sample.

3.5.2. Flexural Strength: Air plasma treated MWCNT reinforced C-epoxy composite laminates have shown higher flexural strength as compared to the raw, He plasma treated and HNO_3 treated MWCNTs reinforced C-epoxy composites. In case of raw MWCNT reinforced C-epoxy composite, failure initiated under the loading point, resulted in the predominant formation of inter laminar cracks due to interface shearing (Fig.4g). It is reported that, the crack propagation through the matrix rich interface zones encounters less resistance [21]. Hence, raw MWCNT reinforced C-epoxy composite failed at a lower strength. With increasing time of air plasma treatment of MWCNTs, flexural strength of the C-epoxy increased indicating that, more is the degree of surface functional groups on MWCNTs, higher will be its reinforcing ability. Flexural strength improvement due to air plasma treated MWCNTs in C-epoxy composites are mainly because of more acidic functional groups on MWCNTs surface, which leads to the enhanced C-fiber-matrix interface area and the ability of the MWCNT reinforced C-epoxy to transmit the load to more area across its thickness (Fig.4h). This indicates that the MWCNTs with more functional groups can improve the mechanical properties better than the MWCNTs which don't have a significant degree of functional groups.

4. Conclusions

1. Plasma treatment of MWCNTs proposed in this study has the potential to avoid conventional chemical methods of generating functional groups on MWCNTs to use them as reinforcements in C-epoxy composites.
2. Elemental analysis in combination with Temperature programmed decomposition studies indicated that more number of acidic groups have formed during air plasma treatment of MWCNTs as compared to the conventional chemical functionalization and He plasma treatment.
3. The plasma treatment has affected the width of the Raman bands of the MWCNTs. Enhanced bandwidth and decreasing in the G/D ratio of the MWCNTs after chemical and plasma treatment indicates enhanced disorder.
4. Air Plasma treated MWCNTs can significantly increase the flexural and tensile strength of the C-epoxy composites due to higher acid functional groups on the surface, which improves interface compatibility between the MWCNTs to the epoxy matrix.

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