Mechanical properties of multi-walled carbon nanotubes reinforced polymer nanocomposites

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Carbon nanotubes (CNTs) are considered to be one of the novel reinforcement for developing advanced nanocomposites due to their outstanding thermo-mechanical properties. Multi-walled carbon nanotubes (MWCNTs) are developed by arc discharge method. To enhance the dispersion of CNTs in polymer matrix, CNTs are modified with chemical treatment and processed by ultrasonication process. Surface characterization of CNTs is examined by XPS technique to confirm the different functional groups attached to the surface. Epoxy based polymer composites are developed by dispersing of pristine and surface modified CNTs as reinforcement in different concentrations varying from 0.2 to 1.0 wt% and found that with 1 wt% gives the best result. Detailed rheological studies are carried out to know the dispersion of CNTs in matrix. FESEM studies are carried out to observe the morphology of reinforcing materials as well as its dispersion in the polymer matrix and the effect of reinforcement on fractography is also investigated. The thermal stability of the composites is measured using thermo-gravimetric analysis (TGA) and observed that composites made with surface modified CNT showed higher thermal stability as compared with pure epoxy and pristine CNTs. Enhancement in flexural properties is observed with surface modified CNTs.

Keywords: Carbon nanotubes, Dispersion, Flexural properties, Nanocomposites

Ever since the paper on carbon nanotubes was published in 1991 by S Iijima most of the research activities focused more on the evolution of nanotubes properties themselves as well as their high potential as nano-structured filler for polymer composites and expected novel material properties. Carbon nanotubes (CNTs) have diameter in few nanometers and length in few microns; so the aspect ratio of this material is very high. These small dimensions mean that they have much higher surface area per unit mass and with less density. CNTs are novel crystalline form of carbon; unique nanostructured materials with remarkable physical and mechanical properties such as high flexibility, high Young’s modulus and predicted thermal conductivity was 3000 W/mK for MWCNTs and 6000 W/mK for SWCNTs. However, experimentally these values are not yet been attained and the attained values are for strength is around 63 GPa and thermal conductivity around 200W/mK. In spite of these facts CNTs are still considered as best candidate material as reinforcement due to its structures, extreme aspect ratio and very high surface area for futuristic advanced composites.

The recent research extensively focused on the epoxy resin based carbon nanotubes composites because the epoxy resin is one of the most common class of thermosetting resin which is having high tensile strength, chemical and corrosion resistance, high adhesion and dimensional stability with wide range of application in electronics, aeronautics, astronautics industries and other engineering applications. However, developing advanced composites with CNTs as reinforcement also have challenges due to their poor dispersion in the polymer matrix due to the agglomeration, as CNTs have diameters on the nanoscale and there is substantial van der waals attractions between them, so CNTs tend to agglomerates. The high surface area of CNTs results in a high viscosity of the nanotube/epoxy mixture particularly when fabricating composites with high loading level of nanotubes, which makes the dispersion of nanotubes extremely difficult. So, controlled particle size distribution and dispersion are the key factors for development of the composite materials. The small size of the fillers leads to an exceptionally large interfacial area in the composites. It can be a region of altered chemistry, altered polymer chain mobility, altered degree of curing of

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polymer and altered crystallinity. The interface controls the degree of an interaction between the filler and the polymer and thus control the properties. Therefore, the greatest challenge in developing polymer composites may be learning to control the interface. Many research groups all over the world are working to resolve the challenges for development of advanced composites. Ajayan et al.\textsuperscript{14} in early stages, observed the weak interfacial bonding between the nanotubes and matrix by TEM. Eitan et al.\textsuperscript{15} modified MWCNTs by means of epoxies-based functionalization with carboxyl along their walls. Measurement of the rheological property is useful to examine changes in dispersion state and interfacial bonding affected by surface modification of CNT/polymer composites. Potschke et al.\textsuperscript{16} investigated rheological properties of the unmodified CNTs dispersed epoxy and confirmed the increase in viscosity with increase in filler concentration. Kinloch et al.\textsuperscript{17} studied the rheological behavior of oxidized CNTs and it was found that the composites filled with functionalized CNTs had better dispersion. So, the surface modification of carbon nanotubes is the crucial factor which decides the effective dispersion and improves the micro-mechanical interlocking between the filler and matrix.

Therefore, this work is an attempt to study the role of CNT concentration as reinforcement and affect of surface modification of the CNT which will modify the interface of the CNT and the polymer in the composites.

**Materials and Methods**

**Synthesis of multi-walled carbon nanotubes**

Carbon nanotubes were produced by arc discharge method\textsuperscript{18}. Arc discharge set-up consists of double walled stainless steel chamber with high rate of cooling by water circulation. Graphite was taken as electrodes; one of the electrodes (anode) is rod type whereas the other electrode (cathode) flat surface of bigger diameter. To keep uniform arcing during experiments, the anode was attached to a manipulator (step-motor), which controls the gap between two graphite electrodes by moving forward or backward. The chamber is pumped out to a base pressure of 100 m Torr and then helium gas is purged to desired pressure. Voltage was kept constant of 40 V and variation of current was observed during the entire experiment till the anode was consumed completely. The gas pressure was kept at 300 Torr. MWCNT deposited at the cathode was collected for further processing.

**Purification and surface modification of MWCNT**

As synthesized MWCNT which was found in the cathode deposits contain other carbonaceous materials and amorphous carbon which requires to purify. Purification of the carbon nanotubes was carried out in multi-step processing which includes chemical treatment followed by thermal treatment and finally the physical filtration. The purity of the MWCNT was estimated by TGA as well as microscopically around 90%. These CNTs were functionalized by acid treatment of $\text{H}_2\text{SO}_4$ and $\text{HNO}_3$ in 3:1 ratio and washed thoroughly after the treatment.

**Fabrication of polymer composites**

Nanocomposites were developed by mixing the variable amount of CNTs (0.2-1.0 wt%) to the epoxy and homogeneously dispersed by ultrasonication process. For the preparation of composite, one of the challenging tasks is dispersion. CNTs were agitated in acetone for 30 min with the help of high intensity probe type ultrasonicator to de-agglomerate the CNTs. Pre-calculated amount of pristine CNTs and Epoxy AW-106 grade resin were taken and mixed together. CNTs and resin is mixed under ultrasonicating condition for one hour. The sonication was carried out in ice bath to maintain the temperature throughout the sonication process. Once the sonication was completed, Epicure curing agent HV 953 was added and mixed using mechanical stirrer for 10 min. The mix ratio of epoxy to curing agent was 4:1. The mixing of resin and curing agent initially produce highly reactive, volatile vapor which could creates voids and can affect the properties of the final product. To reduces the chances of voids, the resin and CNT missed was kept under vacuum for 30 min at 80°C and after that the mixture was transferred to stainless steel mold of 75 mm × 50 mm. Curing was done for 4 h at 120°C under vacuum. The composites with CNTs and without CNT were made in same procedure.

**Characterizations of MWCNTs and their polymer composites**

The morphology of CNTs, fracture surfaces of composites and the dispersion of the nanotubes in the matrix was observed under FESEM using S4300 SE/N HITACHI Japan at 20 kV. Composites were coated with a thin gold layer by sputtering process to make them conducting for SEM analysis. Thermo-
gravimetric analysis (TGA) was conducted with NETZSCH STA 449 Jupiter model from ambient temperature to 500°C with heating rate 10°C/ min in Aron atmosphere. Surface elemental compositions of modified CNTs were analyzed by X-ray photo-electron spectroscopy (XPS). Rheological studies were carried out with Brookfield Rheometer (R/S plus) having cone and plate geometry (diameter 25 mm, 0.9 radians cone angle, gap 0.01 mm) at room temperature. The rheology of CNT/epoxy mix included the measurement of viscosities of 0.1, 0.5, 1.0 wt% of CNTs at different shear rates. The three-point bend test was conducted using Instron-5500R universal tester at room temperature with a crosshead speed of 2.0 mm/min. The dimension of the testing samples was: 60 × 10 × 3 mm. Average values of three readings of all the measurements are reported in this study.

Results and Discussion

Figure 1 shows the SEM images of as synthesized and purified multi-walled carbon nanotubes. From Fig. 1a, it was noticed that there are numerous entangled carbon nanotubes were seen along with some other carbonaceous materials. These carbon nanotubes were purified multi-step technique\(^{19}\) and Fig. 1b shows the carbon nanotubes after purifications.

Studies of surface groups of carbon nanotubes by XPS analysis

The synthesized carbon nanotubes and functionalized carbon nanotubes which were treated with mixture of HNO\(_3\) and H\(_2\)SO\(_4\) were characterized by XPS technique. Surface elemental composition of pristine and chemically modified CNTs were analyzed by XPS which is one of the best surface analytical techniques, which can provide useful information on the nature of the functional groups and also the defects on the surface of the sample. Each peak is fitted by using binding energy of standard carbon, 284.5 eV. Figure 2a shows the spectrum of untreated sample the XPS C1s and O1s peaks. Deconvolution of the C1s peak of the untreated CNTs a main peak at 284.022 eV, attributed to the graphitic structure (sp\(^2\) C=C) as shown in Fig. 2b. Moreover, a peak at 284.38 eV (sp\(^3\) C-C) was attributed to defect on the surface of the sample. Figure 3 shows the spectra of chemically modified carbon nanotubes. From this figure, it is observed that the peak at 284.904 eV corresponds to the carbon atom attached to the different oxygen containing moieties. Deconvolution of O1s peak at 532.40 eV of treated CNTS conformed the presence of carboxylic and hydroxyl functional groups as shown in Fig. 3c. The results indicated that various functional groups were introduced on CNTs surface due to the surface modification. Significant increase in oxygen content was observed in surface modified CNTs as compared to pristine CNTs.

Rheological study

The viscosity of the mixture has a direct correlation with the spatial and orientation distribution of nanotubes in the matrix. This can be used as a physical sign with which to monitor the quality of dispersion, as long as the interpretation of the rheological signal is calibrated. The viscosities of different compositions of CNT/epoxy resin samples were measured at room temperature and it was observed that the increase in viscosity increases with higher concentration of CNTs loading as shown in Fig. 4. The result suggested that dispersing of CNTs...
Fig. 2 – XPS of pristine carbon nanotubes (a) XPS spectrum, (b) C1s spectrum and (c) O1s spectrum

Fig. 3 – XPS of acid treated carbon nanotubes (a) XPS spectrum, (b) C1s spectrum and (c) O1s spectrum
in epoxy is limited to 1 wt%, whereas, higher amount of filler materials the chances to form agglomerations increases which leads to inhomogeneous dispersion. Functionalization or chemical treatment of nanotubes can provide multiple bonding sites between CNTs and polymer matrix, so that the network formation increases. The viscosities of functionalized CNTs reinforced composites were increased compared to pristine nanotubes reinforced composites for the same amount of filler materials as shown in Fig. 4b. These measurements of viscosities for different systems were illustrated in Fig. 4.

The viscosity increases drastically and dispersion of CNTs becomes very difficult due to increasing susceptibility of agglomeration of CNTs due to their high surface energy, large aspect ratio which makes them difficult for homogenous mixing.

**Flexural properties of the polymer composites**

The three point bending tests were performed in order to evaluate the influence of the carbon nanotubes in general and especially the relevance of the acid treated of the MWCNTs. The flexural strength, flexural modulus of composites with different concentration of pristine MWCNTs were measured by three point bend test as shown in the Fig. 5. From this figure, it is clear that by increasing the weight percentage of carbon nanotubes increases the flexural strength of the composites. Just by adding 1 wt% pristine CNTs reinforced composites shows the strength of 77 MPa and is a significant enhancement in flexural strength of the composite material. Moreover, after functionalized or chemical treatment to MWCNTs have shown a drastic increase in the flexural strength of about 104 MPa with same 1 wt% of CNT. Functionalised CNTs have the potential to be more efficient as reinforcing agents than pristine MWCNTs as surface modified nanotubes consist of reactive sites and uniform dispersion in organic solvents. The functional groups attached to the surface of CNTs react with the matrix during the curing process and build covalent linkage which leads to higher strength of the composites.

Comparing with pristine MWCNTs, functionalized MWCNTs have better dispersion in the matrix, which indicates that the interfacial bonding enables an effective stress transfer between the epoxy matrix. The flexural strength of containing 1 wt% of
MWCNTs have the higher flexural strength than other composites.

Figure 6 shows SEM images of the fracture surfaces of pure epoxy and nanotube reinforced composites. The pure epoxy fails in catastrophic mode (Fig. 6a). Figure 6b shows the fracture surface of the polymer composites made with pristine carbon nanotubes, which shows the agglomerates of carbon nanotubes in the composites. Figures 6c and 6d show the fracture surface of composites made with functionalized carbon nanotubes. Micrographs show the very good dispersion of carbon nanotubes in the polymer matrix. In the case of composites made pristine carbon nanotubes, macroscopic cracks were observed and then continued to propagate, resulting in the failure of whole composite samples. Once cracks started, they spread quickly along the crack direction and then developed into macroscopic failure. However, in the case of composites made with functionalized carbon nanotubes these cracks occurred more on the interface between CNTs, and fibre pullout was observed which absorbs the energy and composites fails at higher load.

In most locations, the crack damage started from the interface, then CNTs suffered from the external force and were pulled out, leaving the smooth resin matrix which exposed the weak interfacial bonding. It was discovered that there were many CNTs existing surrounding their agglomerates, which might have been caused by the shear force around the CNTs during the manufacturing process, or by poor dispersion. CNT pullout was also found in this composite system, which demonstrated the weak interfacial bonding between the matrix and CNTs. The resin surrounding the CNTs was still tightly attached to the CNTs.

**Thermo-gravimetric analysis**

Thermo-gravimetric analysis (TGA) studies were carried of the composites samples made with pristine as well as chemical treated carbon nanotubes with 1 wt% to know the thermal stability of these composites. Figure 7 show the Thermo-grammetric analysis of the two composites. From this figure, it was observed that surface modification of CNTs can alter the thermal stability of the composite materials.

It is observed from the figure, that composites made with pristine MWCNTs, which have only slightly affected the thermal decomposing temperature of epoxy resin whereas the acid-functionalized MWCNTs have a great effect on the onset decomposing temperature. Introducing different
acid-functionalized MWCNTs to epoxy resin can increase the initial decomposing temperature of neat epoxy resin. Because of the strong interaction between the epoxy resin and acid-functionalized MWCNTs, the diffusion of small molecules can be retarded under high temperature. The surface modified CNTs could significantly enhance interfacial interaction between the CNTs and matrix in the composites. Functionalization would modify the CNT surface characteristics and enable higher polarity so that CNTs can form covalent bonds with the polymer matrix, resulting in enhanced thermal stability. Therefore, functionalization becomes an important step which will facilitates the effectiveness of the reinforcement.

Conclusions
In the present study composites with carbon nanotubes with different concentrations as reinforced in epoxy resin have been developed. Rheological studies indicates that the viscosity of epoxy composites increases with increasing the filler material in the matrix, which can be useful for evaluating the dispersion in matrix. Viscosity of functionalized carbonanotubes reinforced epoxy composite increased compared to pristine CNT/epoxy composites. The mechanical properties of MWCNTs/epoxy composites are improved significantly with the addition of MWCNTs. The combination of a chemical functionalisation of MWCNTs is useful approach to improve dispersion state of the CNTs and the interfacial adhesion to the epoxy matrix. The most significant improvement of strength 58% in pristine MWCNTs and 100% improvement in acid treated MWCNTs at 1wt% content is observed. It is also observed that the fracture surface of carbon nanotubes/epoxy composites that CNTs are agglomerates of around 20 microns and their dispersion is random in the resin.

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References