DISPERSION OF CARBON NANOTUBES IN PHENOLIC RESIN: INFLUENCE ON THE MECHANICAL PROPERTIES OF THE RESULTING COMPOSITES

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1.0 Introduction

Since their discovery in 1991[1], carbon nanotubes (CNTs) have generated huge activity in most areas of science and engineering due to their unprecedented physical and chemical properties. No previous material has displayed the combination of superlative mechanical, thermal and electronic properties attributed to them. These properties make nanotubes ideal, not only for a wide range of applications [2] but as a tool to understand fundamental science[3].

In particular, this combination of properties makes them ideal candidates as advanced filler materials in composites. Researchers have envisaged taking advantage of their conductivity and high aspect ratio to produce conductive plastics with exceedingly low percolation thresholds[4]. In another area, it is thought that their very high thermal conductivity can be exploited to make thermally conducting composites[5]. However, probably the most promising area of composites research involves the mechanical properties enhancement of plastics using carbon nanotubes as reinforcing fillers.

In more recent times, fibres made from materials such as glass, alumina, boron, silicon carbide and especially carbon have been used as fillers in composites. However, these conventional fibers have dimensions on the meso-scale with diameters of tens of microns and lengths of order of millimeters. Their mechanical properties are impressive with carbon fibres typically displaying tensile strength and stiffness in the ranges 1.5-7.0 GPa and 230-725 GPa respectively [6]. In recent years carbon nanofibers have been grown from the vapor phase with diameters of the order of 100 nm and lengths between 20 and 100 μm.   These small dimensions mean they have much higher surface area per unit mass than conventional carbon fibres allowing much greater interaction with composite matrices. They also tend to have impressive mechanical properties with tensile strengths between 2.5 and 3.5 GPa and Young's modulus in the range of 100-1000GPa [7].

However the filler material with unprecedented mechanical properties must be carbon nanotubes. Nanotubes can have diameters ranging from 1 to 100 nm and lengths of up to several hundred micrometers [8]. Their densities can be as low as 1.3 to 1.4 g/cm^3 and their Young's moduli are superior to all carbon fibres with values greater than 1 TPa [9]. In any case, their strength is what really sets them apart. The highest measured strength for a carbon nanotube was 63 GPa [10]. This is an order of magnitude stronger than high strength carbon fibres. Even the weakest type of carbon nanotubes have strengths of several GPa [11].

Several studies have been undertaken to develop both thermoplastic and thermosetting polymer composites with nanotubes as reinforcement. Qian et al [12] have reported that by addition of 1% of multi-walled nanotubes (MWNTs) into polystyrene matrices resulted in increase of overall tensile modulus and strength by approximately 42 and 25% respectively.   Andrews et al. [13] have used bundles of nanotubes and petroleum-derived pitch matrix to form composites. Different authors have used different matrix systems e.g. epoxy [14], polyamide [15], PMMA [16], polystyrene [12] and phenolics [17] for making CNT reinforced composites. Most of them have found an over all increase in the strength of the composites with very small fraction of CNTs loadings. However, the increase in the properties over the neat resin properties is not at all near to the expected values. Rather in some of the cases a negative effect on the mechanical properties due to poor interaction between the MWNTs and the epoxy matrix is reported [18]. It seems despite several attempts by different authors, a large amount of work will have to be done before we can really make the most of the exceptional mechanical properties of carbon nanotubes in composites.

There are four main system requirements for effective reinforcement. These are large aspect ratio, good dispersion, alignment and interfacial stress transfer. Dispersion is probably the most fundamental issue. Nanotubes must be uniformly dispersed to the level of isolated nanotubes individually coated with polymer. This is imperative to achieve efficient load transfer to the nanotube network. This also results in more uniform stress distribution and minimizes the presence of stress concentration centers. The effect of poor dispersion can

be seen in number of different systems when the nanotube loading level is increased beyond the point where aggregation begins. This is generally accompanied by a decrease in strength and modulus [17].

Probably the most important requirement for a nanotube reinforced composite is that external stresses applied to the composite as a whole are effectively transferred to the nanotubes.

There seems to be hardly any study, especially on the phenolic resin based CNT composites which would demonstrate substantial improvement in the composite properties, approaching close to CF based composites. The present study is therefore an attempt to understand the influence of one of the above parameters i.e. dispersion of CNTs in the polymer matrix by applying different dispersion techniques. It will be demonstrated how the proper dispersion of CNTs in the phenolic resin matrix help in improving the mechanical properties of the resulting composites by more than 100%.

2.0 Experimental

2.1 Production of Carbon nanotubes

Multi-walled carbon nanotubes (MWNTs) were synthesized by a chemical vapor deposition (CVD) technique on a setup described elsewhere [19, 20]. Briefly, a mixture of toluene and ferrocene (amounts) was used as source of hydrocarbon and Fe catalyst respectively. This mixture was injected into a quartz reactor (ID 42 mm) that was kept at a constant temperature of ~750°C. Typical run times were kept at 2 hrs. High purity Argon gas was used as a carrier gas. MWNTs deposited on the inside wall of the reactor were harvested and characterized by thermal gravimetry, electron microscopy and Raman spectroscopy for their structure and purity.

2.2 Characterization of the as produced carbon nanotubes

2.2.1 Thermal gravimetry

Thermal gravimetric analysis (TGA) is one of the important tools that can be used to determine the nature of different impurities present in carbon nanotubes. TGA of the as-produced carbon deposit was carried out in a Mettler Toledo, TGA/SDTA 851^e thermal analysis system. A constant supply of dry air at 10ml/min was maintained and the temperature was raised at 10^0C/ min from room temperature to 1000^0C and kept for 15 min. isothermally at the maximum temperature. The recorded weight loss curve is shown in Fig 1. As observed in the figure, sharp weight loss is initiated at 450^0C due to oxidation of the carbon nanotubes and a total weight loss of 90% upto 550^0C was recorded. The weight loss after this temperature is negligible. The remaining 10% material could be either metal or its oxide. The curve also shows that there is no weight loss around 300^0C ensuring absence of amorphous carbons in the deposit. It may therefore be concluded that in our experiments the yield of carbon nanotubes is 90% (minimum).
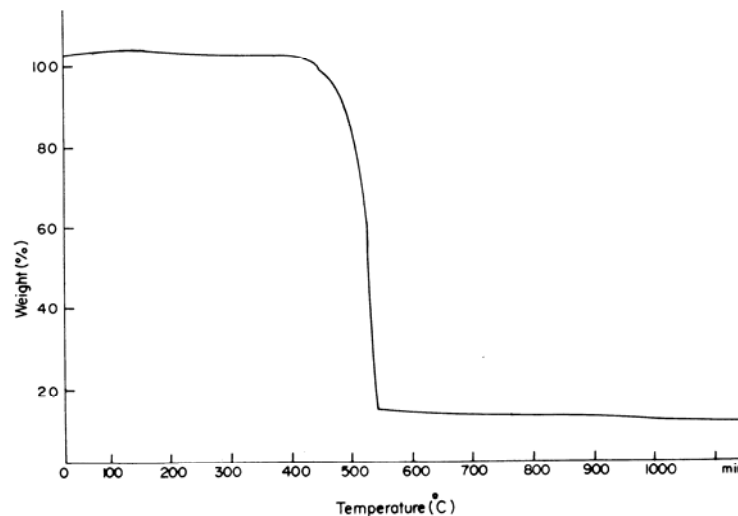

Fig. 1 TGA curve of as produced CNTs

2.2.2 SEM

The surface morphology of the nanotubes was observed using scanning electron microscopy (SEM). In addition, a qualitative analysis of the metal impurities in the sample was performed using a electron dispersive x-ray spectroscopy (EDS) unit fitted with the SEM. The EDS spectra were collected from various spots on the MWNT sample, and the average amount of Fe catalyst present in the as-produced carbon deposits was found to be ~9 weight %. The SEM micrograph shown in fig. 2 of the as-produced deposit shows large bundles of aligned MWNTs nearly 200 μm in length. The micrograph taken at higher magnification reveals that the tubes are of uniform diameter, individually as well as collectively (Fig.3). The diameter of the tubes is around 60-70 nm, suggesting them to be MWNTs. This was further confirmed by transmission electron microscopy (TEM) and Raman spectra of these tubes.

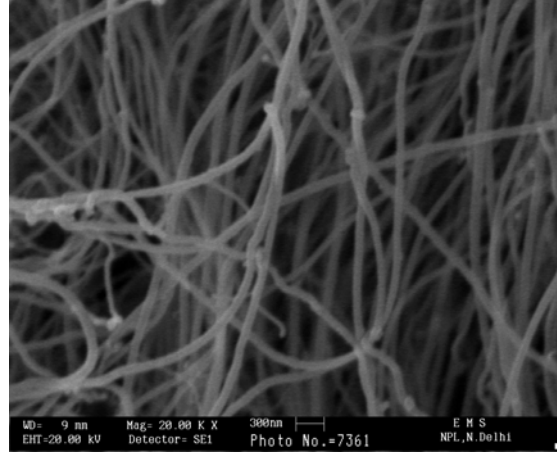Fig. 2. SEM micrograph of a large aligned bundle of as grown CNTs

Fig. 3. SEM micrograph of as grown CNTs at high magnification

2.2.3 TEM

TEM micrographs in Figs. 4 clearly shows bunch of pure carbon nanotubes with Fe catalyst particle at the tip. The thickness of the wall of the tube encapsulating the metallic particles reveals that the tubes are MWNTs. However, different scans of the samples under TEM show that these tubes are very clean with almost no impurities of amorphous or graphite nanoparticles or shells, as evidenced by the TGA study also.

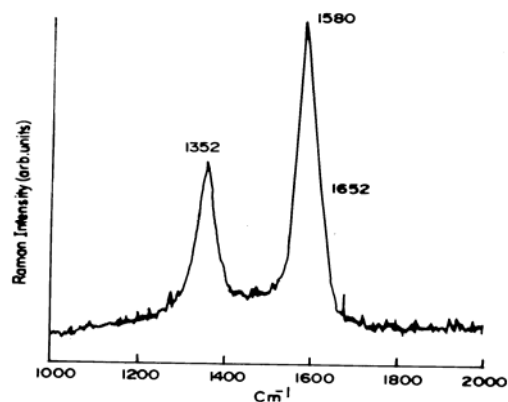Fig. 4. TEM micrograph of bunch of carbon nanotubes

Fig.5. Raman spectra of as grown CNTs

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2.2.4 Raman spectroscopy

Raman scattering studies were performed at room temperature using an Ar ion laser (514.5 nm excitation) and an ISA Triax 550 single grating spectrometer equipped with liquid nitrogen cooled CCD detector. All Raman scattering data were collected in the back-scattering geometry.

Raman spectra , obtained in the range 1000 – 2000 cm^{-1}, show the tangential band at 1580 cm^{-1} (G band) due to the $A(g_1)$, $E_1(g)$ and $E_2(g)$ vibrational mode of MWNTs and a disorder induced band at 1352 cm^{-1} (D band) due to $A(g_1)$ mode shown in Fig. 5 [21]. The disorder occurs due to the absence of long range order of the grapheme layers in the as produced soot.

2.3 Fabrication of CNT/polymer composites

For the CNT-polymer composites, the MWNTs were used as the reinforcement and the Novolac type dry phenolic resin powder procured from IVP Industries, India, was used as matrix precursor. Composites were prepared with different volume fractions of the MWNTs. Two different techniques were adopted to disperse these tubes in the matrix before the usual hot compression molding step to obtain CNT-phenolic composites bars of size 50mm x5mm x 3mm.

2.3.1 Dispersion by wet mixing technique

In this technique , about 0.2 – 2.0 gms of carbon nanotubes (depending on the volume percent as reinforcement) and dry phenolic resin (Novalac) were dispersed in acetone separately and sonicated for different times. Sonication of the tubes was continued till a visible uniform dispersion was achieved. No further improvement in dispersion was observed with further increase in sonication time. The two were then mixed together and sonicated again for two hours. This mixture was poured into a petri-dish and solvent was allowed to evaporate. The slurry containing the tubes and resin was molded into composite bars of size 50 x 5x 3 mm^3 in special die-steel molds by conventional hot pressing technique. The mold temperature was kept at 80^0 C. After molding, the composites were cured in air at 180^{0}C for two hours. For comparison, samples with 100% resin (0 vol% MWNTs) were also prepared.

2.3.2 Dry mixing technique

In this technique the dry powdered resin and as-produced carbon nanotubes were mixed thoroughly in a specially designed mixer without the use of a solvent before molding into composite bars of same size as discussed above. The complete process sequence (algorithm) is given below. For comparison, samples with 100% phenolic resin powder (0% MWNTs) were also prepared with similar dimensions.

3. Results and Discussion

3.1 Dispersion of carbon nanotubes in the matrix

Fig. 6 shows the SEM micrographs of the CNT/polymer slurry with 10 vol.% MWNTs after evaporation of the solvent. Several regions were scanned and the tubes were found to be dispersed quite uniformly. No agglomeration as such is visible except some of the tubes are either bunched up or shows a thick resin coating over them.

However, in the SEM micrograph of the composites prepared using the dry mixing technique the nanotubes could not be distinguished from the polymer (Fig. 7) and appear to be completely covered by the powder resin.

3.2 Mechanical *Properties of the composites prepared by the wet mixing technique*

Flexural strength and modulus of the composite samples was measured on INSTRON model 4411 using three point bending technique (ASTM D 790). The span to depth ratio for the test samples was kept as 13:1 and the cross head speed was maintained at 0.5 mm/min. Fracture surfaces of the samples were also examined under SEM.
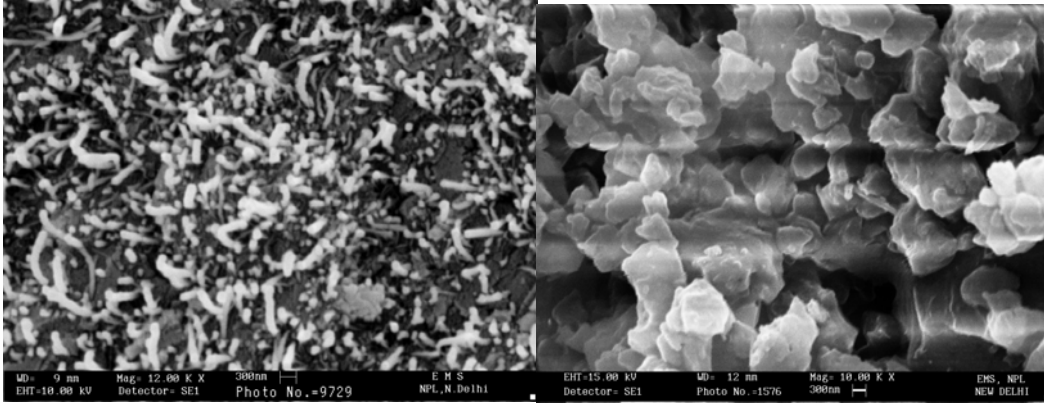
Fig. 6. SEM micrograph of dispersed carbon nanotubes Fig 7. SEM micrograph of dispersed carbon nanotubes
in phenolic resin by wet technique in phenolic resin by dry technique

Figure 8 shows the variation in the flexural strength and the modulus of the composites, with increasing volume fraction of MWNTs. As shown in the figure initially there is a sudden drop in the strength as compared to that of the neat (control) resin, however, it picks up after 5% loading of MWNTs and continues to increase up to 20% loading of MWNTs, beyond which it just tapers off. The reason for the initial drop in strength could be due to the fact that small amounts of MWNTs act as inclusions or defect centers rather than as reinforcement. This occurs due to pockets of agglomerated nanotubes in the matrix resin during its gelling stage just before the curing cycle. However, with higher percentage of tubes, the effect of agglomeration is overtaken by the load sharing by the large amount of the reinforcement and stress transfer to MWNTs which act as reinforcement.

As observed from the curve, the strength of the composite does not increase beyond 20 vol% of MWNTs; rather it shows a slight decrease when the MWNTs as reinforcement approaches 35 vol.%. The reason for this could be the large volume of interface provided by the nanotubes as compared to mesoscopic reinforcements like carbon or glass fibres. As a result, the amount of resin is unable to wet the total surface area provided by the nanotubes, which leads to poor adhesion and porosity in the sample. This might be the major cause for the failure of the composites at lower loads. Moreover, the maximum strength achievable for the composites even with 20% MWNTs is less than that of the control sample (~60 MPa), by using the wet dispersion technique. Fracture of the samples occurs due to debonding when either the nanotube-matrix interface fails or the matrix fails under the large shear stresses near the interface. In either case it is necessary to consider the interaction between the polymer and the nanotubes in the vicinity of the interface. It would be therefore instructive to observe the fracture surfaces of the composites after the flexural test.

The fractured surfaces of the composite samples were observed under SEM and reveal nanotubes pullout from the matrix, as shown in the images of the 20 vol.% MWNTs sample in Fig. 9 (a,b). The nanotubes pull-out reveals a weak interface between the tubes and the matrix. However, as shown in Fig 9b, the stresses or shear forces generated at the tube/matrix interface during the flexural test causes the alignment of the nanotubes.
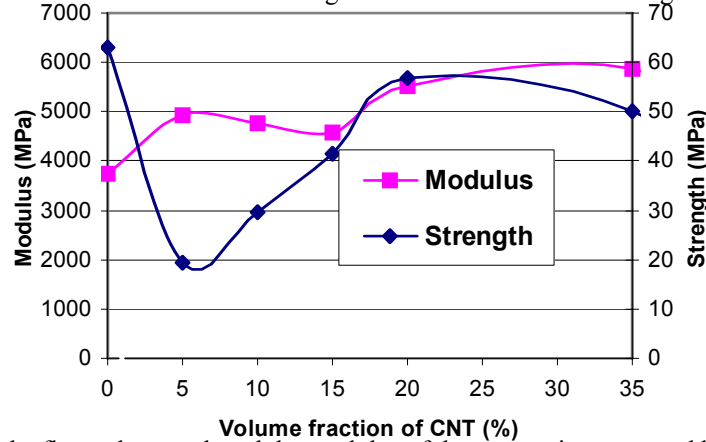

Fig. 8. Variation in the flexural strength and the modulus of the composites prepared by wet technique, with increasing volume percent of nanotubes

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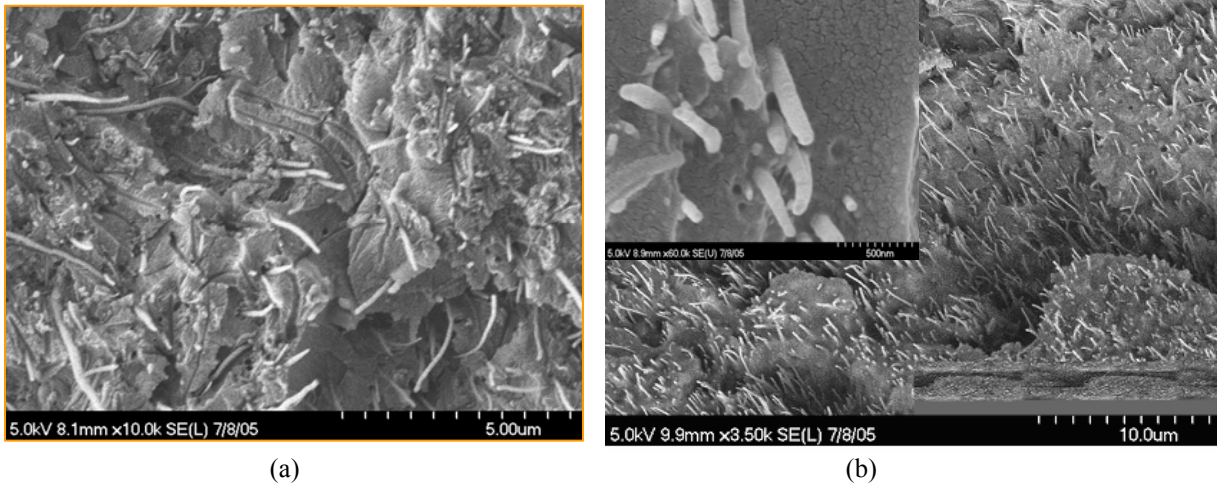| (a) | (b) |

Fig. 9. SEM of fractured surface of CNTs reinforced composite prepared by wet technique

The flexural modulus of the composites, as opposed to the strength, increases gradually with the volume % of reinforcement and reaches a saturation value around 6 GPa with 20-35 vol.% MWNTs. Total improvement in the modulus achieved over the neat resin value is ~60% which is the contribution from the higher stiffness of the nanotubes.

Curve 1 in fig.10 shows the stress-strain behaviour of the neat phenolic resin sample. It clearly shows plastic deformation near the yield point, typical for a cross linked thermoset resin. However, incorporation of 20 to 35 % CNTs does not change the fracture behaviour (curves 2 and 3) which still remains that of a neat resin suggesting no load transfer on the CNTs. This type of behaviour further confirms poor bonding of CNTs with the matrix.
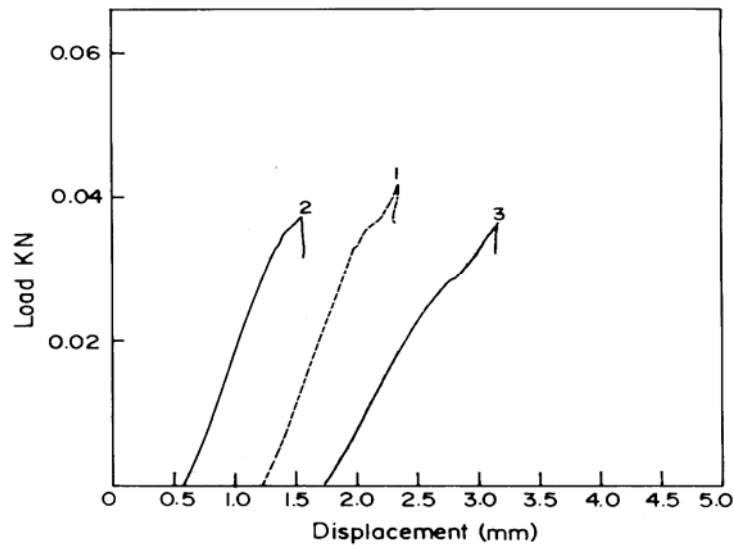

Fig. 10. Stress-strain behaviour of the CNT reinforced composites
Curve1: Neat crossed-linked resin (0% MWNTs), Curve2 with 20% MWNTs, Curve3 with: 35% MWNTs

3.3 Mechanical properties of composite samples prepared by dry mixing

Figure 11 shows the change in the flexural strength of the composites with 2 vol% of CNTs dispersed in phenolic resin powder by ball milling for different timings ranging from 10, 20, 25, 30 and 40 hrs. As seen from the figure the strength of the resulting composites shows gradual increase and reaches a maximum average value of 140 MPa after 40 hrs. of ball milling. Different samples show a scatter of 127 to 157 MPa. This is an an increase of more than 100% over the neat resin value (~60 Mpa) with only 2 vol% of MWNTs in the

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composites. CNT-phenolic composites possessing such high values of flexural strength have not been reported so far. The gradual improvement in the flexural strength suggests better dispersion of the tubes and stress transfer with increasing mixing time. The study suggests that large energy is needed to break the bundles of the nanotubes or in other words overcome the van der wall forces between the individual nanotubes. It is very much evident that further experimentation is required to see the effect of mixing time, in the ball mill , on the flexural strength with 2% of MWNTs loadings.

A uniform dispersion of tubes will ensure uniform stress distribution inside the composite samples and the stress concentration centers will be minimized. This results into increase in the composite strength as observed. As in the previous case the fractured surface of these composites was also observed under the SEM and shown in Fig.12 which shows very little CNTs pull out unlike the composites prepared by wet technique (Fig. 9). It also shows polymer coating on the tubes, i.e. the tubes are not bare. There seems to be some adhesion between the nanotubes and the matrix at mixing stage itself.
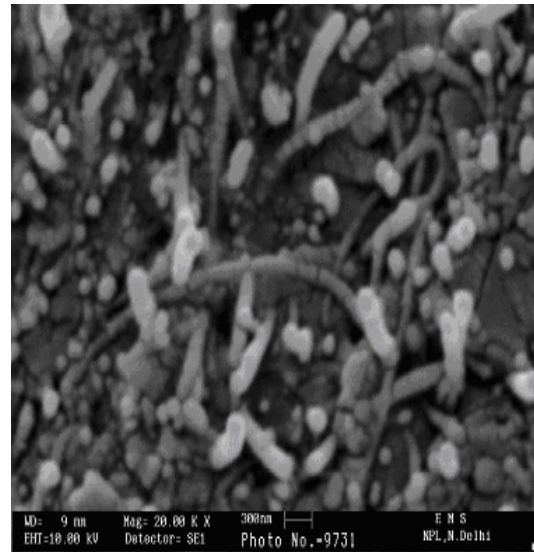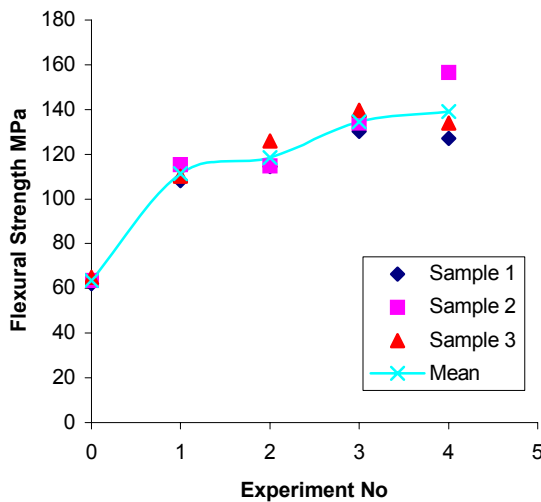

Fig.11. Flexural strength of the composites prepared with Fig.12. SEM of fractured surface of CNTs reinforced
2 vol% CNTs dispersed in the resin by dry mix technique   composite prepared by dry technique

The stress-strain behaviour of the CNT reinforced composites shown in figure 13 is also different than that of the wet mixed samples (fig. 10) which shows a plastic deformation. In the present case the composite fails like a brittle material without any plastic deformation even with very low percent of CNT i.e. 2% reinforcement as shown for samples 2-5. This suggests that there is a definite stress transfer from matrix to the tubes. Interestingly, the curve is not completely linear, suggesting a mixed mode of failure i.e. CNT pull out and debonding. There, however, is no evidence of fractured CNTs itself in the micrograph shown in Fig. 12.

The average modulus with this loading does not change with the dispersion and remains almost constant around 5 GPa. The value is similar to the composites prepared with the wet mixed technique.

Encouraged by the above results the studies were further extended to prepare composite samples with 5 vol% of CNTs (fig.14). It shows that as expected the strength of the composites further increased with mixing time and the average value of flexural strength reached to a value of 161 MPa as compared to 140 MPa with 2% CNTs. Further the range of scatter increased from 145 MPa (min.) to 187 MPa (max) ensuring a definite possibility to achieve still higher strength values for MWNTs - phenolic isotropic composites.

4.0 Conclusions

Although carbon nanotube-reinforced polymer composites show a lot of promise for high strength, light weight and high performance composites, earlier studies did not show actual performance enhancement compared to traditional carbon fibre based composites. The present study has highlighted the importance of proper dispersion of carbon nanotubes in the polymer to achieve the desired goal. CNT-phenolic resin composites possessing flexural strengths as high as 160 MPa could be developed even with small volume i.e 5
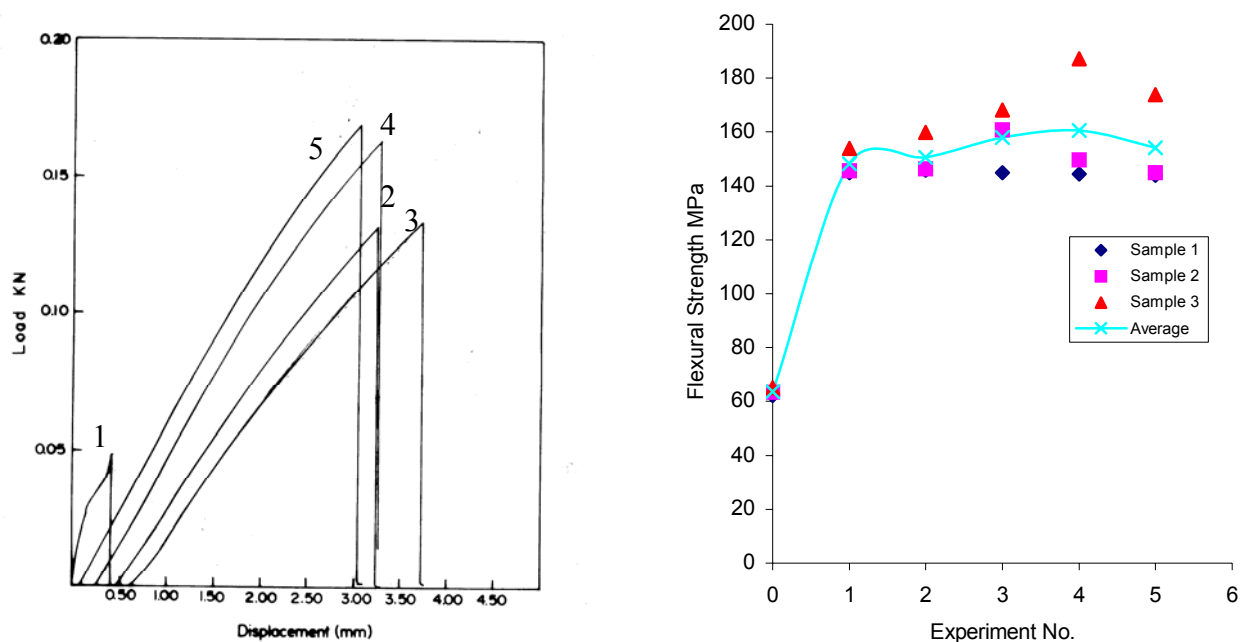
Fig.13. Stress-strain behaviour of the CNT
reinforced composites, Curve1 : Neat resin (0% MWNT),
Curves2-5: different vol. fractions of MWNT reinforcements

Fig14. Flexural strength of the composites prepared with 5 vol% CNTs dispersed in the resin by dry mix technique

% of CNT loadings, which is not possible with carbon fibres as reinforcement at this reinforcement level. Further improvement in the composite properties is anticipated when surface functionalized carbon naotubes will be used as reinforcement.

5.0 Acknowledgements

6. References

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