Effect of doping of multi-walled carbon nanotubes on phenolic based carbon fiber reinforced nanocomposites

Sadaf Saeed1,*, Saira Hakeem1, Muhammad Faheem1, Rashid Ahmed Alvi1, Khawar Farooq1, Syed Tajammul Hussain2, and Shahid Nisar Ahmad2

1 National Institute of Vacuum Science and Technology, Islamabad, Pakistan
2 National Center for Physics, Quaid-i- Azam University, Islamabad, Pakistan

*E-mail : sadaf03_2000@yahoo.com

Abstract. We report on the effect of multi-walled carbon nanotubes (MWCNTs) on different properties of phenolic resin. A low content of MWCNTs (~ 0.05 wt%) was mixed in phenolic resin and a stable dispersion was achieved by ultrasonication, followed by melt mixing. After curing the characterization of these composites was done by using scanning electron microscopy (SEM), thermogravimetric analysis (TGA), and Fourier transform infra-red spectroscopy (FTIR). The thermal and ablative properties of carbon fiber reinforced MWCNTs-phenolic nanocomposites were also studied. The addition of MWCNTs showed improvement in thermal stability and ablation properties.

1. Introduction
Fiber reinforced thermosetting resins have found a widespread use in variety of applications like household items, auto body-panels, aerospace structural components, sports equipments, printed circuit boards (PCBs), high-performance composites, and many more. Phenolic resin, the first synthetic thermoset polymer, is inherently fire resistant. Phenolic resins are commonly based on phenol (carbolic acid) and formaldehyde. High char yield, good thermal stability, low smoke production on burning, and low flammability are the characteristics that make phenolic resins attractive candidate for various applications in the electrical, automotive, construction, and appliance industries. The phenolic resins are widely used in thermal insulation materials, molding compounds, coatings, and composite materials [1-3].

The extraordinary properties of carbon nanotubes (CNTs) have brought new structural concepts in the field of composite materials, and the use of CNTs as nano-fillers for reinforcement of composites has attracted tremendous attention [4-8]. Small addition of CNTs to polymer matrix may drastically change the properties of the polymer in terms of strength, flexibility, thermal conductivity, and electrical conductivity. The doping of carbon nanotubes in polymer composites as nano-filler has been studied for thermal management [9-12]. Although, the CNTs have been extensively exploited for their use as nano-fillers in various polymers [13-17], but, when it comes to phenolic resins, the field is still open and...
relatively less attention has been paid to these resins. Mostly pristine CNTs were directly mixed in the phenolic resin for the preparation of CNTs filled nanocomposites [18-20].

Two elements are essential to achieve the desired properties of the nanocomposites; homogeneous dispersion of CNTs in the resin, and degree of interaction between the CNTs with the host matrix [21]. CNTs tend to agglomerate due to strong van der Waal interactions present among them. So they bundle up in the resin, and homogeneous dispersion of CNTs in the resin becomes a difficult task. Even at higher loading of CNTs, poor dispersion may result in a failure to achieve the expected properties of the nanocomposites. The homogeneous dispersion of multiwalled carbon nanotubes (MWCNTs) in poly matrix may stabilize the morphology and improve the properties of the host matrix. This may be attributed to the fact that when CNTs are homogeneously dispersed in the resin matrix, the interactions between MWCNTs and the resin matrix becomes stronger [22, 23], and the load is efficiently transferred from CNTs to the resin. Also, hydrogen bonding between CNTs and polymer chains can enhance the degree of dispersion of CNTs in polymeric matrix. Thus the effective utilization of CNTs in composites strongly depends upon their homogeneous dispersion in the host matrix, which plays a key role to maximize properties of composite system.

We have incorporated MWCNTs into phenolic resin using melt mixing technique. A low loading (0.05 wt%) of MWCNT was dispersed in the phenolic resin. Test samples of CNTs dispersed composites were prepared from prepregs, using compression molding technique, to study the thermal properties of the nanocomposites. The major goal of this study is to evaluate the effect of MWCNT on thermal properties of carbon fiber/phenolic nanocomposites.

2. Experiment

2.1 Materials

Multiwall carbon nanotubes used for the preparation of nanocomposites were obtained from NCP, Islamabad. They were produced by chemical vapor deposition method (purity 95%). Two types of CNTs were present; extra long filaments of carbon with larger diameters, and CNTs in the diameter range of 50-150 nm. The properties of the phenolic resin and carbon fiber used for the preparation of samples are summarized in table 1 and 2, respectively. Ethanol used was 99.9% pure.

| Property                          | Value                        |
|----------------------------------|------------------------------|
| Appearance                       | Dark red                     |
| PH                               | 7.4                          |
| Dry material content (%)         | 78-78                        |
| Viscosity (cp)                   | 258 at RT                    |
| Free phenol content (%)          | 3.54                         |
| Free formaldehyde content (%)    | < 0.7                        |
| Gel time (sec)                   | 120 at 90°C                  |
Table 2. Specification of carbon fiber

| Property             | Value   |
|----------------------|---------|
| Trade name           | T800H   |
| Filament count       | 12000   |
| Density (g/cm\(^3\)) | 1.81    |
| Tex count (g/1000m)  | 445     |
| Filament diameter (µm)| 5       |
| Tensile strength (MPa)| 5490    |
| Tensile modulus (GPa)| 294     |

2.2 Nanocomposite preparation

Purification of as received MWCNTs was done by heating at 400 °C. To achieve a better state of dispersion, the MWCNTs were first dispersed in ethanol by sonication for 2 hours. This was followed by centrifugation at 6000 rpm to separate the carbon filaments and CNTs. The suspended CNTs were decanted, followed by drying at 60 °C. These CNTs were put in ethanol and sonication was done for 30 minutes. Phenolic resin was added to the CNTs solution and mechanical mixing was done for 2 hours. The apparently homogeneous mixture was then melt-mixed. Melt mixing was done by magnetic stirring of the mixture on a heating plate, and a temperature of 450 °C was maintained for 8 hours. Finally, evacuation was done in a vacuum chamber to remove the remaining solvent. Chopped carbon fiber was impregnated with phenolic resin-CNTs mixture to form a prepreg, using a fiber to resin ratio of 66: 34. The composite samples were prepared from the prepreg by compression molding method at 165 °C. A pressure of 5MPa was applied for 30 minutes. The diameter and thickness of the samples were 34.6mm and 5mm, respectively.

2.3 Sample characterization

The characterization of the mixture and the cured composites included the following analysis:

a. Thermal Analyses: Thermogravimetry (TG) was conducted in a Netzsch (STA 449C) equipment. Heating of the samples was done at a heating rate of 10 °C/min from 25°C to 900°C.

b. FTIR Analysis: Fourier transform infrared spectroscopy (FTIR) analysis was done in Perkin-Elmer with a resolution of 4 cm\(^{-1}\), from 4000 to 400 cm\(^{-1}\), in transmission mode.

c. Ablation Test: To evaluate the ablation performance of the composites, the oxyacetylene flame test was carried out according to ASTM-E-285-80.

d. Morphological Characterization: Morphological characterization of the samples was carried out using a scanning electron microscope (Jeol 6480, LV).

3. Results and discussion

The multi-walled carbon nanotubes used in this work were produced by chemical vapor deposition method. The infrared (IR) spectroscopy method has been adopted by many researchers to study the surface properties of CNTs and the bonding between the CNTs and the host matrix.

3.1 FTIR data

The comparison of FTIR data of neat phoenolic resin and CNTs incorporated phenolic resin is shown in figure 1. It suggests that once the nanotubes were incorporated into the Phenolic resin a band at 1699 cm\(^{-1}\) was generated due to the formation of linkage between CNTs and the phenolic resin.
3.2 SEM data

The SEM images of raw CNTs and the processed CNTs (after purification and centrifugation) are shown in figure 2. These images are taken almost at the same magnification. The difference in the diameters between the as received and processed CNTs can clearly be seen. The raw CNTs show a broad size distribution; maximum diameter of ~450 nm was observed in this case (shown in part (a) of the figure 2). On the other, the CNTs after centrifugation have a size distribution in the range of 50-150 nm (shown in part (a) of the figure 2).

3.3 Thermal behavior (TGA data)

The effect of the MWCNTs on the thermal stability of phenolic resin was studied using thermogravimetric analysis (TGA). The TGA curves for phenolic resin and MWCNTs/Phenolic resin nanocomposites, at a heating rate of 20°C/min under an inert atmosphere, are presented in figure 3. The
data reveals that thermal degradation of pure phenolic resin and MWCNTs/phenolic resin nanocomposites exhibits three thermolytic temperature zones. The zone of 100-350°C is the thermal decomposition zone of free or imperfectly cross linked molecules [24]. These molecules include water, unreacted phenol and formaldehyde. The weight loss by the evolution of unreacted monomers contributes up to 5-8%.

The second and third zones at 400-625°C and 625-900°C, respectively, can be attributed to the decomposition of the cross linked nanocomposites with the evolution of carbon mono oxide, carbon dioxide, methane, phenols and cresols. The release of these molecules can be correlated to the post cure reactions and the formation of dihydroxy benzophenone linkages.

![Figure 3. TGA curves of phenolic resin (a) and CNT dispersed phenolic resin (b) nanocomposite](image)

The residual weight (i.e. char yield) is an important performance index for phenolic resin and its composites. Table 3 summarizes the residual weights at 900°C.

| Material                  | Residual wt % at 900°C |
|---------------------------|------------------------|
| 0% CNTs-phenolic resin    | 47                     |
| 0.05% CNTs-phenolic resin | 49                     |

The increased thermal stability can be attributed to better dispersion of CNT in the resin, resin matrix–CNTs interactions, and thermal conductivity of the nanotubes to transmit the heat. Similarly, the char yield of the nanocomposites at 900°C increases with small doping (0.05 wt %) of MWCNTs (the char yield increased from 47% to 49%).

### 3.3 Ablation Test Results

Ablation test was performed using oxyacetylene flame according to ASTM standard. The samples were exposed to the flame for 30 seconds. A comparison of ablation performance of the phenolic resin-CF
composites with and without addition of CNTs is shown in Table 4. The addition of CNTs in the phenolic resin results in the decrease in average weight loss of the Phenolic-carbon fiber composite.

| Concentration of CNT (%) | Exposure time (Sec) | Average wt. loss (g/Sec) | Fractional wt loss | Comparative decrease (%) in mass ablation |
|--------------------------|---------------------|--------------------------|-------------------|----------------------------------------|
| 0                        | 30                  | 0.074                    | --                | --                                     |
| 0.05                     | 30                  | 0.057                    | 0.2297            | 23                                     |

4. Conclusion

The primary objective of this paper was to study the effect of MWCNTs on the thermal properties of carbon fiber reinforced phenolic resin composites. The TGA results revealed that MWCNTs incorporated composites had better thermal stability than those without MWCNTs. Decrease in average weight loss was observed on addition of MWCNTs to carbon fiber reinforced phenolic resin composites. The decrease in mass ablation rate of carbon fiber reinforced phenolic resin, on addition of MWCNTs, suggests that MWCNTs may be used in flame retardant materials to enhance their efficiency. The increase in char yield is also observed on addition of MWCNTs which is also a promising result in this regard. CNTs-phenolic interface can play a major role in thermal resistance of the material. The only major issue is a homogenous dispersion of CNTs in the resin matrix which plays a vital role.

5. References

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