STUDIES ON CARBON NANOTUBES BASED EPOXY COMPOSITES

by

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Dedicated to my Father Late Shri Maharaj Singh
&
My Mother Smt. Kushuma Devi

CERTIFICATE

This is to certify that thesis entitled **“Studies on Carbon Nanotubes Based Epoxy Composites”** being submitted by Mr. Bhanu Pratap Singh to the Indian Institute of Technology, Delhi, for the award of degree of **Doctor of Philosophy** is a record of bonafide research carried out by him. Mr. Bhanu Pratap Singh has worked under our guidance and supervision and has fulfilled the requirements for the submission of this thesis, which to my knowledge has reached the requisite standard.

The results contained in this thesis are original and have not been submitted, in part or full, to any other University or Institute for the award of any other degree or diploma.

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ABSTRACT

Carbon nanotubes (CNTs) are endowed with exceptionally high material properties, very close to their theoretical limits, such as electrical and thermal conductivity, strength, stiffness, toughness and low density. Due to their exceptionally unique combination of properties, incorporation of CNTs into the polymer matrix is expected to enhance the properties of resulting nanocomposites more than any other existing material. Epoxy resin is one of the most important and widely used thermosetting polymer matrix used for the development of advanced composites displaying a series of promising characteristics for wide range of applications. It has very unique mechanical properties, chemical resistance, low cost, ease of processing and good adhesion to a variety of substrates. Therefore, the present study was carried out to study the conductive composites based on CNTs and epoxy resin which may find applications in structural and electromagnetic interference (EMI) shielding.

During the last two decades, several reports have been published on the CNTs-epoxy composites with limited success. Though, there are many studies on the EMI shielding behavior of composites using CNTs but no correlation has been made with respect to their mechanical properties. The main reason has been poor dispersion, wetting, alignment and constraint on the amount of reinforcement (<1%). In addition to this, another reason is the availability of consistent quality of CNTs which could ensure the comparison of large amount of data. Therefore, it was of great interest to investigate these aspects systematically to improve the performance of CNTs-epoxy composites especially for their mechanical and EMI shielding properties using in-house grown CNTs.

The thesis reports the bulk synthesis of consistent good quality of MWCNTs using in-house developed chemical vapor deposition reactor. The characterization of in-house developed

MWCNTs was done using SEM, TEM, Raman spectroscopy [morphology, length and structure] and thermogravimetric analysis [purity]. MWCNTs prepared had 87% purity with diameter of 26 nm and length of 350 µm (bundle length). Commercially available MWCNTs [Nanocyl 7000] were also procured for comparison purposes. Nanocyl-MWCNTs [9.5 nm outside diameter and 1.5 µm length] had much lower aspect ratio as compared to in-house grown MWCNTs. Nanocomposites were prepared by mixing varying amounts of MWCNTs [in house grown designated as l-MWCNTs and Nanocyl 7000 MWCNTs designated as s-MWCNTs] with epoxy resin [LY 556] and hardener [HY5200]. The ratio of epoxy resin to hardener was fixed as 100:23 by weight. All the samples were cured under similar conditions [cured for 2h at 80°C and 4h at 150°C] and then characterized. Special attention has been paid to explore the industrially viable dispersion process of CNTs into epoxy resin. The influence of length of CNTs on the properties [mechanical, electrical, and EMI shielding] of composites has also been studied.

The second challenge was how to disperse higher amounts of MWCNTs in polymer matrix without agglomeration to make use of their properties. Efforts have been made to evolve a method for incorporating large amounts of CNTs [upto 20.4 %] into the epoxy resin. Composites prepared using higher loading of l-MWCNTs had much better electrical and EMI shielding properties with improved mechanical properties.

In order to improve the compatibility of MWCNTs with epoxy matrix, we carried out the surface modification of CNTs to introduce some functional groups such as amine on the surface of MWCNTs. For this purpose, first oxidation [treatment with conc. nitric acid to introduce –COOH group], acylation [with thionyl chloride to incorporate –COCl groups] followed by reaction with excess amine [Huntsman 5200 to introduce $–NH_2$ group] and designated as Am-MWCNTs. Structural and morphological characterization of functionalized nanotubes was done using FTIR, Raman, EDX, SEM and TEM. The length of MWCNTs decreased and defect structures increased upon modification. Such modification is expected to enhance its compatibility with epoxy resin. Several samples were prepared by blending varying amounts of Am-MWCNTs and investigated its effect on mechanical, electrical, and EMI shielding behavior. In spite of lower length of MWCNTs after modification, improvement in mechanical properties was higher as compared to l-MWCNTs. However, the electrical conductivity and EMI shielding effectiveness was lower with Am-MWCNTs as compared to l-MWCNTs. In order to match or surpass the carbon fiber-epoxy composites properties, CNTs-carbon fiber/epoxy hybrid composites have been developed and characterized for their electrical, thermal, mechanical and EMI shielding properties. We have grown varying amounts of MWCNTs on carbon fiber fabric and hybrid composites were prepared. Such hybrid composites [30 % loading - 3% MWCNTs and 27% carbon fiber fabric] showed much better performance properties as compared carbon fiber fabric reinforced composites at 50 % loading.

The thesis has been divided into six chapters. **Chapter 1** presents a brief introduction to polymer nanocomposites followed by detailed study carried out on CNTs including their structure, properties and synthesis techniques. Fabrication methods for CNTs-polymer composites especially with epoxy resin, their dispersion, functionalization and alignment in polymers and their mechanical properties, electrical properties, EMI shielding properties and thermal conductivity is also discussed. Application part of CNTs-polymer nanocomposites is also discussed in brief.

The detailed methods used for the synthesis of MWCNTs, MWCNTs-epoxy composites, MWCNTs-carbon fiber/epoxy hybrid composites are given in **chapter 2** of thesis. The techniques used for the characterization and evaluation of the properties of these composites are also described in this chapter.

The effect of length and loading amount of MWCNTs on the properties of epoxy composites fabricated by two different approaches are given in **chapter 3**. The effect of length of MWCNTs on mechanical, electrical and EMI shielding properties of MWCNTs-epoxy nanocomposites fabricated by industrially viable dispersion technique upto 0.5 wt.% MWCNTs loading is investigated. The percolation threshold was obtained at 0.02 wt. % for l-MWCNTs based epoxy composites compared to 0.11 wt. % for s-MWCNTs based epoxy composites. Due to very low percolation threshold and enhanced electrical conductivity (1.37 x 10^{-3} Scm^{-1} for 0.5 wt. % l-MWCNTs based epoxy composites and 0.95 x 10^{-3} Scm^{-1} for 0.5 wt. % s-MWCNTs based epoxy composites), absorption dominated EMI shielding effectiveness was achieved -16 dB for l-MWCNTs based composites compared to -11.5 dB for s-MWCNTs based composites with 0.5 wt. % loading in Ku band (12.4-18GHz). This is the highest reported value for MWCNTs-epoxy composites for such a low loading level of 0.5 wt. % at 2.5 mm thickness from the best of our knowledge. In addition to this, flexural strength of the composites was found to be 125 MPa at 0.3 wt. % for l-MWCNTs based composites and 113 MPa at 0.3 wt. % for s-MWCNTs based composites from 95 MPa of pure cured epoxy. This study clearly reveals that the l-MWCNTs based epoxy composites have overall better performance over s-MWCNTs based composites.

In order to further improve the EMI shielding effectiveness of composites, further improvement in the electrical conductivity is required which necessitates higher loading of CNTs. A new technique to incorporate large amounts of CNTs into epoxy resin for formation of CNTs-epoxy composites is also discussed. The fabricated CNTs-epoxy composites are characterized for electrical, mechanical and EMI shielding properties. Using this novel technique, upto 20.4 wt. % of MWCNTs loading in the composite was achieved which resulted in EMI shielding effectiveness of – 60 dB. Additionally, these composites show an improvement of 40% in the strength over the neat epoxy resin value.

The realization of superior mechanical properties in the CNTs reinforced epoxy requires a strong interfacial interaction between the nanotubes and the epoxy. Chemical functionalization of the CNTs surface could enhance the compatibility of CNTs with matrix and may act as curing agent resulting in the formation of covalent bonds. In **chapter 4**, amine functionalized MWCNTs was used as reinforcement in the fabrication of epoxy composites and several samples were prepared having loadings ranging from 0.1 - 0.75 % w/w. The effect of loading of functionalized MWCNTs on the mechanical, electrical and EMI shielding properties of epoxy composites was investigated and the results are described in this chapter. It was observed that flexural strength of amine modified MWCNTs based epoxy composites reached upto 163 MPa at 0.5 wt. % MWCNTs loading compared to 95 MPa of pure cured epoxy, an overall improvement of 72%. Therefore, these composites can be used as high strength composites.

Unless the CNTs-polymer composites surpass the mechanical properties of the conventional carbon fiber based polymer composites, the commercial applications in structural reinforcements will not be feasible. Failure to achieve superior mechanical properties by neat CNTs-polymer composites has led us to adopt different routes, notably in the form of hybrid composites. MWCNTs were grown on carbon fiber fabric substrate by CVD that resulted in strong anchoring of these tubes on the carbon fiber surface. This has been described in **chapter 5**. These hybrid preforms were used as reinforcement in epoxy resin matrix to develop hybrid carbon fiber-MWCNTs/ epoxy composites. The flexural strength as well as the flexural modulus of these composites was found to increase with increasing amount of CNTs grown on carbon fiber surface. Flexural strength of the hybrid composites improved by 80%, i.e., 560 MPa compared to 310 MPa for the base composite (carbon fiber-epoxy) prepared under identical conditions. Flexural modulus of these composites also improved by 120%, i.e. 55 GPa for the hybrid composite compared to 25 GPa for the base composite. The interlaminar shear strength improved from 23 MPa for carbon fiber-epoxy composites to 50 MPa for hybrid composites. In addition to mechanical properties, in-plane and transverse thermal conductivity of these hybrid composites improved from 17.68 W/mK and 1.79 W/mK, respectively, for base composite to 29.05 W/mK to 2.61 W/mK for hybrid composite. The incorporation of MWCNTs on the carbon fiber fabric produced a significant enhancement in the EMI-shielding effectiveness i.e. from −29.4 dB for carbon fiber-epoxy composite to −51.1 dB for MWCNTs-carbon fiber/epoxy hybrid composite. This indicates their usefulness for making heat dissipative structurally strong microwave shields.

The summary and conclusions are given in **Chapter 6**. Suggestions for future work are also given in this chapter.

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