Fabrication and characterization of carbon nanofiber (CNF) based epoxy composites

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Abstract. The behaviour of epoxy based nanocomposites containing 1.5, 2 and 2.5 wt.% of carbon nanofibers (CNFs) have been analysed through mechanical and viscoelastic characterizations. The nanocomposites thus fabricated were allowed to cure at two different temperature conditions- one was at room temperature (27 ºC) and other was at low temperature (4 ºC). Among all the room temperature cured (RTC) and low temperature cured (LTC) composites, maximum improvement in flexural modulus (83% & 128%), storage modulus (34% & 21%) and glass transition temperature (34% & 35%) were found in case of 2 wt.% CNF loaded samples (CNF2). In addition, LTC composites at 2 wt.% were showing enhanced flexural and thermal properties in comparison to the RTC composites. However at relatively higher concentration less increment in flexural modulus was noticed for both RTC and LTC composites. Microscopical investigation supported the above results by showing the interfacial arrangement between carbon nanofibers and epoxy matrix.

Keywords. Carbon nanofiber, epoxy composite, flexural modulus, glass transition temperature.

1. Introduction

For about a decade and more, carbon nanofibers (CNFs) are acting as extraordinary filler constituents offering overall improvement in mechanical and physical properties of the polymer matrix material. Due to light weight, high specific modulus ~ 500 GPa and high specific strength ~3 GPa of individual nanofibers, CNFs-reinforced polymer becomes eye-catching structural materials [1]. Further electrical conductivity ~ 10$^4$ S/cm, thermal conductivity ~ 1900 Wm$^{-1}$ K$^{-1}$ and huge specific surface area (SSA) of up to 1000 m$^2$/g together with their low manufacturing cost make them suitable for improving the performance of polymeric materials in numerous applications like in automotive, aerospace, electronics or biotechnology [2]. In polymer, epoxy resin is most often used as the polymer matrix due to its series of interesting properties like high specific strength, good stiffness, chemical resistance, dimensional stability and also strong adhesion to the embedded reinforcement [3-6]. Enhancement in mechanical properties of CNF based epoxy composites have been well illustrated in the literature [7-12] by the achievement of strong interfacial adhesion between the composite phases. Previous research showed that CNFs are prone to agglomerate because of their surface properties and the process of
fabrication [13-17]. So the significant improvement in CNF dispersion in the composite is very much necessary as it facilitates the stress transmission from matrix to the reinforcing agent. In the present study, the entanglement and agglomeration of CNFs were removed by using the solvent to the CNFs and by curing of the fabricated specimen at low temperature. Our group already worked on this procedure [18] and fabricated CNF/epoxy composites by the incorporation of low wt.% of CNFs (0.5, 0.75, 1 wt.%) where qualitative dispersion has been reported. The originality of present work is to study the influence of reinforcing strategies of CNF/epoxy composites of higher wt.% (up to a maximum 2.5%) of CNFs in the epoxy matrix.

2. Materials and Methods

2.1. Materials
Epoxy polymer matrix in the current study was prepared by mixing epoxy resin (araldite LY-556 based on Bisphenol A) and hardener HY-951 (aliphatic primary amine) in wt. ratio 100/12. Epoxy and hardener were procured from CIBA-GEIGY, INDIA. This epoxy resin (5.3-5.4 equiv/kg) was of low processing viscosity and good overall mechanical properties. Carbon nanofibers (CNFs) used for experimental study were procured from Nanostructured & Amorphous Materials Inc. (Nano Amour), USA. They are 10-50 μm long and 200-500 nm in diameter. The purity of the nanofibers was >95%.

2.2. Preparation of composites
The Carbon nanofibers (1.5 wt.%, 2 wt.% and 2.5 wt.%) were first dispersed in acetone by sonication for 4 hours. The obtained powder was then again dispersed in acetone and sonicated. This process assisted to de-bundle the nanofibers at this higher concentration which was optimized to be the best dispersion, confirmed through optical microscope. Finally the powder of nanofibers were mixed to epoxy resin and sonicated at controlled power levels for 6 hours. Then the CNF and epoxy resin mixture were kept in vacuum oven for 12 hours to eliminate the moisture and air bubbles. Thereafter with manual stirring hardener was added to the mixture inside a water bath to avoid further reaction. Another degassing process was conducted to the mixture in vacuum oven for a few minutes. The mixture was injected into two molds one of which was kept in room temperature atmosphere (27 ºC) and other was in low temperature (4 ºC). These prepared samples were then post cured at 90 ºC for 6 hours.

The fabricated specimens in this work are named as follows:

| Room temperature cured specimens | RTC |
|----------------------------------|-----|
| Low temperature cured specimens  | LTC |
| 1.5 wt.% CNF based epoxy composites | CNF1.5 |
| 2 wt.% CNF based epoxy composites | CNF2 |
| 2.5 wt.% CNF based epoxy composites | CNF2.5 |

3. Characterization
As the content of CNFs, mixed in the form of reinforcement to the epoxy is not so large, hence it is expected that the volume occupied by the fillers is small. The fibers were oriented in a random way throughout the matrix which results the nanocomposites isotropic in behaviour. Hence, a test standard for polymeric materials was used to evaluate the mechanical properties of nanocomposite materials.

3.1. Flexural test
Flexural tests were accompanied according to ASTM D790–02 “Standard Test Methods for Flexural Properties of Un-reinforced and Reinforced Plastics and Electrical Insulating Materials” on an
universal testing machine (Instron 5967). The mode of test was three point bending and the rate at which the load was imposed was 2.0 mm/min. The span between two supports, width and thickness of the specimen was shown in the figure 1. In order to reproduce the results five specimens were tested in each group.

![Diagram of flexural testing specimen configuration](image.png)

**Figure 1.** Flexural testing specimen configuration showing thickness = B, width = W, span = S and applied force = P.

3.2. Dynamic mechanical analysis (DMA)

Viscoelastic properties of composites were analyzed using Gabo Qualimeter (Eplexor 150N, Germany) in dual cantilever mode. Treatment conditions included a frequency 1 Hz with a strain of 0.1%. A temperature range from 20-260 °C was applied at a heating rate of 2 °C min in air.

3.3. Microscopical investigation

Field emission scanning electron microscope (Nova NANOSEM 450) was used to observe the fracture surface topography of all the composites specimens.

4. Results and Discussion

4.1. Flexural test results

Figure 2 (a) and (b) represented the elastic moduli of parent epoxy and nanocomposites for CNF1.5, CNF2 and CNF2.5 for both RTC and LTC specimens respectively. Earlier we have reported [18] the behaviour of mechanical properties of CNF/epoxy composites by incorporating low wt.% of CNFs (0.5, 0.75, 1 wt.%). In the present studies higher CNF contents were taken and flexural modulus values were evaluated.

![Graphs of flexural modulus](image.png)

**Figure 2.** Flexural modulus of (a) RTC samples and (b) LTC samples.
For RTC samples the evaluated flexural modulus of neat epoxy was 2344 MPa. Modulus was increased by 50% and 83% for CNF1.5 and CNF2 respectively. Similar trend was observed in the LTC specimens. The modulus values for the CNF1.5 and CNF2 were found to be 3736 MPa and 5356 MPa i.e. increment in modulus by 25% and 79% respectively in comparison to the neat epoxy (2976 MPa). The modulus was almost double for CNF2 in case of LTC specimens compare to the neat epoxy of RTC specimens. This result is well agreed with earlier reported result [19] where the mechanical properties of CNF/epoxy composites were increased due to the addition of CNFs below 3 wt.%. The increment in modulus value was attributed to the qualitative dispersion of CNFs with the epoxy which results formation of strong interface between the filler and the host [20]. The improved interface is in turn facilitates load transfer from matrix to the nanofiller enhancing overall mechanical properties of the composites. However at higher loading of CNFs (CNF2.5) the trend was different. The modulus value obtained was lower than the other nanocomposites, though it was still higher than that of the parent epoxy for both the cases. For the LTC specimens CNF2.5 showed only 16% increment than that of the neat epoxy composite. Due to high aspect ratio and vander Waals’ interaction of CNFs agglomeration may be created at higher concentration. As a consequence the whole nanocomposites may act as a stress concentrator and hence the mechanical properties did not increase to greater extent. These results were in accordance with the study by Gershon et al. [21] and Palencia et al. [11] who established the existence of a limit of dispersion of CNFs in the epoxy matrix which was evidenced by the mechanical properties.

On the otherhand, it was worth noting that LTC specimens showed greater modulus to their RTC counterparts. The result indicates that the low temperature facilitates the curing procedure in an effective manner by delaying the settling time and hence mechanical properties were improved [18]. Flexural stress-strain curves of neat epoxy and CNF filled epoxy were recorded during the three-point bending test of the materials studied shown in figure 3 (a) and (b). All the specimens failed immediately after the flexure stress reached the maximum value. An increased strain to failure was observed in case of some LTC nanocomposites (figure 3(b)) in comparison to RTC nanocomposites (figure 3 (a)).

![Stress vs. Strain behaviour of room temp. cured samples](image1)

![Stress vs. Strain behaviour of low temp. cured samples](image2)

**Figure 3.** Stress vs. strain behaviour of (a) RTC and (b) LTC composites.

4.2. DMA test results

DMA was performed to evaluate the viscoelastic properties of the composites such as storage and loss modulus, glass transition temperature etc. Figure 4 (a) and (b) show the effect of temperature on the storage modulus of the LTC and RTC composites respectively. It was found that compared to the neat epoxy composites the value of storage modulus was increased upon increasing CNF contents up to 2 wt.% for both LTC and RTC specimens.
Figure 4. Storage modulus vs. temperature plot of (a) LTC (b) RTC composite samples.

The value of the storage modulus of neat epoxy composites was found to be around 133 MPa for both the cases. In case of RTC specimens for CNF1.5, CNF2, and CNF2.5 the percentage of increment in modulus were 32%, 34% and 12% respectively. CNF2 showed the maximum enhancement in modulus (179 MPa) among the RTC specimens. On the other hand in LTC specimen CNF1.5 and CNF2 demonstrated almost equal modulus values (162 MPa) which is 21% greater than the neat epoxy. The increase in modulus may be due to the uniform dispersion of the CNFs as well as confinement of CNFs to the epoxy polymer [22]. However CNF2.5 displayed lowest value of storage modulus (115 MPa) among all. The modulus is even lesser (13% decreased) than the respective neat epoxy. Lower modulus value clearly indicates that reinforcement effect of CNFs was decreased when concentration of CNFs went towards higher side attributing the agglomeration of CNFs and weak interfacial bonding between CNFs and epoxy matrix [23].

Tan delta is defined as the ratio of loss to storage modulus of a composite where delta represents the phase angle. The phase angle is very much sensitive to the structural change of the materials and decreases with increasing filler contents [24]. The peak of tan delta is used to determine the glass transition temperature (Tg) of a material from the onsets of the sharp drop in tandelta vs. temperature graphs. The evaluated Tg value for different composite samples from the graph were presented here in tabulated form. In case of RTC the value of Tg for the neat epoxy was found to be 65°C and that of LTC specimens was 67 °C. It was observed that as the CNF content goes higher, Tg values for both the RTC and LTC nanocomposites were increased. This was increased by 26%, 34% & 31% for RTC and 24%, 35% and 10% for LTC for CNF1.5, CNF2 and CNF2.5 respectively compare to their neat epoxy composites. These results indicated significant enhancement in glass transition temperature compare to the parent epoxy. Maximum enhancement in Tg was recorded for CNF2 (90.7°C) among all the samples. The increase in Tg of the nanocomposites was due to the addition of CNFs which restricts the mobility of polymer chains, made the nanocomposites brittle in nature and hence improves the thermal stability of the composites [25-27]. However at higher wt.% (for 2.5) the Tg for the LTC samples showed lower value than the others (still higher than neat epoxy). The detrimental results were may be due to presence of aggregated phases of nanofibers at higher
concentration which eventually prevented from achieving uniform dispersion. As a result the interface between CNFs and epoxy became much weaker which in turn made the composite less stiff compared to others. There were some other reason behind the reduction in $T_g$ according to which changes in chemical equivalent between matrix and curing agent may decrease the cross linking density of the composites and hence $T_g$ was decreased [7]. Another observation from present study revealed that the LTC samples were showing greater $T_g$ values than RTC specimens except higher loading. The same trend was noticed in mechanical results also. The possible reason is that at low temperature the nanofibers were well dispersed and cured by delaying the settling time which enhanced the overall mechanical and thermal properties of the composites.

4.3. Microscopical results

Figure 5-7 shows the micrograph of fracture surfaces of RTC and LTC specimens. It was clearly observed in figure 5(a) i.e. in the case of CNF1.5 (RTC) nanofibers were intimately attached to the matrix. As a result of this bonding matrix can transfer the applied load on the composites to the high modulus CNFs. In figure 5(b) i.e. in the case of CNF2 (RTC), nice integration of CNFs with the epoxy resin was found. This is in turn denoted good interfacial strength of the composites even if the fracture occurred. In the case of LTC CNF1.5 (figure 6(a)) adequate wetting of CNFs inside the matrix were seen. It seems like fractographs were much denser where CNFs were attached to the epoxy and

(figure 6(a) and (b)) very less number of CNFs were removed after the application of load. This indicated wrapping of polymers around the nanofibers suggesting stronger bonding compare to the RTC specimens. That is why significant enhancement in mechanical results was seen in case of LTC samples. Another worth noting from figure 6(a) was that most of the CNFs were aligned in the same direction which was along the direction of application of load. Since load is transferred effectively in the axial direction hence in LTC, the CNF1.5 specimen showed greater flexural and storage modulus than that of the RTC samples. Further figure 6(b) showed the bridging and spanning of nanofibers between the composite cracks that offers resistance to the crack propagation. It has already been reported that bridging of nanofillers inhibits the crack initiation [26, 28]. Hence, the presence of CNFs in the form of a bridge between the crack regions can be the reason for increased mechanical behaviour in LTC samples.
Now according to the observation under mechanical test it was found that at higher concentration of CNFs (for CNF2.5) the overall mechanical properties were decreased for both the RTC and LTC specimens. The prediction of the detrimental effect was may be due to the presence of aggregated phases of CNFs. It was observed that the prediction shows well agreement after the microscopical investigation was performed. The investigation revealed the formation of aggregates of CNFs at CNF2.5 for both the cases shown in figure 7(a) and (b). This aggregation are very much responsible for creating voids and internal damages inside the composites [8] resulting lower mechanical properties.

According to Bal [18], low improvement (49%) in flexural modulus value was found in case of 1 wt.% RTC samples in comparison to the RTC 0.75% (i.e. 60%) than neat epoxy (1682 MPa). Comparatively, in the present investigation, remarkable improvement was found in case of RTC CNF1.5 (50%) as well as in RTC CNF2 (83%) specimens. So the curing procedure followed in this study facilitates better dispersion for relatively higher concentration. Further investigation is however required for complete removal of agglomeration of CNFs for more than 2 wt.%.
5. Conclusion

This study investigated the influence of adding higher amount of carbon nanofibers on the mechanical and thermal properties of RTC and LTC epoxy composites. Flexural modulus was improved to 50% and 25% for CNF1.5 and 83% and 79% for CNF2 respectively. Storage modulus and glass transition temperature demonstrated improved results for these specimens attributing to good interfacial adhesion. The micrographs of fracture surface revealed the interfacial attachment of nanofibers and matrix in composites that supports the results obtained from mechanical and viscoelastic studies. On the contrary, CNF2.5 failed to show further improvement due to the appearance of aggregated phases in the composites evidenced by micrographs.

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