Effect of nano and macro carbon fillers on flexural properties of glass fiber/epoxy composite laminates

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Abstract. In this work, symmetrically designed glass fiber composites with epoxy matrices modified with multi wall carbon nanotubes (MWCNTs) and short carbon fiber fillers (SCFF) have been manufactured using hand layup technique assisted by press molding machine. The flexural test (three point bend test) was performed on MWCNTs reinforced and MWCNTs with short carbon fiber fillers (SCFF) or hybrid reinforced GFRP using Hounsfield H50KS universal testing machine at a strain rate of 1mm/ min. The result showed that the addition of nano and macro fillers (i.e. MWCNTs and SCFF) improved flexural strength of GFRP laminate. This increment is more evident in the case of composite filled with MWCNTs (0.5wt %) and SCFF (0.5wt %) both.

1. Introduction
Fiber reinforced polymer (FRP) composites have expanded markedly as high strength structural materials and they have found applicability in many industries such as aerospace, marine, automobile and military mainly due to their high stiffness to weight ratio and process ability easiness [1,2]. Wide researches in FRP composites have achieved excellent inplane properties of these materials. Still, these composites show poor out of plane performance that is dominated by the polymer matrix [3]. Thus, it is important in the field of composite to enrich the properties dominated by matrix. Many attempts have been made to improve the mechanical properties controlled by the matrix. The incorporation of different nano, micro and macro reinforcements (fillers) like MWCNTs, graphene, micro Al₂O₃, SiO₂, Ti₂O₃, short carbon fibers fillers (SCFF), nano clay etc into the polymer matrix of fiber reinforced polymer composites enables to maximise out of plane properties like bending strength and inter laminar shear strength. Ramesh et al. [4] found that addition of microparticles like Al₂O₃, SiO₂, Ti₂O₃ improve the ILSS and flexural strength. Since, CNTs have high stiffness (500GPa – 1000GPa) and strength (50GPa – 100GPa), diameter dependent specific surface area (SSA) of up to 1300m²/gm, high aspect ratio in the range of several thousand, high thermal conductivity and electrical conductivity [5], they have higher potential to enhance the mechanical properties of FRP. Prashant et al. [6] showed that the addition of 0.5wt % of MWCNTs in GFRP, improved the flexural strength by 44.22%, when compared to neat GFRP. Zhou et al. [7] found that the highest improvement in flexural strength of FRP on addition of 0.3wt % MWCNTs. Macro fillers have also been studied by various researchers. K.K. Singh et al. [8] found that SCFF upto 1wt % has increased the flexural strength fairly.
In this research, a comparative study on flexural properties with nano and macro fillers altogether has been made. Three samples were prepared as (1) neat GFRP, (2) MWCNTS reinforced GFRP and (3) MWCNTS with SCFF or hybrid reinforced GFRP. The hand layup technique is used with the assistance of hydraulic press molding to cure the composite laminate.

2. Manufacturing of composite

Various materials used along with their characteristics, producer and supplier are shown in table 1.

| Serial No. | Material         | Characteristics                                      | Producer       | Supplier                      |
|-----------|------------------|------------------------------------------------------|----------------|------------------------------|
| 1         | Plain woven glass fabric | Nominal weight= 600 GSM, Primary Reinforcement       | Vetrotex       | M.S. Industries, Kolkata     |
| 2         | MWCNTS           | Length: 10 micron, Thickness: 5-10 nm, purity: 98%   | United nanotech innovations private limited |
| 3         | Plain woven carbon fiber | Chopped length: 5- 10 mm, Secondary reinforcement | VetrotexIndia Limited | M.S. Industries, Kolkata     |
| 4         | Bisphenol-A      | Bis (2- Brand name: Lapox K-6 ethyl) (AN312)         | Atul limited, Valsad, Gujrat, India |
| 5         | N-N' - Bis (2- amino ethane -1-2-diamine hardener) |                        |                |                              |

The technique used to prepare symmetrically designed quasi isotropic GFRP laminates of the stacking sequence of 

\[
[(0,90)/(+45,-45)/(+45,-45)/(0,90) // (0,90)/(+45,-45)/(+45,-45)/(0,90)]
\]

was hand layup technique assisted by the hydraulic press as shown in figure 1.

![Figure 1: (a) Ply stacking sequence of the laminate, (b) Various components of press molding machine.](image)
Firstly, the glass woven was cut in two orientations i.e. (0, 90) and (+45, -45). To prepare laminate without any secondary reinforcement, the thermosetting epoxy was mixed with the hardener in the ratio of 10:1 (as recommended by the supplier) while for laminates with MWCNTs, weighted quantity of the same was mixed in epoxy using ultra sonic bath for 1 hour and further hardener was mixed. Then stirring of solution was done for 15 minutes using high speed stirrer at 1300 rpm. In order to manufacture composite laminates, the woven glass sheet was kept on flat surface and wetting (using resin) of glass fiber sheet was done with the help of brush. Then, second fiber layer was kept on the first and brushing action was repeated. In order to remove excess resin, a heavy iron roller was rolled over wet woven sheets. This process was repeated up to eight layers proposed design laminate. Finally, in order to remove the maximum amount of epoxy resin and to cure the laminate, the wet layered laminate was placed in hydraulic press molding machine at the load of 200KN. Furthermore, for preparing hybrid GFRP reinforced with MWCNTs and SCFF, seven equal weights of SCFF were added manually and randomly between each layer.

Thus, three composite laminates were prepared. For each composite laminate, three specimen were cut using diamond cutter as shown in figure 2 with dimensions as per ASTM D7264.

![Figure 2: Samples tested for the three point bending test.](image)

3. Mechanical testing

Bending tests of the manufactured composites were carried out using a fully computerized Hounsfield H50KS universal testing machine having maximum load carrying capacity of 50KN and loading rate varied from 0.01mm/min to 50mm/min as shown in figure 3. A maximum of three tests were conducted for each composite laminate. All tests were conducted at a strain rate of 1 mm/min. The maximum flexural stress and flexural chord modulus of elasticity were calculated using the formulae listed below as per ASTM D7264 [9]. Figure 3 shows the fixture setup used for the flexural test and sample undergoing the test.

\[
\sigma = \frac{3PxL}{2bh^2} \\
E_{chord} = \frac{\Delta \sigma}{\Delta \varepsilon} \\
S_{n-1} = \sqrt{\left(\sum_{i=1}^{n} x_i^2 - n(\bar{x})^2\right)/(n - 1)}
\]

(1)  
(2)  
(3)  

Where,
\[ \sigma = \text{Stress at the outer surface of mid span, MPa} \]
\[ P = \text{Applied force, N} \]
\[ L = \text{Support span, mm} \]
\[ h = \text{Thickness of specimen, mm} \]
\[ b = \text{width of specimen, mm} \]
\[ E^\text{Chord} = \text{Flexural chord modulus of elasticity, MPa} \]
\[ \Delta\sigma = \text{Difference in flexural stress between the two selected strain points, MPa} \]
\[ \Delta\varepsilon = \text{Difference between the two selected strain points} \]
\[ n = \text{Number of specimens} \]
\[ \bar{x} = \text{Sample mean (average)} \]
\[ s_{n-1} = \text{Sample standard deviation} \]
\[ x_i = \text{Measured property} \]

Figure 3.(a) Fixture setup for flexural test as per ASTM D2344, (b) Sample undergoing flexural test.

4. Result and discussion
Load vs displacement curves were converted into stress vs strain curves by substituting the value of the load, deflection and dimensions in the formulae mentioned earlier as per ASTM D7264. Stress vs Strain curves obtained are shown in figure 4. And individual & average flexural properties along with estimated standard deviations are presented in table 2.

Table 2: Flexural properties of the tested specimen.

| Name | Specimen serial no. | Flexural strength, MPa | Average Flexural strength, GPa | SD in Flexural strength | Flexural modulus, GPa | Average Flexural Modulus, GPa | SD in flexural modulus |
|------|---------------------|------------------------|-------------------------------|------------------------|----------------------|-------------------------------|------------------------|
| Neat | 1                   | 315.67                 | 315.43                        | 4.97                   | 16.909               | 16.326                        | 0.8703                 |
|      | 2                   | 320.28                 |                               |                        |                      |                               |                        |
|      | 3                   | 310.344                |                               |                        |                      |                               |                        |
| MWCNT| 1                   | 348.87                 | 330.91                        | 15.64                  | 16.929               | 17.136                        | 0.4461                 |
|      | 2                   | 320.22                 |                               |                        |                      |                               |                        |
|      | 3                   | 323.665                |                               |                        |                      |                               |                        |
| MWCNT+SCFF | 1                   | 367.78                 |                               |                        |                      |                               |                        |
|      | 2                   | 385.72                 | 358.15                        | 33.43                  | 21.4301              | 20.225                        | 1.04798                |
|      | 3                   | 320.96                 |                               |                        |                      |                               |                        |
Figure 4: Stress Strain curves of (a) Neat GFRP, (b) MWCNTs/Epoxy GFRP, (c) Hybrid MWCNT/SCFF/Epoxy GFRP and (d) all specimens under flexural test.

The curves show a large linear behavior followed by a zone of irregularities which may be due to fiber breakage and delamination of lamina during loading. ‘Pinging’ sounds were heard indicating the same.

On analyzing and comparing, it is found that the average flexural strength of hybrid MWCNTs/SCFF modified specimen to be maximum and is equal to 358.15 MPa which is 13.54% higher than that of neat GFRP. It can be credited to the fact that addition of MWCNTs provides a mechanism of matrix strengthening such as crack bridging phenomenon [10]. Also, both MWCNTs and SCFF increase the strength of epoxy matrix as they are very stiffer as compared to epoxy. Their strength are also significantly higher than the strength of glass fiber.
The average flexural strength of 1wt % MWCNTS modified laminate is equal to 330.91 MPa which is 4.91% higher than that of neat specimen. It is lower than that of MWCNTS/SCFF modified GFRP laminate by 7.61%. This is because the effective load transfer from matrix to nanofillers happens only when there is a good dispersion of MWCNTS in matrix [11] which may not so in case of specimen containing 1wt % of MWCNTS resulting in the formation of agglomeration. Appropriate dispersion is there in the hybrid MWCNTS/SCFF GFRP laminate containing 0.5wt % MWCNTS only.

4. Conclusions

A systematic study was carried out to analyse the effect of nano (MWCNTS) and macro (SCFF) carbon fillers on flexural performance of glass fiber reinforced composite laminate. Following conclusions can be drawn from the present study:

1. MWCNTS alone and MWCNTS & short carbon fiber fillers (SCFF) both improve the flexural strength of composite laminate when compared to neat GFFP.
2. Reinforcing GFRP with both 0.5wt % MWCNTS & 0.5wt % SCFF is more effective than with 1wt % MWCNTS only.
3. Addition of MWCNTS optimizes the flexural strength only when there is a good dispersion of carbon nanotubes in epoxy resin.

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