Role Of Surface Modification Of MWCNTs To Improve Mechanical Properties Of Three-Phased GFRP Composite Laminate

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Abstract:

Fiber reinforced polymer composites are highly recommended as light-weighted materials. When these materials are embedded with nanoparticles like multiwall carbon nanotubes, show improvement in mechanical properties. The reason for this improvement is formation of micro-bridging at interfaces of MWCNTs/epoxy and MWCNTs/fiber/epoxy. In this paper, in-house produced MWCNTs by arc discharge method (surface modified and unmodified MWCNTs) are doped with quasi-isotropic GFRP composite. The three samples neat, unmodified MWCNTs-GFRP and modified MWCNTs-GFRP laminates are tested for SBS and flexure properties. Composite laminate is prepared with hand layup technique assisted with vacuum bagging method at 650 mm of Hg pressure. The results of the study justified that the surface modification helps in improving micro-bridging in-between the constituents of composites. Thus, help in better load transfer mechanism.

Keywords: MWCNTs, arc discharge method, GFRP, SBS and flexural testing.

1. Introduction

FRP laminates are used in light weight and high performance structural materials due to its high strength to weight ratio. GFRP laminates are extensively used in various fields such as ship structures, automobile door panels and etc…, because of low cost and better impact damage resistance properties. In 1991 Sumio Ijima discovered the small needle like structures known as carbon nanotubes (CNTs) [1]. These materials shows incredible material properties such high strength upto 1TPa and along with this reason these materials have low density and high aspect ratio. Thus, these materials can be used as secondary reinforcing materials in composite materials to enhance the mechanical strength. Since, CNTs surface is highly inactive it is necessary to activate its surface. Various methods and chemicals are available to modify the CNTs surface but in most of the cases its surface gets distorted.

V Datsyu et. al. [2] modified the CNTs surface using nitric acid solution and ammonium hydroxide solution. From SEM and thermogravimetric analysis it was found that the CNTs treated with nitric acid with a mixture of hydrogen chloride and hydrogen peroxide yielded damaged surface than the basic agents of ammonium hydorixide treatment with hydrogen peroxide**.** Yun Peng et. al. [3] modified the MWCNTs with hydrogen peroxide and found about 46% of atomic in four days of oxidation. Detailed study of CNTs behavior under hydrogen peroxide treatment was carried out by [4-6]. Kim et al [7] studied the electrical conductivity of epoxy polymer reinforced with MWCNTs and found improved electrical conductivity. Here, authors modified the MWCNTs surface with ammonium hybdroxide/hydrogen peroxide solution where, little damage to the MWCNTs structure was observed. Ziegler et. al. [8] studied MWCNTs surface modification with sulphuric acid and hydrogen peroxide solution and found shortening of MWCNTs length. Several studies [9-11] showed the negative side effects of the acidic oxidative treatment of MWCNTs.

Addition of MWCNTs in fiber reinforced composites improves the interlaminar strength and reduces delamination. This improvement is due to better load transfer capacity by the matrix material to fiber and detailed study of improvement in interlaminar shear strength is carried out by [12-14]. Prashant Rawat et. al. [15] investigated the shear and bending performance of GFRP when doped with MWCNTs and at 0.5wt.% of MWCNTs results showed 13.66% and 44.22% enhancement when compared to neat GFRP laminate.

In this work MWCNTs surface is modified with hydrogen peroxide and doped with GFRP laminates at 2wt.% then results are compared with neat and pristine MWCNTs doped GFRP laminates under three point loading condition.

2. Materials and fabrication

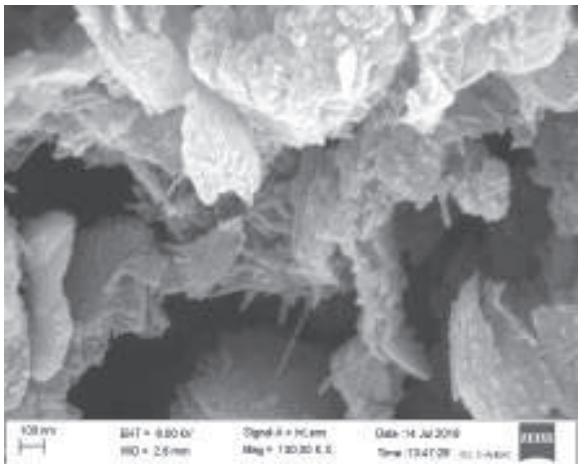
2.1 Materials Used:

Bidirectional plain woven 600GSM glass fibers are procured M. S. Industries, Kolkata, India. Bisphenol A and K-6 are supplied from Atul Industries Gujurat, India. MWCNTs are manufactured using in house arc discharge method.

2.2 Fabrication

2.2.1 Arch discharge method

MWCNTs are fabricated using arc discharge method using 99.9% pure graphite electrode rods by connecting to an AC current [16]. Then soot obtained from the arcing is crushed and heated at 620-680^{0}C for 60minutes. Further, stirred it on a magnetic stirrer and impurities are removed by washing it with toluene for about 300-330minutes. Washed MWCNTs are heated in an air oven at 80-120^{0}C. Quality of synthesized MWCNTs are checked by field emission scanning electron microscope (FESEM) and x-ray diffraction spectroscopy (XRD) (Fig. 1 (a) and (b)).



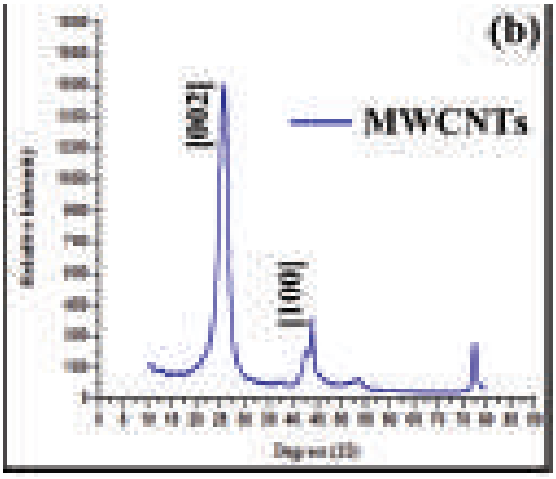


Figure 1: Synthesized MWCNTs (a) FESEM (b) XRD

3. Surface modification and dispersion of MWCNTs in epoxy

MWCNTs surface modification helps in better formation of bonding with epoxy. Here, MWCNTs are initially washed with ethanol and then washed with distilled water. Then washed MWCNTs are dried in an oven at an elevated temperature. Finally, dried MWCNTs are treated with hydrogen peroxide for about one hour. At the end of the reaction MWCNTs surface are modified with –OH and –COOH groups on it (Fig. 2). This helps in better formation of bonding with epoxy material which intern influence the strength of the FRP laminate. Surface modification of MWCNTs is confirmed by FESEM (Fig. 3).



Figure 2: Schematic Diagram of Surface Modification of MWCNTs

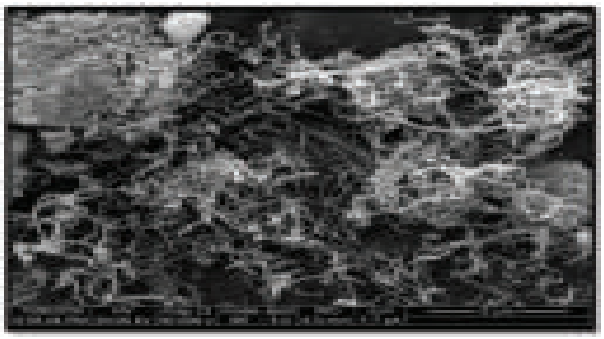


Figure 3: FESEM of Surface Modified MWCNTs

2.2.3 Laminate Preparation

Laminates are fabricated by vacuum bagging method assisted by hand lay-up method. Plies are placed one by one according to $[(0/90)/(+45/-45)/(+45/-45)/(0/90)]_S$ laminate design after applying MWCNTs doped resin mixture. Figure 4 shows brief procedure involved in preparing the laminate.

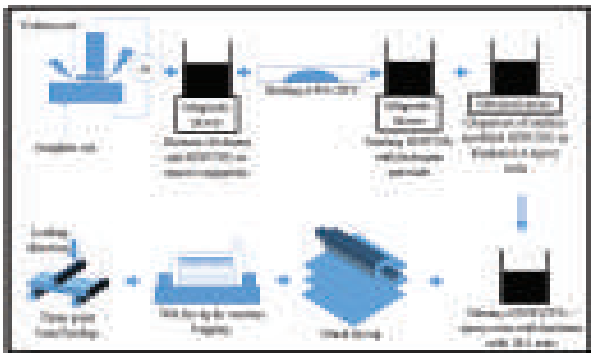


Figure 4: Detailed fabrication process of GFRP laminate

4. Experimentation

3.1 Flexural

This test is conducted on three point bend test according to ASTM D7264/D7264M standard [17]. Sample specification is as shown figure 5. In this analysis span to thickness ratio is equal to 16.

$$\sigma = \frac{3PL}{2bh^2}$$

Where,

ó = Stress at outer Surface at Mid Span (MPa)

P = Applied Force (N)

L = Support Span (mm)

b = Width of Beam (mm)

h = Thickness of Beam (mm)

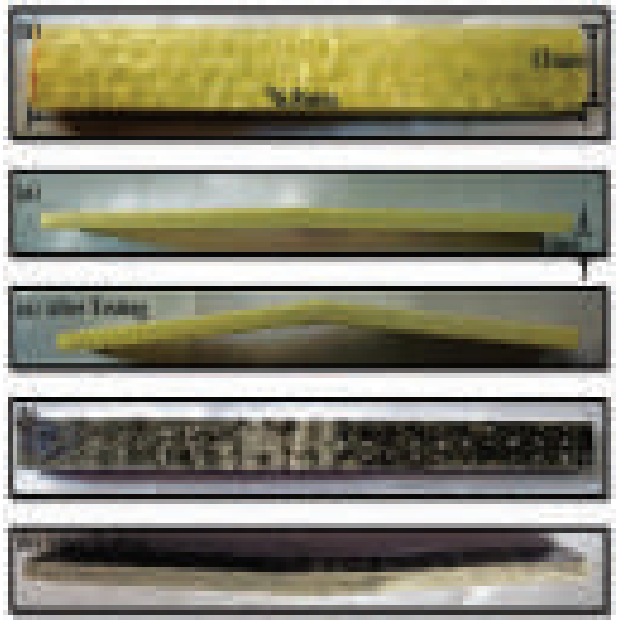


Figure 5: Flexural Sample according to ASTM D7264 (a) Neat GFRP (b) Tested Sample (c) 2wt.% MWCNTs Doped GFRP

3.2 Short Beam Shear Strength

ASTM D2344/D2344M standard is used to conduct the test on three point bend fixture [18]. Sample size is shown in figure 6.

$$F^{SBS} = 0.75 * \left(\frac{P_m}{b * h}\right)$$

Where,

F^{SBS} = Short Beam Strength (MPa)

P_m = Maximum Load Observed during the Testing (N)

b = Measured Specimen Width (mm)

h = Measured Specimen Thickness (mm)

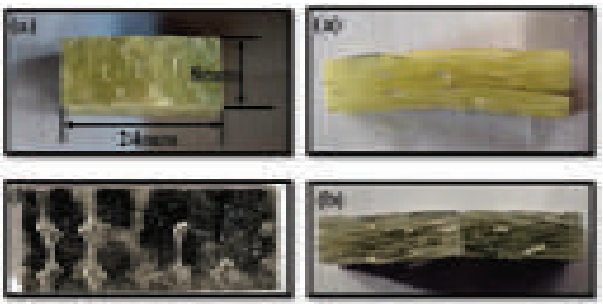


Figure 6: SBS Sample according ASTM D2344 (a) Neat GFRP (b) 2wt.% Surface Modified MWCNTs Doped GFRP

5. Results and Discussion

Figure 7 and 8 shows force vs extension for short beam shear and flexural strength respectively. From figure 10 it is observed that 2wt.% doped MWCNTs performed better than neat GFRP laminate as well as pristine MWCNTs doped GFRP under both flexural as well as short beam shear loading conditions. Flexural strength for neat pristine MWCNTs and surface modified MWCNTs doped GFRP are found to be 155.53, 171.092 and 188.109MPa respectively. While short beam strength is found to be 15.1451, 16.425 and 18.7925MPa for neat, pristine and surface modified MWCNTs doped GFRP laminate. Increase in strength is mainly due to the presence of MWCNTs which helps in better load transfer between matrix and glass fiber. Moreover, functionalization helps establishing a better communication between matrix and MWCNTs as well as fiber and MWCNTs. Improvement in strength is also attributed by crack arrest during the propagation by the MWCNTs which increases the delamination, interlamination and shear properties of the laminate.

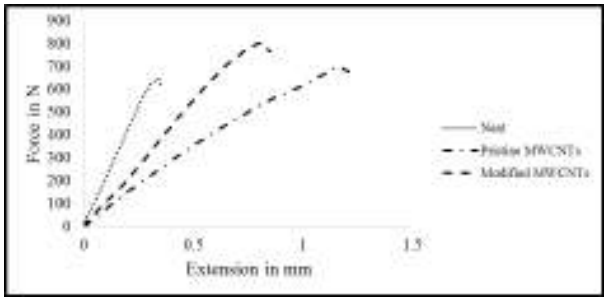


Figure: 7 Force vs Extension Results of Short Beam Shear Strength

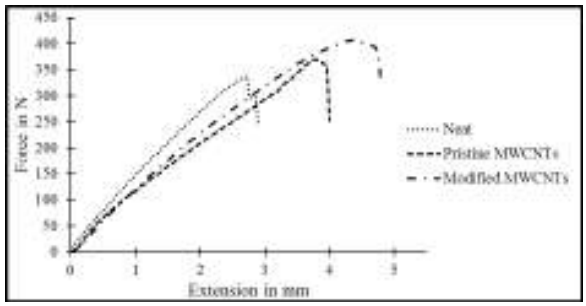


Figure 8: Force vs Extension Results of Flexural Strength

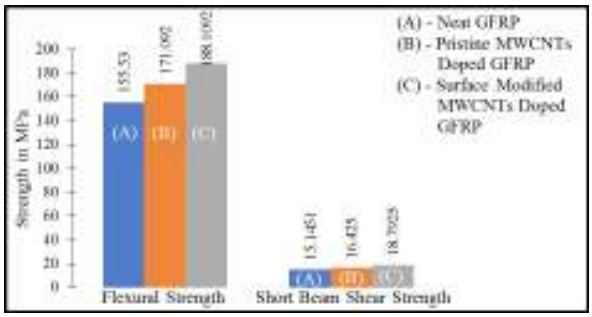


Figure 9: Results of Flexural and Short Beam Shear Strength

6. Conclusion

In this work MWCNTs are synthesized using in house arc discharge method. Then, MWCNTs surfaces are modified using hydrogen peroxide. To investigate the influence of surface modification effect on flexural and short beam shear strength is carried out on three point bend test. From experimental results 19.40% and 12.59% enhancement is observed for surface modified MWCNTs doped GFRP laminate when compared to neat and pristine MWCNTs doped GFRP laminate in case of short beam shear strength. While 17.31% and 9.04% improvement is observed in case of surface modified MWCNTs doped GFRP laminate when compared to neat and pristine MWCNTs doped GFRP laminate for flexural strength. This enhancement is may be due to improved load transfer between resin and fiber which is caused by enhanced bonding between them aided by surface modification of MWCNTs. Moreover, MWCNTs constrained the crack growth, improved the interlaminar strength and reduced the delamination between the plies.

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