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Functionalized carbon nanotubes *(F-CNTs)* Integration on Glass fiber by Solution Dip coating and Characterization via Nano-indentation

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ABSTRACT

This work deals with processing of Carbon nano tubes through different chemicals in order to improve its interaction abilities. Similarly, the processed Carbon nano tubes - Functionalized Carbon nanotubes are fabricated on Glass fiber by Solution Dip coating method. Different experimental variables-temperature, Concentration, soaking time, Agitation speed- were changed for better deposition of the nano particles on the Glass fiber. The processed Glass fiber were cut into proper dimension to form different laminates. The laminates were joined with each other through epoxy-resins- to form a composite product. Different characterization tests of the composite were conducted in order to know about the properties of the composite material. The results of the test manifested that increasing the concentration of the *F*-CNTs and number of layers of Glass fiber the strength of the composite material enhances. The composite can be utilized in different industries i.e. aerospace, sports goods, Automobile, Wind Turbine Blades.

Keywords:

Functionalized Carbon nanotubes (*F-CNTs*)
Glass fiber
Epoxy
Nano- indentation

1. Introduction

Carbon nanotubes (CNTs) are thin sheets of graphene which were discovered in 1991. The rolling of graphene sheets in single walled CNTs exist in various forms i.e. Armchair, Zigzag, and Chair shaped. The CNTs can be wrapped into different forms that results in changing its structure and electronic properties. The CNTs exist in single sheet-Single Walled nanotubes (SWNT) or multiple sheets-multi Walled nanotubes (MWNTs) form. SWNT possess single cylindrical structure that ranges in diameter of 0.5-0.2 nm, having length in the range of 50-150μm .Similarly, it possess micro-porous surface with surface area that ranges up to 1300 m^2/g(outer surface).SWNTs have strong mechanical and electrical behaviors. The electrical properties depends on two factors: Tube diameter, Helicity. The presence of Electrical conductivity, surface curvature make the CNTs different than Activated carbon. MWNTs are formed by placing several SWNTs concentric. The concentric spacing of the wall is kept 0.34nm.Similarly, MWCNTs possess an outer diameter of 2-100nm which depend on the number of coaxial tubes present in it. As compare to SWNTs, MWNTs are more stable [1]. Carbon nanotubes are prepared by number of ways.

Different methods used to manufacture the composite include; Electric Arc discharge, Laser Ablation, and Chemical vapor deposition. Electric Arc discharge is the most efficient method used to manufacture CNTs. In this method, current is passed between two electrodes of graphite. The anode possess metallic oxide catalysts (Ni, Co, Fe, -oxides). Helium, Argon or Methane is provided for making the environment cold for synthesis of CNTs. The nature of electrodes, Current amount, and Catalyst quality of CNTs. In Laser ablation, graphite rod is hit by Laser in an inert gas environment that sublimes the graphite where the vapors are recollected to get CNTs. Pyrolysis of Hydrocarbons (Propane, Butane, Hexane, Benzene, and Toluene) is the most used method for getting CNTs. It is also known to be Chemical Vapor Deposition method. In this method CNTs are produced in enormous quantity at temperature range of 500-1300 $C^{\cdot}$ in presence of catalysts (Ni, Co, Fe).In this process, initially, the vapors are dissociated and saturated in metal nano-particles. Afterwards, the vapors are precipitated. The catalysts used in this process act as a nucleation sites .Metallic catalysts not only provide space for deposition of vapors but also play role in decomposition of hydro-carbon. The vapors are deposited on the catalyst in Root Growth manner or Tip growth manner [2].

1.1. Functionalization of CNTs

CNTs possess a variety of impurities, catalyst particles, that need a separate step of purification which not only make the process more complex but also less economical [3]. In addition to it, In order to improve the interaction of the Carbon nanotubes, CNTs are treated either physically (Covalent) or chemically (non-covalent) in order to improve its surface which is known as Functionalization.

1.2. NonCovalent functionalization

This method involve adsorption or wrapping of polymer to CNT surface. The polymer and the CNTs interact via π-π-interaction [4]. Non-covalent functionalization does not affect the structure of the aromatic ring of CNTs. Beside polymer surfactants, sodium dodecyl benzene sulfonate are also used for non-covalent functionalization. This method effects the side walls but it does not oxidize CNTs up to great extent.

1.3. Covalent Functionalization

Covalent functionalization oxidizes CNTs up to greater extent as compare to Non-covalent functionalization. As the end caps of CNTs are more reactive than the side walls, therefore, the side walls need proper treatment, in order, to improve its reactivity. For this purpose, CNTs are treated with chemicals having functional groups: -COOH, $-NO_2$,-OH, -H,=O,HNO_3,H_2SO_4 as they change the sp^2 hybridization into sp^3 [3]. However the major concerns of this method includes the surface damage of CNTs during Ultra-sonication and its length breakage, resulting in degradation of its mechanical properties. Similarly, the chemicals damage the surface as they are either not easy to be used, or they may have a weak interaction with polymer matrix or may have a re-agglomeration with the matrix [5].

1.4. Friedel-Crafts Acylation

In order to get rid of the aforementioned defects, Acylation is the most recent process to prepare functionalized CNTs, via Frieda-Crafts Acylation technique [6]. The attached groups alter the nature of the CNTs from Hydrophobic to Hydrophilic resulting in increase in the interaction and alignment of CNTs with other substances, without effecting and altering the shape and structure of CNTs [7]. With such improved interaction of *F-CNTs*, it is widely used in manufacturing nano-composites.

1.5. Carbon nanotube and Glass fiber composites

Glass fibers are widely used as reinforcement material because of their low cost, more reliabilities and availabilities in manufacturing composites like shopped strand mat, and woven fiber because of its high stiffness, strength, good chemical and thermal resistance [8, 9].Such fibrous materials are usually doped with nano-fillers and reinforced with polymeric matrix as it result in high strength, good electrochemical behavior [10]. Functionalized Carbon Nano-tubes are efficient fillers in this regard as they possess strength of 22GPa and Young modulus of 1TPa [11].Various conventional techniques are used for manufacturing the *F-CNTs* nano-composites. As, In Melt processing the polymer is blended with CNTs .Shear mixing is carried out in order to disperse the nano-fillers on substrate efficiently. Similarly, In Situ polymerization the changes are brought at the monomer level resulting in a nano-composite material [5]. Bin Hai, and Peng-Cheng Mai used Electrophoretic deposition to manufacture a composite of CNTs , graphene and Glass fibers by depositing the nano-fillers on the substrate using electric current and electrodes[1]. Delong, Benue, and Hang experimented by depositing CNTs on Glass fiber by Chemical Vapor deposition (CVD) [12]. Similarly, Solution mixing method was carried out to embed CNTs into polymeric matrix [13].Furthermore, Rapid nano welding of carbon nanotubes by electrical and thermal shocks witness coating of CNTs on Glass fiber [14]. However, all the conventional techniques have various drawbacks that effect the factors responsible for efficient functioning of the composite materials, including Improper alignment, interaction and dispersion of CNTs on the substrate material resulting in malfunctioning of the composite including; Delamination, micro-cracking, and fiber breaking of the composite material [1, 12, 15-19]. Therefore, to overcome the flaws associated with conventional techniques, the solution Dip coating method is an appropriate method to follow for manufacturing *F-CNTs* and epoxy (Glass fiber) composite. These F-*CNTs* based Glass fibers have the potential to be utilized in light weight, automotive product, fuel cells, Satellite, Armor and Sports.

2. Methodology

Initially, Carbon nano tubes were treated with different chemicals(Benzene-ticarbo-oxallic acid(BTC), Poly-phosphoric acid(PPA), Phosphorus penta oxide(P_2O_5) in order to carryout its Fnctionalization which increases

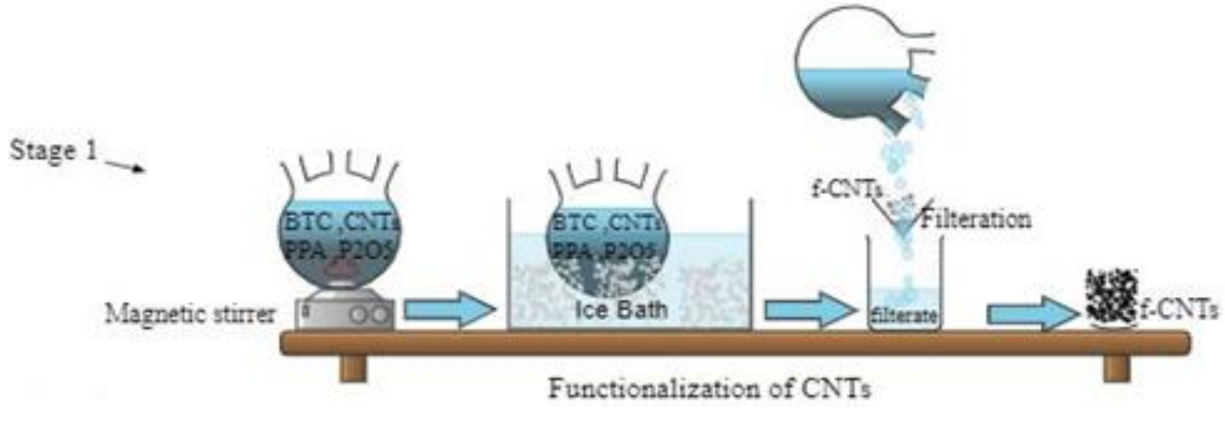

Fig. 01: Functionalization of CNTs

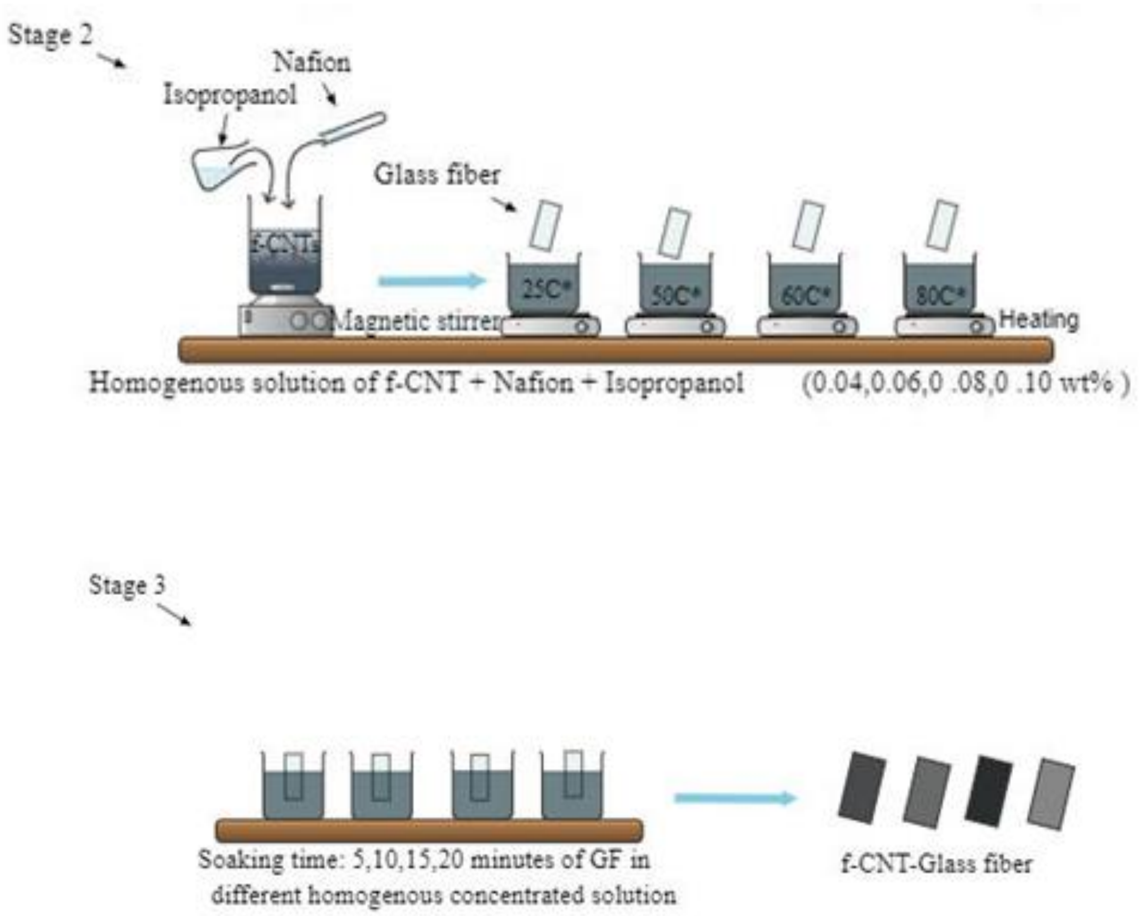

Fig. 02: Solution Dip Coating Process(stage 2, stage 3)

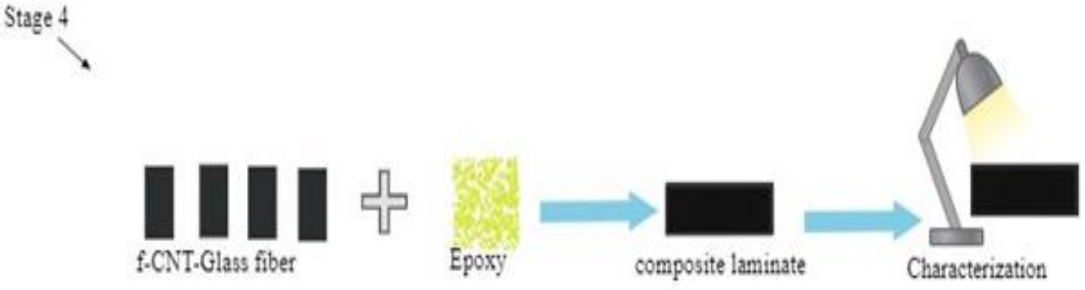

Fig. 03: Characterization of the composite

its interaction and dispersion abilities. Secondly, solution dip coating method was used for fabricating the Glass fiber with the Functionalized Carbon nanotubes. The treated carbon nano tubes were fabricated onto the glass fiber surface by manupulating different experimental variables; Agitation speed, Concentration of Functionalized Carbon nanotubes (*F*-CNTs) , Soaking time, and Temperature. The processed glass fiber sheets were cut into different laminates form .Different number of laminates were selected. They were joind *via* resin in order to form a strong composite. The composite was cured for some time. Once the product samples were ready they were tested via different tests which showed the improved abilities of the composite. A schematic series of experimental work is depicted in figs. 01-03.

3. Results

Cylindrical Samples with requirements of Length and diameter to be 1cm and 2cm inches were prepared for crushing test (fig. 04).

Fig. 04: *f*-CNT-Glass fiber composite

The samples were tested via Universal testing machine (model number UH-200A, Capacity of 200tons).The pinnacle plate of UTM was impacted at different impact rate on the sample. Loading impact was continued over the sample till it crashed/fractured. On such occasion the UTM machine showed the maximum value of compressive load at which the sample fractured. The UTM analysis shows the increasing strength of the composite material as depicted in fig. 05.

The instrument used for nanoindentation was Nanoscope IIIa scanning probe microscope equiped with a dimension 3100 AFM head and with a Hysitron TriboScope nanoindentor head. The nanoindentor samples were glued on a steel stage where a particullar load was applied for a particullar span of time . With the help of Berkovich indenter the load was applied over the sample for a particular period of time. The Nano indentation manifested the improved Modullus of the composite (Fig. 06).

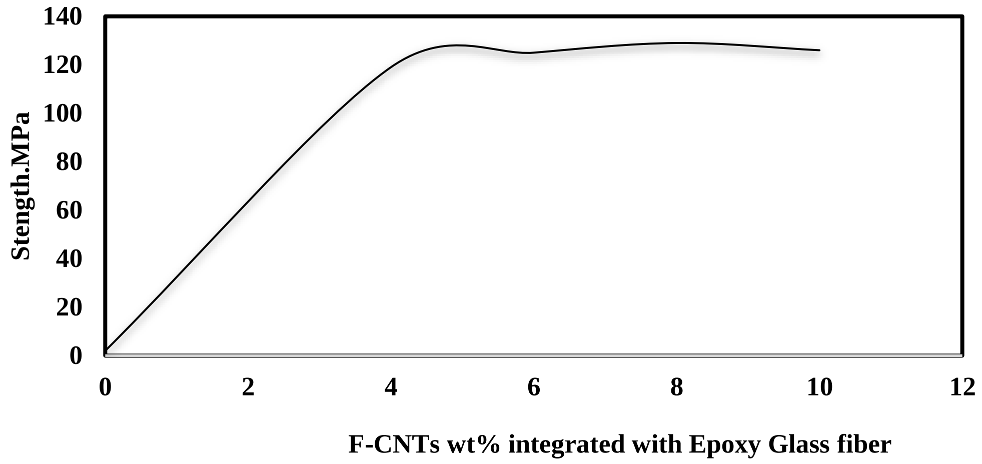

Fig. 05: Strength of the *F-CNTs* glass fiber composite

4. Conclusion

This work evaluate the processing of *F-CNTs* by Solution Dip coating method for manufacturing *F-CNTs* and epoxy (Glass fiber) composite. The said method improves the factors responsible for better functioning of the composite i.e. Dispersion, alignment and interaction of *F-CNTs* with epoxy (Glass fiber). The product composite formed is tested via several characterization tests. The results manifested that increasing the concentration of *F-CNTs* on glass fiber enhances the properties-strength, E-Modulus- of the composite material. With such high strength properties the composite can be utilized in Aerospace, sports, Automotive Product, Satellite etc.

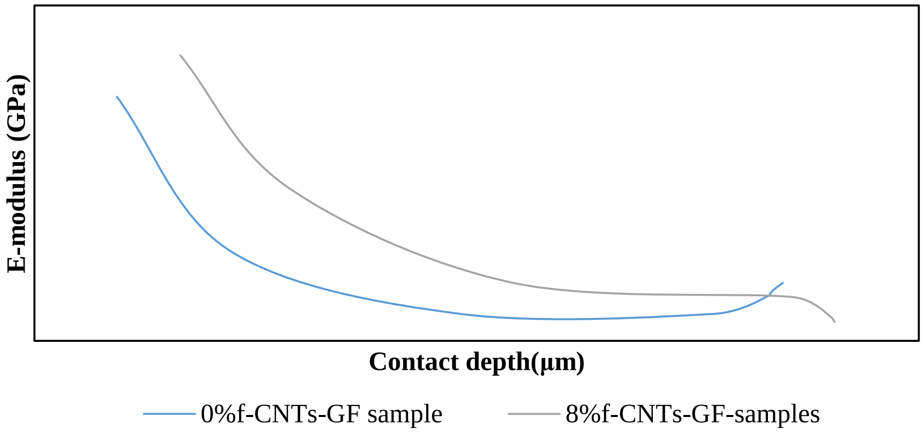

Fig. 06: E-Modullus as a function of Contact Depth

References

1. Bin Hao and *et al.*. Comparative Study On Monitoring Structural Defects In Frps Using Glass Fibers With Carbon Nanotubes And Graphene Coating. Conference, 2015.
2. Gogotsi, Y., Nanomaterials Handbook 2017. 2nd Edition.
3. In-Yup Jeon and *et al.*. Functionalization Of Carbon Nanotubes. *Carbon Nanotubes (Polymer Nanocomposites),* 2011.
4. Díez-Pascual, A.M., Chemical Functionalization Of Carbon Nanotubes With Polymers. *Macromol*, 2021: P. 64–83.
5. Garima Mittal and *et al.*. A Review On Carbon Nanotubes And Graphene As Fillers In Reinforced Polymer Nanocomposites. *Journal Of Industrial And Engineering Chemistry*, 2014: P. 18.
6. Chang D. and *et al.*. Mild And Nondestructive Chemical Modification Of Carbon Nanotubes (Cnts): Direct Friedel-Crafts Acylation Reaction. *Physical And Chemical Properties Of Carbon Nanotubes*, 2013.
7. Zhang J. and *et al.*. Functional Interphases With Multi-Walled Carbon Nanotubes In Glass Fibre/Epoxy Composites. *Carbon*, 2010. 48: P. 2273-2281.
8. Ramlee R. and *et al.*. Properties Of Glass Fiber-Carbon Nanotube (Cnt)/Epoxy Composites. *Journal Of Polymer Materials,* 2013. 30: P. 103-116
9. Tang X. and *et al.*. Dip-Coating For Fibrous Materials: Mechanism, Methods And Applications. *Sol-Gel Sci Technol*, 2017. 81.
10. Wang L. and *et al.*. Enhancing The Mechanical Performance Of Glass Fiber-Reinforced Polymer Composites Using Multi-Walled Carbon *Nanotubes. Advance Engineering Material*, 2020.
11. Mahato K. K. and *et al.*. Tensile Behavior Of Mwcnt Enhanced Glass Fiber Reinforced Polymeric Composites At Various Crosshead Speeds. *Iop Conf. Series: Materials Science And Engineering*, 2017. 178 012006.
12. He D. and *et al.*. Design Of Electrically Conductive Structural Composites By Modulating Aligned CVD-Grown Carbon Nanotube Length On Glass Fibers. ACS Appl. Mater. Interfaces, 2017. 9, 3: P. 2948–2958.
13. Rane A. V. and *et al.*. Methods For Synthesis Of Nanoparticles And Fabrication Of Nanocomposites. *Synthesis of Inorganic Nanomaterials*, 2018: P. 121-139.

14. Shang Y. and *et al.*. Rapid Nano-Welding Of Carbon Coatings Onto Glass Fibers By Electrothermal Shock. *Applied Materials And Interfaces*, 2020.
15. Warrier A. and *et al.*. The Effect Of Adding Carbon Nanotubes To Glass/Epoxy Composites In The Fibre Sizing And/Or The Matrix. *Composites Part A: Applied Science and Manufacturing,* 2010. 41: P. 532–538.
16. Jamnani B. D. and *et al.*. Grafting Carbon Nanotubes On Glass Fiber By Dip Coating Technique To Enhance Tensile And Interfacial Shear Strength. *Journal Of Nanomaterials*, 2015. 2015: P. 7
17. Liu F. and *et al.*. Mechanical Properties Of Epoxy And Its Carbon Fiber Composites Modified By Nanoparticles. *Journal Of Nanomaterials*, 2017. 2017: P. 10.
18. Tehrania M. and *et al.*. Integration Of Carbon Nanotubes Into A Fiberglass Reinforced Polymer Composite And Its Effects On Electromagnetic Shielding And Mechanical Properties. *IMECE,* 2013: P. 7.
19. Rathinasabapathi G. and *et al.*. Exploration Of Nano Fillers (Multi Walled Carbon Nano Tubes And Graphene Powders) In The Reinforcement Of Epoxy/Glass Fibre Polymers (GFRP). *International Journal Of Innovative Technology And Exploring Engineering*, 2019. 8(12): P. 5.