Synergetic Impact of carbon nanotube and/or graphene reinforcement on the mechanical performance of glass fiber/epoxy composite

Krishna Chaitanya Nuli*, Abhinav Omprakash Fulmali, Nagesh, Bhaskar Sen, Rajesh Kumar Prusty, Bankim Chandra Ray

FRP Composite Laboratory, Department of Metallurgical and Materials Engineering, National Institute of Technology, Rourkela-769008, India

**Email id:* krish.n928@gmail.com

Abstract

The exceptional and distinctive properties of the allotropes of carbonaceous nanomaterials like carbon nanotubes and graphene have attracted many researchers and engineers to enhance the performance of fibrous polymeric composites. This article extrapolates the synergetic impact of carbon nanotube (CNT) and multi-layered graphene (MLG) reinforcement onto the mechanical performance of glass fiber/epoxy composites. Magnetic stirring and ultra-sonication process have been carried out under optimized parameters for incorporation of CNT-MLG into the epoxy polymer. Incorporation of 0.1wt% of carbon nanotube to the glass fiber/epoxy composites enhances a flexural strength of 10% and addition of 0.1 wt. % of multi layered graphene to the glass fiber/ epoxy composites enhances a flexural strength of 6% when differentiated with neat GE. Embodiment of 0.1 wt. % carbon nanotube and multi-layer graphene to the glass fiber/epoxy composites in three different ratios like 1:1, 1:2 and 2:1 showcases a 13%, 12.25% and 14.7% enhancement in the flexural strength respectively with respect to the neat glass fiber/epoxy composites when tested at room temperature. Among them, the ratio 2:1(CNT: MLG) contributes higher strength due to the combined action of high aspect ratio of CNT and higher specific surface area of multi-layered graphene thus, facilitating efficient stress transfer from matrix to the reinforcements. Thermal characterization have been carried out using differential scanning calorimetry (DSC). The fractography of the samples is examined through the scanning electron microscope.

Keywords: Carbon nanotube, multi-layered graphene, FRP composite.

1. Introduction

In recent times, Fiber reinforced polymer (FRP) Composites are increasingly used in advanced engineering structures for various applications like in marine, structural and industrial sectors [1]. These applications demand materials with multifunctional properties like high strength as well as durability, good electrical and thermomechanical properties. Fiber reinforced polymer Composites serves in most of these applications but due to their poor out of the plane properties, these can't sustain loads in transverse direction which limits their utility. Additionally these composites fail due to various failure modes and hence for high stress applications, certain modifications of either the matrix, the fiber or both is required[2–4]. Various nanofillers are used for the embedding in the polymer resin for improving the performance of the FRP composites. Though these nanofillers mostly seem to have positive impact on the properties but they also have limitations and under certain environmental conditions may prove to be harmful. Nanofillers like Carbon nanotubes (CNT) etc. are selected based on the properties required for the final composite. Carbon nanotubes have high aspect ratio which help to improve the room temperature properties like flexural strength, flexural modulus etc. of the FRP composites by increasing the efficiency of load transfer between the fiber and the matrix. Fiber matrix interface plays a vital role in governing the overall properties of the composite and controls the behavior of the system under loading conditions [5]. Graphene (mono-layered, multi-layered) is also attracting the researchers due to its various properties [6–8]. As a results of its multi-functional properties, it is in competitive demand with CNT nanofillers. Graphene has very high surface area which helps in enhancing various properties of the composites like tensile strength [9], fracture toughness [10] etc. Also, Research including Graphene nanoparticulates by Zakaria et.al.[11] showed that 1 wt% Graphene nanoparticulates (GnP) embedded resin increased the tensile and flexural of the nanocomposite up to 26% and 29% as compared to neat epoxy. Seretis et al. [12] also reported improvement in flexural and tensile strength of the glass fibre/epoxy composite laminate up to a GnP content of 5 wt %.

Mash up of Carbon nano tubes (CNT) and Multi-layererd Graphene (MLG) is a new research concept which aims at studying the synergistic effect of them in hybrid composites and to investigate any beneficial utility. As reported by S. Chatterjee et al.[13] among samples of different concentrations and ratios of mixture of CNT and Graphene nanoparticulates (GnP), CNT;GnP ratio of 9:1 displayed the highest increase of 17% as compared to 9% CNT and 5% with pure GnP. From similar research works, it is evident that different species in mixture may have synergistic effect on the composite system by contributing to the overall improvement of the properties of the composite Very limited literature is available regarding the impact of the combination of mixture of different nanofillers on the properties of FRP composites. The aim of this present work is to investigate the vast field of fibre reinforced polymer composites embedded with a mixture of nanofillers and comparing them with CNT, MLG and Glass fibre/epoxy (GE) composite and study the contribution of each nanofiller when combined in a mixture. Hence, composite laminates embedded with CNT, MLG and mixture of nanofiller in the ratio of (CNT;MLG) as 1:1, 2:1,1:2 are fabricated using hand layup method followed by flexural testing at room temperature and analysis of Field Emission Scanning Electron Microscope (FESEM) images by observing the fracture surfaces for the mode of failure and dispersion of nanofillers.

2. Experimental section

Five sheets of e-glass fiber were used to fabricate each composite laminate using hand lay-up method. To fabricate GE composite laminate, the weight of the 5 e-glass fiber sheets were noted and same amount of epoxy resin was taken in a container. Hardener of 10 wt% of epoxy resin was mixed with the resin so as to start the hardening process. First sheet of e-glass fiber was laid and the mixture of epoxy and hardener was applied to it using a brush. After it, another sheet was put on it and roller was used to properly distribute the mixture. This process was repeated until all the layers are put. The laminate was then put in hot press to cure for 20 min and left at room temperature for 24 hours. To fabricate the CNT composite, first in a conical flask, 150 mL acetone was taken. To the acetone 0.1wt % amount of CNT was added. It was then stirred with the help of magnetic stirrer at 1000 rpm for 30 min followed by sonication in a bath ultrasonicator to break the agglomerates [35]-M2, disperse the powder particles properly and achieve homogenization. Meanwhile, in a separate flask, epoxy was taken and heated at 400 rpm, 70 C for 30 min. This is done so as to reduce the viscosity. Then the mixture of CNT with acetone was mixed with the epoxy resin. This epoxy/CNT/acetone mixture was then again stirred at 70 C at 1000 rpm till whole acetone evaporates. Then this whole mixture is sonicated again in a bath ultrasonicator for 1hr at 70 C followed by vacuum degassing for 18 h to remove entrapped air or other gasses. TETA Hardener 10 wt% of epoxy resin was added and mixed. Hand layup method was used to fabricate the laminate in similar manner as that of GE composite laminate followed by hot press compression for 20 min at 60 C. MLG composite and 1:1, 1:2, 2:1 CNT: MLG composites were also prepared in the same way. Samples were then cut as per the ASTM-D7264 standards for flexural testing. The samples were polished well and irregularities were removed to obtain uniform dimensions.

3. Results and discussion

3.1 Flexural test

Fig.1. portrays the stress- strain response of the CNT and/ or graphene embedded to the glass fiber epoxy composite. Embodiment of 0.1 wt.% of carbon nanotube (CNT) to the neat glass fiber epoxy composite intensifies the flexural strength and modulus by 10% and 7% respectively, due to superior transfer of load from matrix to nano filler.[14] Increment of 6%and 5% flexural strength and modulus has been observed on addition of 0.1 wt.% of multi layered graphene to the GE composite, reveals a substantial intrinsic surface area causes to effective transfer of stress from matrix to multi layered graphene.[15] Steady enhancement of flexural strength and flexural modulus with amelioration of CNT loading through synergetic CNT and MLG ratio. Dispersion of CNT and MLG of ratio 2:1 into the glass fiber epoxy composite attributes an excellent flexural strength and modulus when simulates with neat GE because the multi walled carbon nanotube (MWCNT) fastens on high surfaces of multi layered graphene sheets precipitates to 3dimensional hybrid structures, impede the agglomeration of MLG. Perhaps the extortionated surface area across the matrix and hybrid nano fillers increases, results in achieving superior strength and modulus. Moreover the MWCNTs in the 3 D structure act as a bridges between the matrix and nano fillers in the composite. [16] However there is decrement in the 1:2 ratio when compared with 2:1, as the 2D structured multi layered graphene sheets stacks together bonding π- π interactions among them. Hence, these agglomerations act identical to micrometer size defect provoke to stress concentration sites.[17]

3.2. DSC analysis

Fig.2. portrays the effect of incorporation of nano fillers content on the glass transition temperature (Tg) of the GE composite. The Tg value for a five layered neat GE composite is 103ºC. Dispersion

of 0.1 wt.% of alone nanotube, nano sheet (MLG/ MWCNT) to the glass fiber epoxy composite dimishes the Tg in simulation to neat GE by 14ºC and 8ºC respectively. This stipulates that polymer chains are not engaged to some extent by virtue of remnant(fragmental) polymer adsorption on the facet of nano fillers thus making polymer chains stock-still.[15]

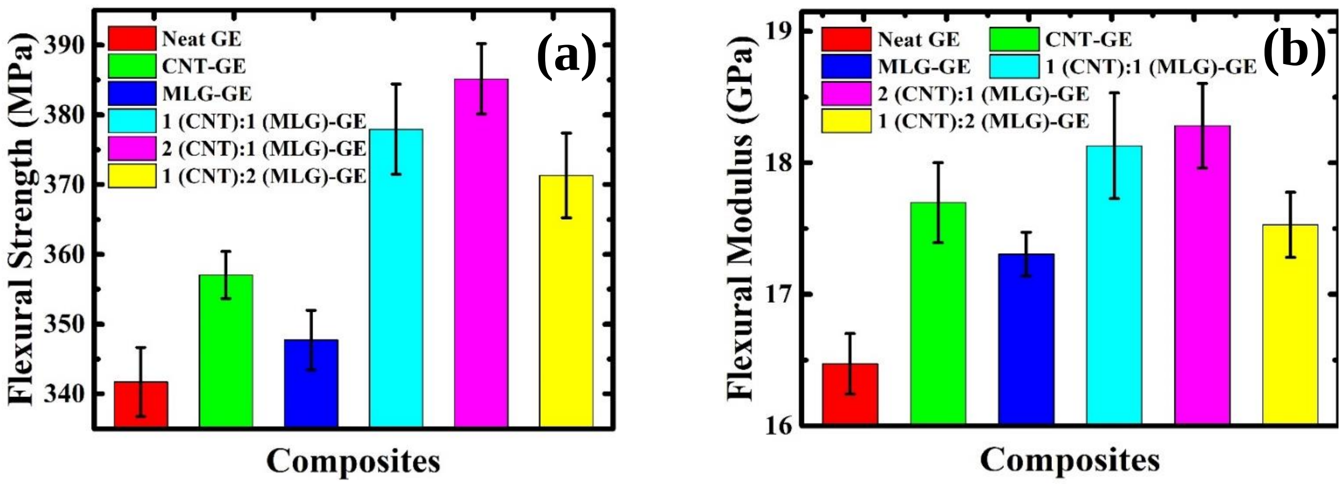

Fig.1. Diversification of a) flexural strength b) flexural modulus with different CNT-MLG contents embedded in GE composite

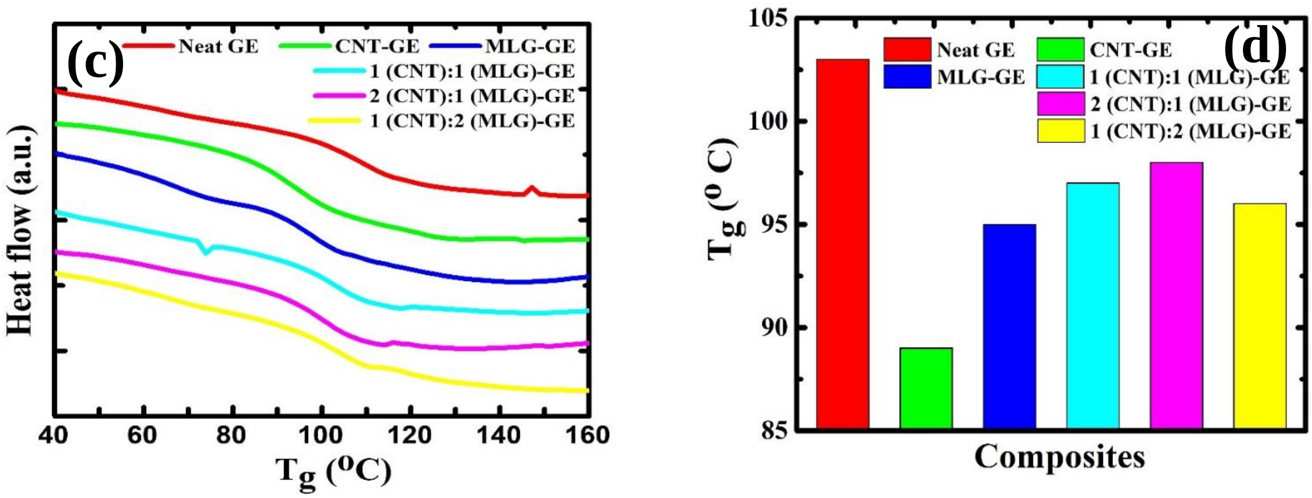

Fig.2. Depicts the c) DSC analysis, d) diversification of glass transition temperature by incorporating different ratios of CNT-MLG in GE composite

In the MWCNT-MLG embedded glass fiber epoxy composite, a meagre increment of glass transition temperature in analogy to alone nanotubes or sheets doped GE (glass fiber epoxy composite) as result of acid-base mechanism. MWCNT in the three dimensional hybrid act as bridge between the graphene and the polymer thus lessen the immobility of polymer liking thereby curbing the inter phase volume.[18] However, there is a curtailment of glass transition temperature in the nanofillers embedded hybrid GE composite.

3.3. Fractography

Enhancement of mechanical properties is pivoted by the interfacial strength among the matrix and fiber or nano fillers. Fig.3. depicts the fractography surfaces of samples examined at room temperature. Fig.3. (a) illustrates the weedy interfacial bonding between fiber and epoxy matrix. However for 2:1 (CNT:MLG) embedded glass fiber/epoxy composite showcases prolific interfacial bonding between fiber and matrix (yet small debonding sites) manifest us that this amalgamation accords us efficient load transfer from fiber to matrix. Fig.3. (c, d) stipulates the deformation characteristics of the samples tested at room temperature. The aligned shear cups across the spacing of fibers reveals the finer transfer of load from fiber to fiber via matrix. [14]Increment of river lines in the nanofillers embedded composite attributes to finer dispersion of CNT and MLG into the epoxy. From fig.3. (e, f) arrows and dotted circles shows that Multi layered graphene impede the fissures provoked in the striated area and CNT deflects the minor crevices through pinning and pull out mechanisms.

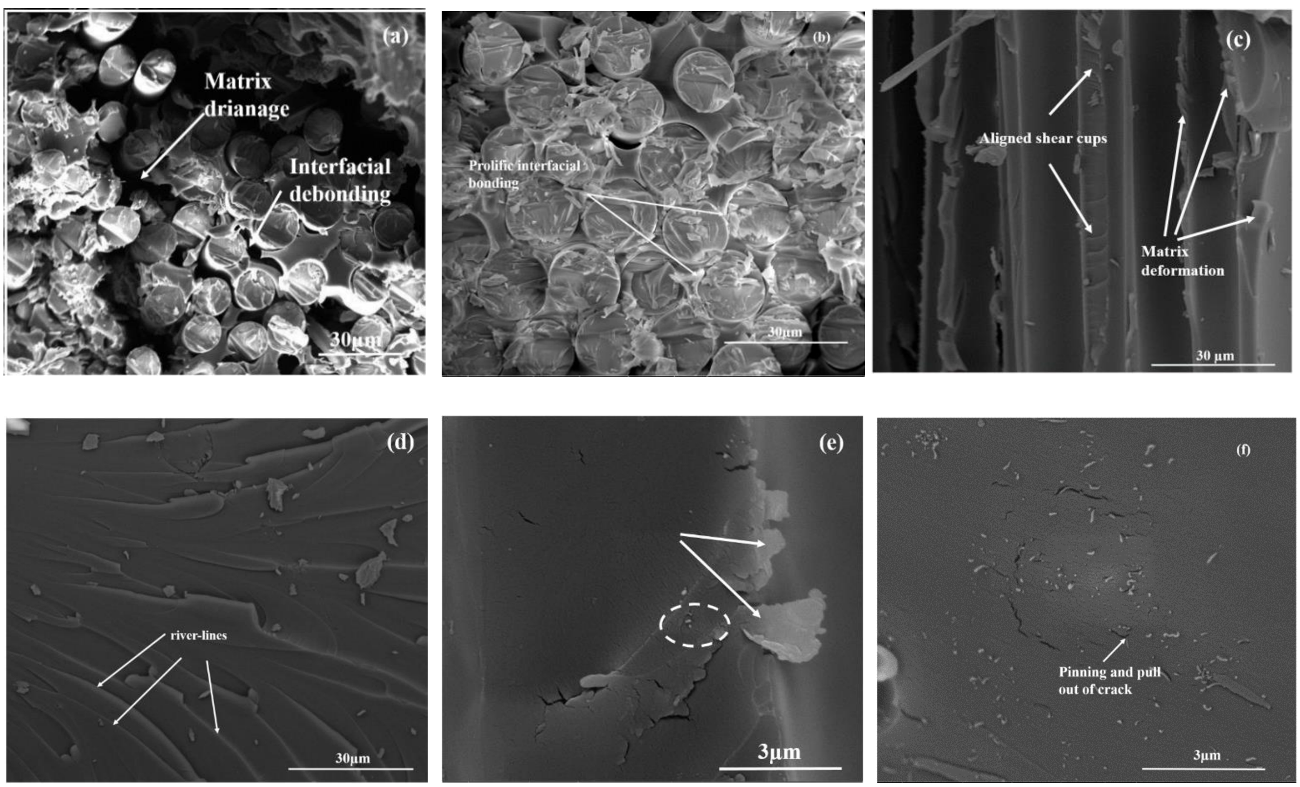

Fig.3. Depicts the FESEM images of deformation behaviour, interfacial zone, crack mechanism of a) GE composite embedded with b, d) CNT:MLG(2:1), C, f)CNT:MLG(1:1), d, e)CNT:MLG(1:2) nanofillers.

4. Conclusion

Incorporation of MWCNT-MLG hybrids to the glass fiber epoxy composite imparts a substantial synergetic impact on FRP composite. Embodiment of CNT:MLG (2:1) gives superior strength and modulus of 14.7% and 12.1% respectively by virtue of better dispersion of CNT and MLG in the matrix. However during DSC analysis there is decrement in glass transition temperature on incorporation of nanofillers due to occupation of CNT and graphene sheets in between the polymer chains. In FESEM, the fractured images of varied ratios of nanofillers incorporated GE composite samples interprets that addition of nanofillers to GE improves the mechanical performance of FRP composites. Furthermore, CNT and MLG impedes the minor crack and major respectively.

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References

[1] M. J. Shukla, D. S. Kumar, D. K. Rathore, R. K. Prusty, and B. C. Ray, "An assessment of flexural performance of liquid nitrogen conditioned glass/epoxy composites with multiwalled carbon nanotube," *J. Compos. Mater.*, vol. 50, no. 22, pp. 3077–3088, 2016.

[2] I. Srikanth, S. Kumar, A. Kumar, P. Ghosal, and C. Subrahmanyam, "Effect of amino functionalized MWCNT on the crosslink density, fracture toughness of epoxy and mechanical properties of carbon-epoxy composites," *Compos. Part A Appl. Sci. Manuf.*, vol. 43, no. 11, pp. 2083–2086, 2012.

[3] I. Scarlatescu, M. Spunei, A. Chis, S. Negru, M. Bunoiu, and N. Avram, "Experimental dosimetric checkup under positioning errors according to gamma criterion," *UPB Sci. Bull. Ser. A Appl. Math. Phys.*, vol. 80, no. 1, pp. 271–280, 2018.

[4] B. C. Kim, S. W. Park, and D. G. Lee, "Fracture toughness of the nano-particle reinforced epoxy composite," *Compos. Struct.*, vol. 86, no. 1–3, pp. 69–77, 2008.

[5] T. Tsuda *et al.*, "Stress transfer efficiency in aligned multi-wall carbon nanotubes sheet/epoxy composites," *Compos. Part A Appl. Sci. Manuf.*, vol. 67, pp. 16–21, 2014.

[6] Q. Cheng, J. Tang, J. Ma, H. Zhang, N. Shinya, and L. C. Qin, "Graphene and carbon nanotube composite electrodes for supercapacitors with ultra-high energy density," *Phys. Chem. Chem. Phys.*, vol. 13, no. 39, pp. 17615–17624, 2011.

[7] M. Tian *et al.*, "Enhanced mechanical and thermal properties of regenerated cellulose/graphene composite fibers," *Carbohydr. Polym.*, vol. 111, pp. 456–462, 2014.

[8] Z. Xu *et al.*, "Organosilane-functionalized graphene oxide for enhanced antifouling and mechanical properties of polyvinylidene fluoride ultrafiltration membranes," *J. Memb. Sci.*, vol. 458, pp. 1–13, 2014.

[9] D. Višnjić, H. Lalić, V. Dembitz, and H. Banfić, "Metabolism and differentiation," *Period. Biol.*, vol. 116, no. 1, pp. 37–43, 2014.

[10] D. R. Bortz, E. G. Heras, and I. Martin-gullon, "[21] Bortz elt 2011 Impressive Fatigue Life and Fracture Toughness.pdf," pp. 238–245, 2012.

[11] M. R. Zakaria, M. H. Abdul Kudus, H. Md. Akil, and M. Z. Mohd Thirmizir, "Comparative study of graphene nanoparticle and multiwall carbon nanotube filled epoxy nanocomposites based on mechanical, thermal and dielectric properties," *Compos. Part B Eng.*, vol. 119, pp. 57–66, 2017.

[12] G. V. Seretis, G. Kouzilos, D. E. Manolakos, and C. G. Provatidis, "On the graphene nanoplatelets reinforcement of hand lay-up glass fabric/epoxy laminated composites," *Compos. Part B Eng.*, vol. 118, pp. 26–32, 2017.

[13] S. Chatterjee, F. Nafezarefi, N. H. Tai, L. Schlagenhauf, F. A. Nüesch, and B. T. T. Chu, "Size and synergy effects of nanofiller hybrids including graphene nanoplatelets and carbon nanotubes in mechanical properties of epoxy composites," *Carbon N. Y.*, vol. 50, no. 15, pp. 5380–5386, 2012.

[14] B. C. R. Dinesh Kumar Rathore, Rajesh Kumar Prusty, Devalingam Santhosh Kumar, "Mechanical performance of CNT-filled glass fiber/epoxy composite.pdf." .

[15] S. K. Ghosh, P. Rajesh, B. Srikavya, D. K. Rathore, R. K. Prusty, and B. C. Ray, "Creep behaviour prediction of multi-layer graphene embedded glass fiber/epoxy composites using time-temperature superposition principle," *Compos. Part A Appl. Sci. Manuf.*, vol. 107, no. August 2017, pp. 507–518, 2018.

[16] C. Kostagiannakopoulou, X. Tsilimigkra, G. Sotiriadis, and V. Kostopoulos, "Synergy effect of carbon nano-fillers on the fracture toughness of structural composites," *Composites Part B: Engineering*, vol. 129. pp. 18–25, 2017.

[17] A. A. Moosa, A. R. S. A, F. Abdul, K. Kubba, and M. Raad, "Synergetic Effects of Graphene and Nonfunctionalized Carbon Nanotubes Hybrid Reinforced Epoxy Matrix on Mechanical , Thermal and Wettability Properties of Nanocomposites," vol. 7, no. 1, pp. 1–11, 2017.

[18] G. Tsagaropoulos and A. Eisenberg, "Dynamic Mechanical Study of the Factors Affecting the Two Glass Transition Behavior of Filled Polymers. Similarities and Differences with Random Ionomers," *Macromolecules*, vol. 28, no. 18, pp. 6067–6077, 1995.