MultiCraft

International Journal of Engineering, Science and Technology
Vol. 11, No. 3, 2019, pp. 30-39

INTERNATIONAL JOURNAL OF ENGINEERING, SCIENCE AND TECHNOLOGY

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Influence of chemical treatments on thermal and bonding behavior of carbon fiber-phenolic matrix composite

Naresh Kumar Konada[1]*, Koka Naga Sai Suman [2]

[1*] *Department of Mechanical Engineering, Anits Engineering College, INDIA*
[2] *Department of Mechanical Engineering, Andhra University College of Engineering, INDIA*
[*] *Corresponding Author: e-mail: nareshkonada@gmail.com, Tel +91-9949717058*

Abstract

The performance of carbon fiber (CF) -Phenol matrix composite is mainly based on the inter-laminar shear force attraction between all the ingredients present in the composite. Basically, CF surface is smooth in nature in terms of its structure and have poor ability to allow the matrix material to stick to its surface. Hence, in this work an attempt is made to improve the bonding behavior between CF and phenolic matrix by performing three chemical treatment techniques on CF surface. The best chemical treatment method is suggested to use CF more effectively as reinforcement in polymer matrix composites. First, carbon fiber surface undergo thermal oxidation treatment. Second, carbon fiber surface is allowed to undergo HNO_3 treatment and the third by deposition of multi walled carbon nano tubes functionalized (MWCNTs-F) on CF surface. CF-phenol matrix composite sheets are developed along with remaining ingredients using hand layup technique. The ability of uniform dispersion of all the ingredients for three composite sheets was observed by using scanning electron microscope (SEM). Thermo gravimetric (TGA) and Fourier transform infrared spectroscopy (FTIR) analysis is also performed on all sample powders and composite sheets to assess the thermal stability and bonding behavior of CF reinforced composite. Finally, the best chemical treatment method performed on CF is selected for the improvement of thermal and bonding behavior of CF-phenol matrix composite.

Keywords: Multi walled carbon nano tubes; Carbon fibers, chemical treatments, Thermal and bonding analysis.

DOI: http://dx.doi.org/10.4314/ijest.v11i3.4

1. Introduction

Since 1960s, Carbon fiber (CF) reinforcements are used extensively in composites due to its excellent properties interms of its strength, corrosion resistance and wear resistance. Now-a-days these fibers are prominent in the field of marine, aerospace, medical, civil, sports applications due to its high fatigue strength properties (Soutis, 2005). These fibers also possess good wear resistance compared to other fibers (Paiva *et al*., 2009). Bonding behavior between CF and phenol matrix composite can be improved by increase of inter laminar shear force attraction between fiber and matrix and remaining ingredients (Tanaka, 1977). The inter laminar shear force attraction between CF and phenol matrix selected in the present study can be improved to a greater extent by performing chemical treatments on CF to increase the surface roughness of the fiber and improve the absorptive characteristics with respect to phenol polymer matrix. Hence, there have been many efforts performed in the past to improve surface properties of CF by performing different treatment techniques like sizing, plasma, chemical oxidation, γ -ray irradiation, electrochemical, dip coating, MWCNT deposition on CF surface by chemical vapour deposition (CVD) etc. (Song *et al*., 2012).

It is observed from the past research work of many authors that, the inter-laminar shear force attraction between fiber and matrix can be greatly improved by deposition of MWCNT on CF surface. Song *et al*. (2012) have noticed that deposition of carbon nano tubes radially on CF can improve its mechanical properties to a greater extent. Sharma and Lakkad (2011) have observed that, deposition of carbon nano tubes by using chemical vapor deposition (CVD) method on CF, improved the tensile behavior of CF/epoxy/amine polymer matrix composite to a greater extent. Qian *et al*. (2010) also observed that, CNTs deposition by CVD on CF improved inter laminar shear strength of CF and poly methyl methacrylate (CF/PMMA) composite. Sharma *et al*. (2014), in his review paper on carbon fiber surface and composites interface, identified that, there is an improvement in inter laminar shear strength by 175% for CF/epoxy composite and author also mentioned that, MWCNT deposited on carbon fiber surface by chemical grafting improves inter laminar shear strength by 150% for CF/epoxy composite . Based on all these observations, it was observed that, CVD method of deposition of carbon nano tubes on CF surface improves the inter-laminar shear force attraction between carbon fiber and polymer matrix composite to a greater extent. Chemical vapor deposition of grafting CNTs on CF surface is a difficult process to control all the operating variables especially temperature. The cost involved in this process is also very high. Hence, in this work, an attempt is made to treat CF surface by three chemical treatments and the best method is selected for reinforcing CF in to polymer matrix composites. Three treatments are performed on CF surface. First, oxidation treatment is performed on CF in the presence of nitrogen gas and air. Second, HNO_3 treatment and third, chemical grafting of MWCNTs-F on CF surface (Severini *et al*., 2002). Composite sheets are fabricated for three treatment methods performed on CF and the resulting samples are characterized for SEM to check the uniform distribution of all the ingredients across the composite sheet. The fiber crystalline structure, weight loss of the sample and absorptive characteristics of CF reinforced polymer composite were measured by using SEM, TGA and FTIR techniques. The best surface treatment method on CF is selected to extend CF usage in wide range of applications like aviation, automobile, nuclear civil, sporting goods, energy storage devices, wind turbines, and marine application components.

2. Materials and Methods

2.1 Carbon Fiber

CF used for this study is produced by using poly acrylonitrile (PAN) based with carbon fiber content of 95%. Chopped CF are selected for the present study for performing three chemical treatments on CF with ease (Figure 1). Table 1 represents the properties of carbon fiber supplied by the supplier.

Figure 1 Chopped carbon fiber

Table 1 Properties of carbon fiber

Material	Properties						
	Diameter (µm)	Length (mm)	Tensile strength (MPa)	Tensile modulus (GPa)	Sizing	Resistivity Ω/cm	Carbon content
Carbon fiber	6.9	6	4810	225	1-1.2%	1.54×10^{-3}	95%

2.2 Multi Walled carbon nano tubes (MWCNT)

Multi-walled carbon nano-tubes (MWCNT) obtained by using chemical vapor deposition method are used in this study (Figure 2). These MWCNTs contain few metal particles less than 4%. Hence metal particles are removed by performing fictionalization on MWCNT to form MWCNT-F. The obtained functionalized MWCNTs are deposited on the CF surface. The properties of MWCNTs given by the supplier are given in Table 2.

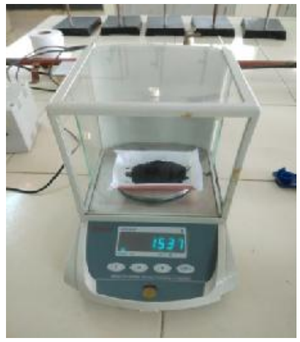


Figure 2 MWCNT Powder

Table 2 Properties of multi walled carbon nano tubes

Material	Properties						
	Diameter (nm)	Length (microns)	Metal particles	Amorphous Carbon	Specific surface area(m^2/g)	Bulk density g/cm^3	Nano tubes purity
MWCNT	10-30	10	<4%	<1%	330	0.04-0.06	>95%

2.3 Carbon fiber surface treatment methods

2.3.1 Carbon fiber HNO_3 treatment

CF was chemically treated to attach carboxylic groups on its surface by deposition of nitric acid on its surface. Initially CF of quantity 150 gms were treated with 30% nitric acid. During this deposition of nitric acid on CF surface releases few gases. After this process, the fibers were washed with distilled water to remove adsorpted gases on CF surface. This process continues until the CF surface is free from nitric acid solution. Finally, CF was dried in the oven for 2 hrs at a temperature of 150^0C followed by drying in the atmosphere for 1 hr. Figure 3(a-c) gives the steps involved in the nitric acid treatment on CF.

(a) (b) (c)

Figure 3(a-c) Steps involved in HNO_3 chemical treatment on CF

2.3.2 MWCNT Surface oxidation treatment on carbon fibers

Carbon fibers are placed in the oven and maintained at a temperature of 650°C for 1 hr. The temperature of the oven is gradually increase from 20°C to 650°C initially in the oven followed by keeping the sample in the air for about 40 min. Figure 4 (a) & Figure 4 (b) are the steps involved in the oxidation treatment of carbon fiber.

Figure 4(a) Chopped carbon fiber

Figure 4(b) Oxidation treatment on CF surface

The surface of MWCNTs are modified to attach carboxylic grops to increase the bonding strength with respect to phenol polymer matrix. About 3 gms of MWCNTs are added 110ml of sulphuric acid and 40 ml of nitric acid and the total quantity of the solution undergoes sonication process for 4 hrs at a temperature of 80^0C . vaccum fitration was done to remove the metal particles present in the mixture. The sample powder is finally sonicated with acetone solution and filtered (Figure 5). Final sample powder is dried in the oven at a temperature of 90°C for 2 hrs followed by drying in atmosphere to form multi walled carbon nano tubes functionalized MWCNT-F.

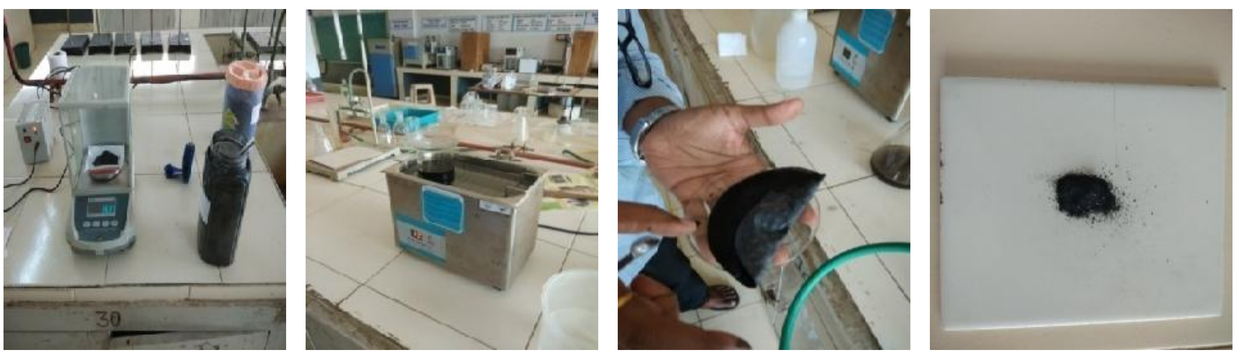


Figure 5. Sequential operations carried out in MWCNT surface oxidation to form MWCNT-F

2.3.3 Grafting MWCNT-F on oxidised CF surface

Multi walled carbon nano tubes functionalized (MWCNT-F) obtained during sonication and drying process is mixed with acetone solution . Carbon fibers are placed on the glass substrate to deposit MWCNT-F manually on its surface using droppler technique.This opeartion is performed slowly to deposit MWCNT-F on CF surface uniformly through out the surface. The obtained chopped carbon fibers after deposition process is placed in an oven at a temperature of 90°C for 2 hrs for the uniform dispersion of solution on CF surface.

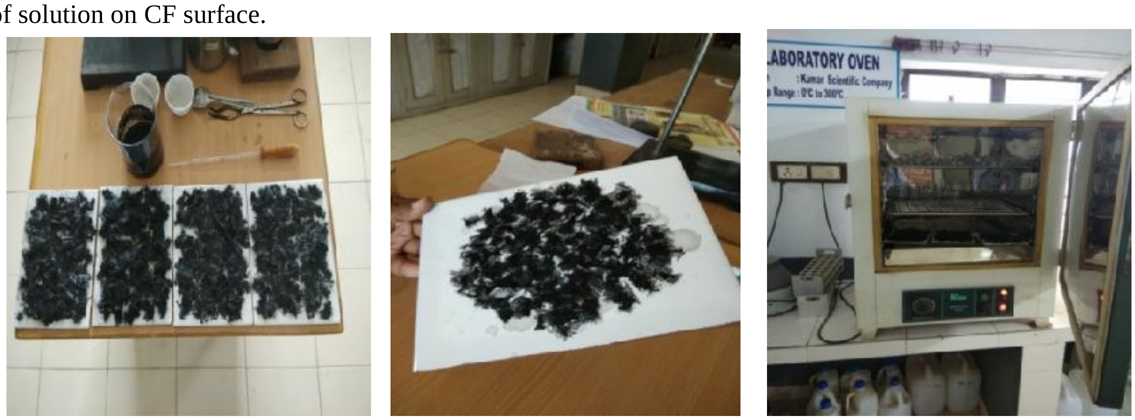
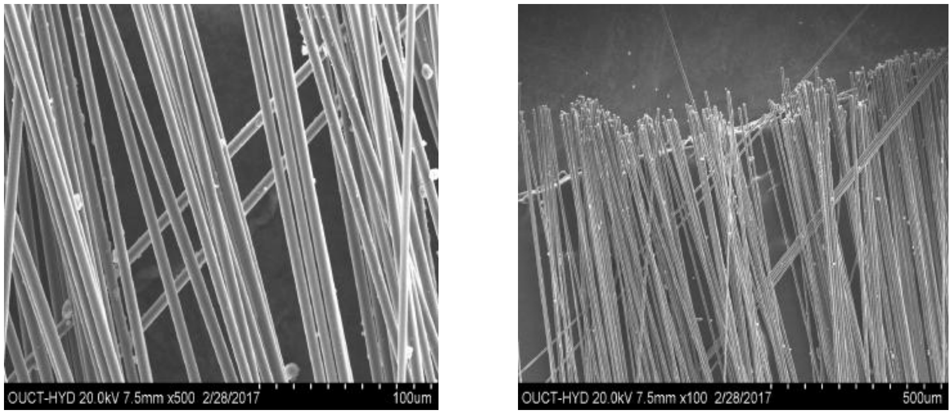


Figure 6 Grafting MWCNT-F on CF Surface

3. Results and Discussions

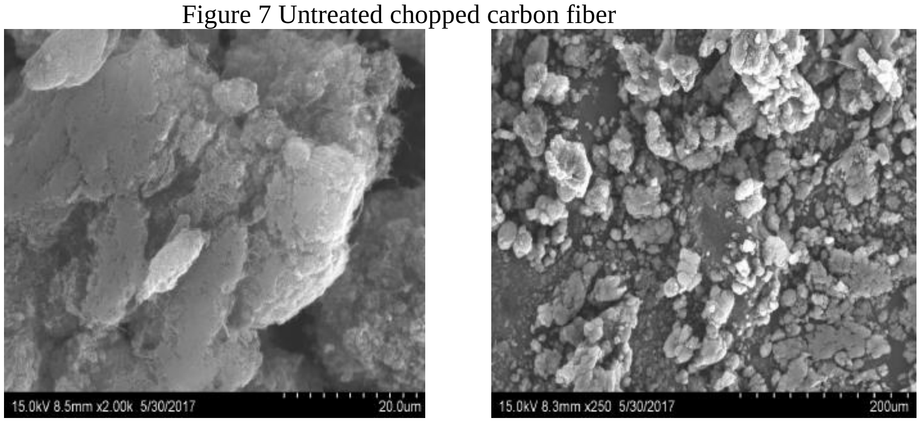
3.1 Scanning Electron microscopy

All the samples of chopped carbon fibers treated with surface oxiadtion, Acid HNO_3 and carbon fibers grafted with MWCNT-F were imaged by using scanning electron microscope (SEM) under hitachi make S-3700N operating at 10 kV. Two magnification images are taken for better visualisation of the surface.



(a) (b)

Figure 7 Untreated chopped carbon fiber



(a) (b)

Figure 8 MWCNT Powder

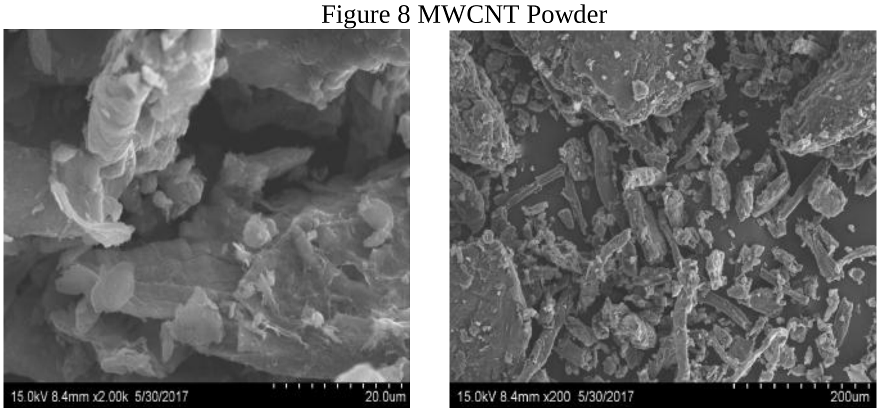


Figure 9 MWCNT surface oxidation treatment

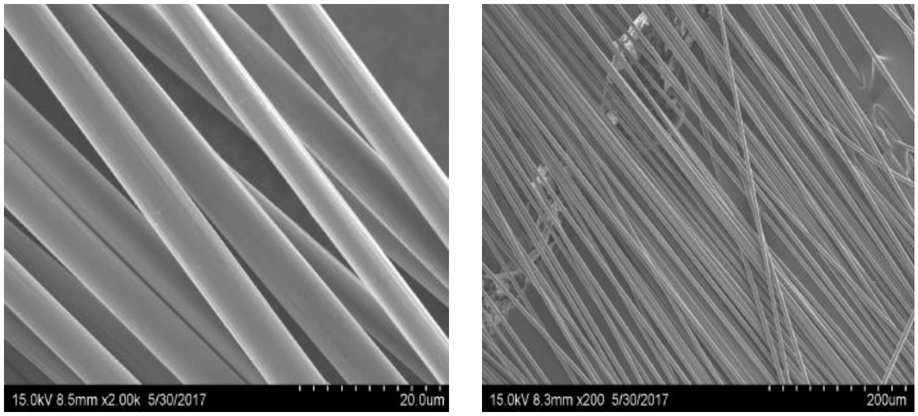


Figure 10 Chopped CF surface oxidation treatment

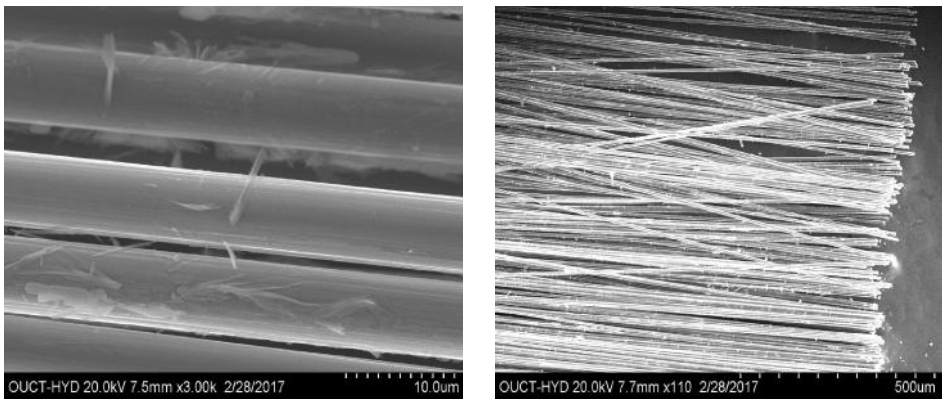


Figure 11 HNO_3 Treated chopped carbon fiber

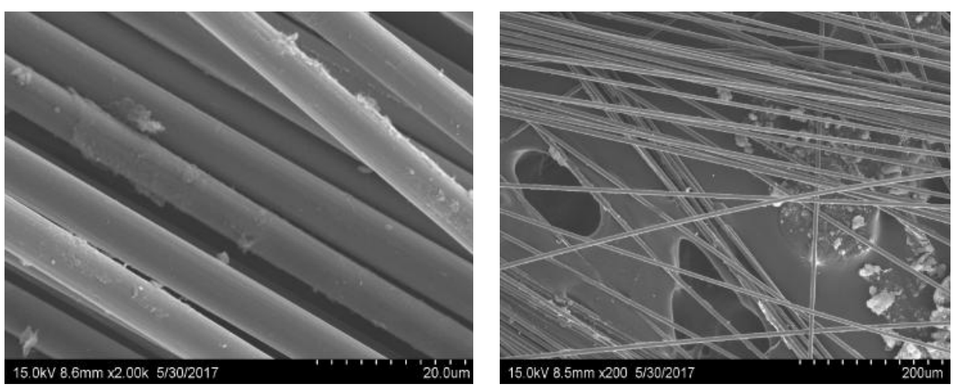


Figure 12 CF grafted with MWCNT-F

Figure 7 (a) & (b), indicates untreated chopped carbon fiber surface is having a very high shiny, smooth surface crystalline structure. This structure clearly defines that; fiber surface is having poor interfacial adhesion with polymer phenolic matrix. Therefore, a proper surface treatment is necessary to modify the CF surface. Figure 8 (a) & (b) indicates MWCNT crystal structure with small granular particles randomly distributed across the surface. Multi walled carbon nano tubes supplied by the supplier contains few metal particles < 4%. These metal particles can be removed by performing fictionalization on carbon nano tubes to form MWCNT-F carbon nano tubes. MWCNTs are modified to form MWCNT-F by performing oxidation treatment on MWCNTs. The surface of MWCNTs after oxidation treatment is observed in Figure 9. MWCNT after surface oxidation treatment is observed to be free from metal particles and have greater possibility of adherence to the CF surface. Performing oxidation treatment on chopped carbon fibers is shown in Figure 10, which will improve the oxygen content level on the CF surface. Initially CF surface is placed in an oven and nitrogen gas is allowed to pass through the surface for 30 min. Then the sample is left in oven under air for 30 min at 600°C. From Figure 10, it was clearly observed that, the surface of CF is modified with oxygen content level on the surface to increase the absorptive characteristic of CF with any chemical substance. There is slight improvement of roughness level after oxidation treatment performed on CF. Figure 11 indiactes acid HNO_3 tratment on CF surface and improves its rougness to meduium level by compromising with the strength of the composite after acid treatment.

From Figure 12, It was observed that, there is a high improvement in the surafce rougness , after CF grafted with MWCNT-F. MWCNT-F prepared by laboratory method by solutions of H_2SO_4 and HNO_3 is vaccum filtered and finally washed with acetone solution to form MWCNT-F powder. Now, MWCNT-F are grafted on oxidated CF surface using a doppler technique. It was clearly observed that , entire CF surface is uniformly grafted with MWCNT-F powder. The crystalline structure of the CF surface is greatly improved with grafting technique.The fiber surface have the greatre ability to stick to the polymer matrix for enhancing the bonding strength between fiber and phenol polymer matrix. Hence, the surface topography of all the surface treatments performed on CF surface, MWCNTs grafting on CF surface posses good rougness and greater ability to stick to the polymer matrix. The strength of the CF base material is not damaged in this technique and noticed that uniform dispersion of MWCNT-F on CF surface improves its roughness to greater extent compared with other techniques like oxidation and nitric acid treatments performed on CF surface. The composites sheets fabricated with three different treatment techniques are shown in Figure 13. It was clearly observed from Figure 13(c) that, the ingredients are uniformly distributed across the composite sheet and possess greater abilty to stick to the polymer matrix for improving the strength of the composite.

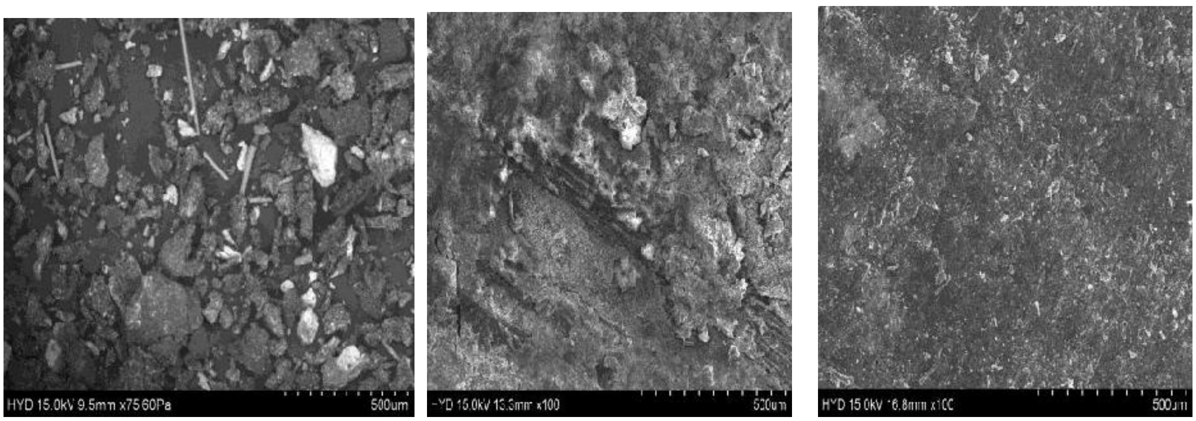


Figure 13 Composite sheets with three different surface treatments on CF (a-c)

3.2 Thermo gravimetric analysis

The abilty of the material to sustain temperatures plays a vital role to assess the perofrmance of CF reinforced composite for a required field of engineering. In this step , thermo gravimetric analysis (TGA) is performed on two samples which possess greater possibilty of fiber and polymer matrix adhesion. First, MWCNT surface oxidation treated and second MWCNT-F grafted on carbon fibers to determine the physical and chemical behaviour of the materials with respect to temperature.This test is performed by placing the sample powder taken fron the each composite sheet fabricated with three different treatment techniques.The mass loss of the samples are observed by placing the specimen powder in the thermo gravimetric analyzer. This analysis was performed with increasing temperature gradually from 42.2°C to 600°C for a time period of 60 min. This analysis gives the information about the ability of the carbon fiber to use in phenol polymer matrix composites subjected to high temperatures.

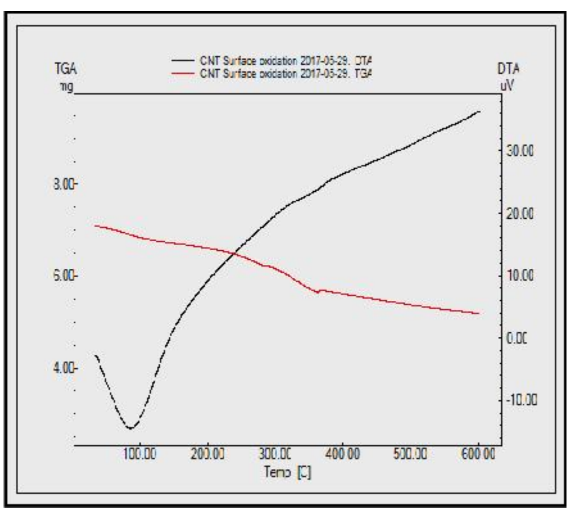


Figure 14 (a) Variation of TGA and DTA oxidation treatment

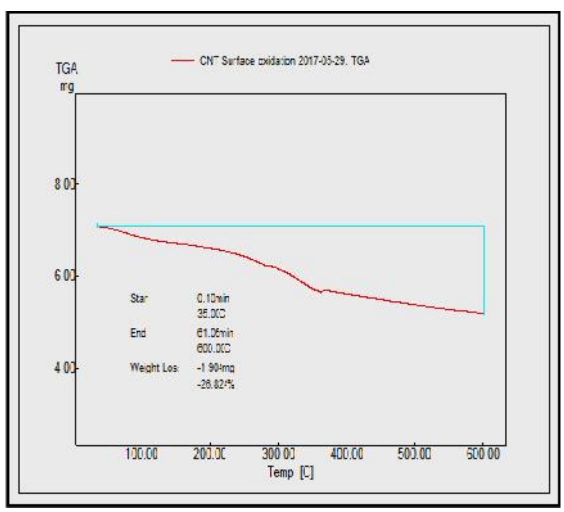
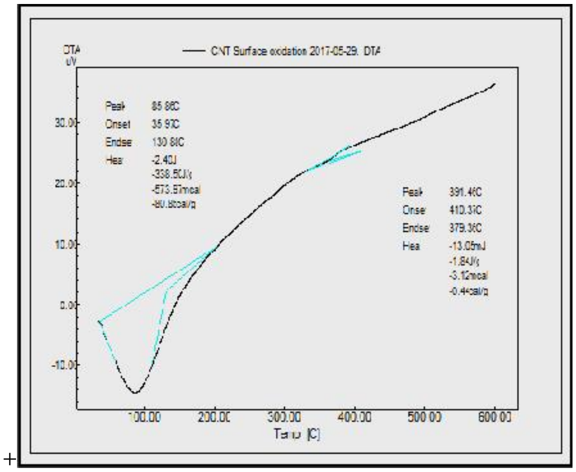


Figure 14 (b) Weight loss of MWCNT surface oxidation



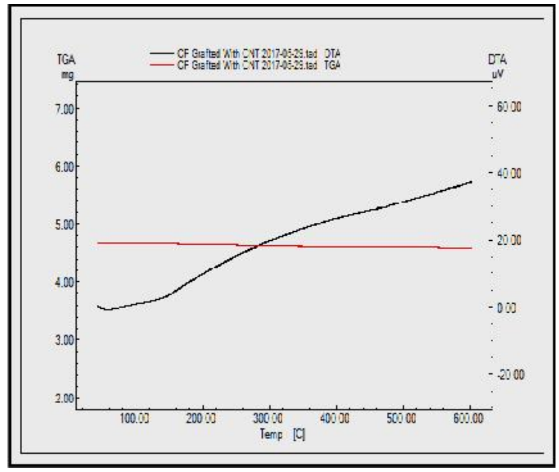
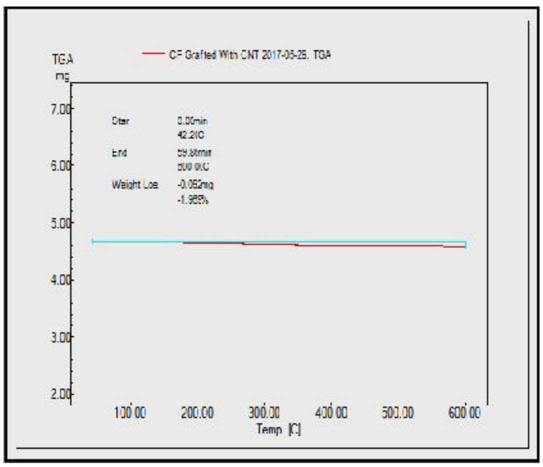


Figure 14(c) Heat energy released for oxidation treatment Figure 14 (d) Variation of TGA and DTA for CF grafted MWCNT-F



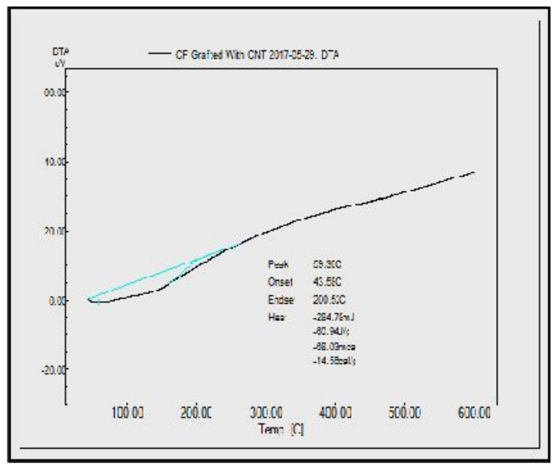


Figure 14 (e) Weight loss of CF deposited MWCNT-F Figure 14(f) Heat energy released for CF deposited MWCNT-F

From Figure 14 (a), it was observed that, when the temperature of the sample is gradually increased from minimum to 600°C, the phase transformation is not severely affected with increase of temperature for surface oxidation treated MWCNTs. It was also noticed from Figure 3.8(b), that there is low weight loss of the sample i.e. 1.90 mg after keeping the sample for a time period of 60 min in thermo gravimetric analyzer. The maximum heat energy released after this test was observed to be 2.40J, which is quite low and the sample can easily sustain the temperatures. After placing MWCNT-F powder sample in the thermo gravimetric analyzer, it was observed from Figure 14(d) and Figure 14(e) that, the sample can easily sustain the temperatures and based on differential thermal analysis curve, there is not much variation occurs in the sample after increasing the temperature from minimum to 600^0C. It was also noticed that, the powder sample after fictionalization can easily sustain the temperatures and the weight loss is observed to be 0.09 mg which is a very less value and hence , MWCNT-F can be used successfully as a grafting member on CF. Therefore, it was observed that MWCNT-F grafted on the CF surface is having a greater chance to posses less weight loss and used as reinforcement in polymers to increase the inter laminar shear strength and temperature with standing capability of the resultant CF reinforced polymer composite.

3.3 FTIR Analysis of MWCNT-F deposited CF surface

Fourier transform infrared spectroscopy (FTIR) analysis gives the information about the bonding behavior of all the ingredients present in the sample with respect to polymer matrix. This analysis uses a high signal infrared rays focusing on the composite specimen. The observations are noted with increase of wavelengths from 2.5µm to 25 µm and wave number rages from 4000cm^{-1} to 400cm^{-1}.

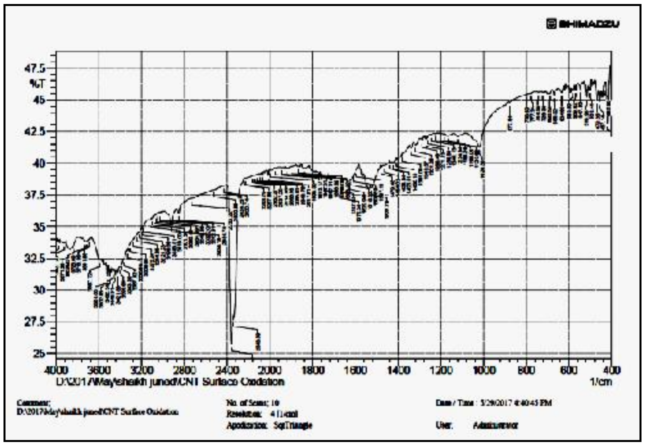


Figure 15(a) Wavelength of CF surface oxidation composite

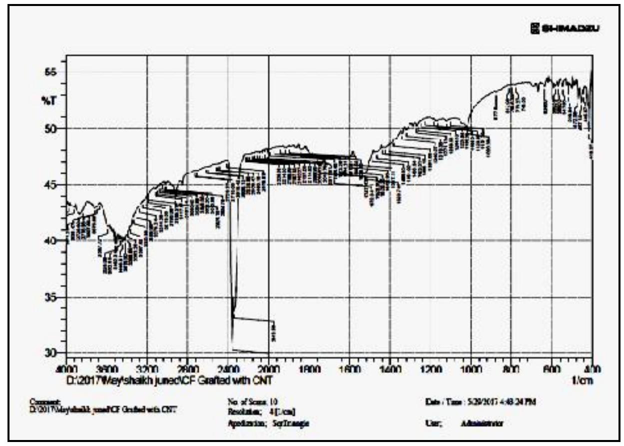


Figure 15 (b) Wavelength of CF $HN0_3$ treated composite

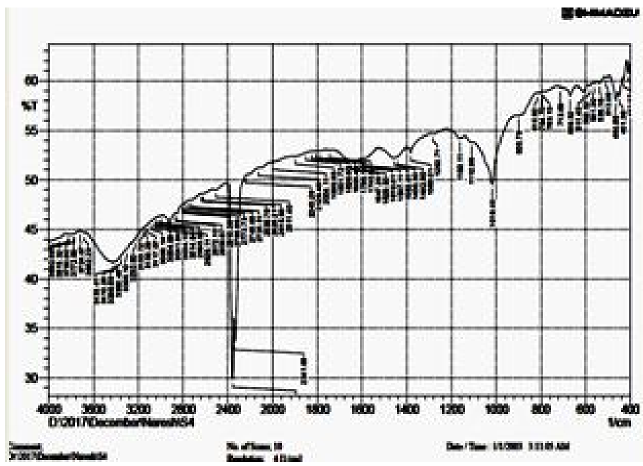


Figure 15 (c) Wavelength of CF grafted with MWCNT-F composite

Figure 15 (a) and Figure 15 (b) is having more fluctuations in the wave length and chemical bonds in the molecuele is not uniformly maintained through put the surafce of the composite. Figure 15 (c) , gives information about uniform dispersio of all the ingreints with the polymer matrix and maintained higher ability to absorb the solid or liquid substances with increase of wave length through out the compoiste.This is mainly, because of increasing the covalent bonding groups (i.e hydroxyl or carboxyl or amino groups) on the fiber surface. The covalent boding strength and interfacial adhesion for MWCNT-F grafted on CF surface is improved to a greater extent compared to other surface treatment methods . Hence based on the absorptivity characteristic of the materail, CF grafted with MWCNT-F can be used as reinforcement in polymer composites to extend its application of usage in several fields of engineering like mechanical,aerospace, nuclear etc. This method of grafting is a cost effective and simple to use and can lead to enhanced mechnaical properties of the composite to a greater extent.

4. Conclusion

Carbon fiber possess excellent mechanical and tribological properties and extensively used as as reinforcement in polymer matrix composites. For better improvement of chemical bonding between all the ingredients and phenol polymer matrix, three chemical treatments are performedon CF . First oxidation treatment in nitrogen gas and air , second HNO_3 treatment and finally CF surface is deposited with MWCNT-F. Among all these methods of CF chemical treatments, MWCNT-F deposition on carbon fiber surface improves CF surface rougness to a greater extent and have a greater chance to adhere to polymer matrix for increasing the interlaminar shear strength between CF, ingredients and phenol matrix. SEM, TGA and FTIR results reveal that, CF deposited with MWCNT-F posses low weight loss with increase in temperature and good absorptivity characteristics with phenol poymer matrix. The surface of MWCNT-F deposited on CF possess uniform dispersion of all the ingredients compared to remaining methods.The laboratory method followed in this work, achieved good results closer to chemical vapour deposition(CVD) process.This method of deposition MWCNT-F on carbon fiber surface is a cost effective and simple to use for achieving good bonding and thermal behavior of carbon fiber phenolic matrix composite . Hence, carbon fibers deposition with MWCNT-F can extend its usage for carbon fiber –phenol matrix composites in several fields of engineering, automobile, marine, civil, aerospace and nuclear applications.

Acknowledgement

The authors would like to thank Anits Engineering College for providing the chemical laboratory facilities for performing this experiment.

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Biographical notes

Naresh Kumar Konada has completed his M.Tech. (Machine Design) from GITAM University in the year 2010. He is presently working as an Assistant Professor at Anits Engineering College since 2010 and studying Ph.D. in the field of machine design from Andhra University, Visakhapatnam, India. His areas of interests include Composites, Nano technology, Vibrations and Machine Design.

Dr. Koka Naga Sai Suman is working as an Associate Professor in the department of Mechanical Engineering, Andhra University College of Engineering, and Visakhapatnam since 2006. He was the recipient of senior research fellow and junior research fellow grants from AICTE. He received best thesis award for his Ph.D work in the year 2010 by Andhra University. His areas of interests include Advanced Composites, Nano technology, Manufacturing.

Received January 2019
Accepted April 2019
Final acceptance in revised form May 2019