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MECHANICAL AND THERMAL CHARACTERIZATION OF CNF-FILLED POLYESTER NANOPHASED COMPOSITE

Mohammad Kamal Hossain, **Muhammad Enayet Hossain**, **Mahesh Hosur and Shaik Jeelani**

Tuskegee University, Tuskegee, USA

ABSTRACT

A high intensity ultrasonic liquid processor was used to infuse carbon nanofibers (CNFs) into polyester matrix which was then mixed with catalyst using a high speed mechanical agitator. Results showed the significant improvement in the dispersion of CNFs in sonication over the mechanical mixing method. Flexure tests performed on the neat polyester (NP), 0.1wt. %, 0.2 wt.%, 0.3 wt.% and 0.4 wt.% CNF-filled polyester (CNF-FP) showed 86% and 16% increase in flexural strength and modulus, respectively, compared to the unfilled polyester with increasing loading percentage of CNF up to 0.2%. Similar trend was found with CNF-filled glass reinforced polyester (CNF-FGRP) composites manufactured by vacuum assisted resin transfer molding (VARTM). Dynamic mechanical analysis (DMA) studies indicated an increasing trend of storage modulus and glass-transition-temperature (T_g) values of all nanophased composites compared to neat polyester. Scanning electron microscopy (SEM) micrographs of fracture surfaces revealed relatively smooth surface of neat polyester compared to the nanophased polyester.

Keywords: Polyester, CNF, Mechanical and Thermal Properties.

1. INTRODUCTION

Fiber reinforced polymer matrix composites due to their high specific strength and specific stiffness to weight ratios have become attractive structural materials in aerospace industry, marine, armor, automobile, railways, civil engineering structures, sport goods etc. [1]. The incorporation of inorganic fillers has proved to be an effective way of improving the mechanical and thermal properties of these materials. However, the typical filler content needed for significant enhancement of these properties can be as high as 10-20% by volume. The processing of the materials often becomes difficult at such high particle volume fractions due to the higher density of the inorganic filler than the resin and the increased density of the filled resin [2]. In this rationale, nanoparticles such as CNFs, CNTs, clay, metallic nanoparticles filled fiber reinforced polymer matrix composites are attracting considerable attention since they can enhance properties that are sometimes even higher than the conventional filled polymers composites at volume fractions in the range of 1 to 5%.

Improvements in mechanical, electrical, and chemical properties have resulted in major interest in nanocomposite materials in numerous automotive, aerospace, electronics and biotechnology applications. These nanoscale materials provide the opportunity to explore new behavior and functionality beyond those found in conventional materials. It has been established that the addition of small amounts of nanoparticles (<5 wt. %) to a matrix system can increase thermal and mechanical properties without compromising the weight or process-ability of the composite [3]. The higher surface area is one the most promising characteristics of the nanoparticles due to its ability of creating a great interface in a composite. An interphase of 1 nm thick represents roughly 0.3% of the total volume of polymer in the case of micro particle filled composites; whereas it can reach 30% of the total volume in the case of nanocomposites [4]. Contribution made by the interphase modified by the low nanofiller loading provides possibilities of enhanced performance by reinforced composites with a small percentage of strong fillers can significantly improve the mechanical, thermal, and barrier properties of the pure polymer matrix [6].

Choi et al. [7] have fabricated and studied the Epoxy/CNF composite with different proportions of CNFs by the in situ process modifying both low and high viscous epoxies. The SEM images showed a high level of dispersion for all materials, although occasional small aggregates were observed in high viscosity epoxy of 20 wt%. The storage modulus and T_g of the polymer were increased by incorporation of CNFs. The results showed the maximum tensile strength and Young's modulus at 5 wt% of CNF and reduction of the fracture strain with increasing filler content. Mechanical, electrical and thermal properties of low viscosity epoxy composites were resulted better than that of the high viscosity composites. Hussain et al. [8] have investigated the effect of nanoscale Al_2O_3 particles in filament wound carbon fiber/epoxy composites and found an increase in modulus, flexural strength, interlaminar shear strength, and fracture toughness when the matrix was filled with 10% by volume of alumina particles of 25 nm diameter. Seferis et al. [9] have shown the ability to incorporate nanosized alumina structures in the matrix and interlayer regions of prepreg based carbon/epoxy composites. Timmerman et al. [10] studied the influence of nanoclay on the carbon fiber/matrix composites under thermal cyclic loading and reported that the transverse cracking in symmetric carbon fiber/epoxy laminates was significantly reduced when nanoparticle fillers were used. Pervin et al. [11] evaluated the thermal and mechanical properties of carbon nanofiber reinforced SC-15 epoxy and documented the significant improvement in the thermal and mechanical properties of this material system. Mahfuz et al. [12] synthesized and characterized the carbon nanoparticles/whiskers reinforced polyethylene filament. SEM and TEM micrographs showed uniform dispersion and unidirectional alignment of carbon whiskers. They also documented the higher tensile strength and modulus by about 15–17% and increasesd thermal stability and crystallinity of the system as compared to the neat polyethylene control samples.

The primary focus of this paper was to characterize the effect of CNF on the mechanical and thermal behavior of the nanophased polyester and its laminate performing the flexure tests, TGA and DMA, respectively. Fracture morphology of the tested specimens was studied by SEM.

2. EXPERIMENTAL

2.1 Materials Selection

Commercially available B-440 premium polyester resin and styrene from US Composite, heat treated PR-24 CNF from Pyrograf Inc., and plain weave E-glass fiber from fiberglasssite.com were considered as matrix, nanoparticle, thinner and reinforcement, respectively, in this current study because of their good property values and low cost. Polyester resin contains two-part: part-A(polyester resin) and hardener part-B (MEKP- methyl ethyl ketone peroxide).

2.2 Resin Preparation

Ultrasonic cavitation technique is one of the most efficient means to disperse nanoparticles into a polymer [13]. In this study, sonication was performed using a high intensity ultrasonic irradiation (Ti-horn, 20 kHz Sonics Vibra Cell, Sonics Mandmaterials, Inc, USA) for 60, 90, and 120 minutes, respectively, adding 0.1, 0.2, 0.3, and 0.4 wt.% CNF with corresponding percent polyester resin with and without 10 wt% styrene in a glass beaker. The mixing process was carried out in a pulse mode of 30 sec. on/15 sec. off at amplitude of 50%. Continuous external cooling was employed by submerging the beaker in an ice-bath to avoid temperature rise during the sonication process. The intense mixing of polyester and CNF with or without styrene produced highly reactive volatile vapor bubbles at the initial stages of the reaction, which could detrimentally affect the properties of the final product by creating voids. To reduce the void formation, high vacuum was applied using Brand Tech Vacuum system for about 90-120 minutes. Once the bubbles were completely removed from the mixer, 0.6 wt% catalyst was mixed with the mixer using a high-speed mechanical stirrer for about 2-3 minutes and vacuum was again applied for about 6-8 minutes to degasify the bubbles produced during the catalyst mixing. In parallel, neat polyester samples were fabricated by using the same method to compare with the nanophased system. The whole mixing system is shown in Figure 1.

1a. Sonication

1b. Degasification

1c. Mechanical Mixing

Fig 1. Mixing Method

2.3 Composite Fabrication

Both conventional and nanophased E-glass/CNF-polyester composites were manufactured by VARTM process. Arrangement of the fabrication process is detailed schematically in Figure 2. The VARTM process uses vacuum pressure to remove air from the fabric lay-up before and during the resin infusion to the fabric reinforcement. The pressure difference between the atmosphere and the vacuum is the driving force for infusion of the resin into the lay-up. Vacuum was maintained until the end of cure to remove any volatiles generated during the polymerization, in addition to maintaining the pressure of one atmosphere. The panel was cured for about 15-18 hours at room temperature. The room temperature cured material was taken out from the vacuum bagging and trimmed, and test samples were machined according to ASTM D 790-02. They were thermally post cured at 110 °C for 3 hour in a mechanical convection oven.

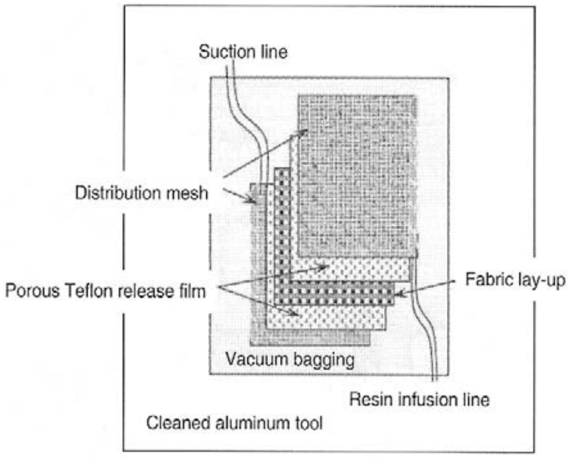

Fig 2. VARTM Layup Sequence

2.4 Test Procedure

2.4.1 Flexure Test

Flexural tests under three-point bend configuration were performed on the Zwick Roell testing unit shown in Figure 3 according to ASTM D790-02 to determine the ultimate strength and young modulus of the polymer nanocomposites and its laminates. The machines were run under displacement control mode at a crosshead speed of 2.0 mm/min [11] and tests were performed at room temperature.

Fig 3. Zwick Roell Setup

2.4.2 Thermogravimetric Analysis (TGA)

Thermo gravimetric analysis (TGA) was conducted with a TA Instruments Q 500, shown in Figure 4, which was fitted to a nitrogen purge gas. The temperature was from increased from ambient temperature to 500 °C at a ramp rate of 10 °C/min.

2.4.2 Dynamic Mechanical Analysis (DMA)

Storage modulus, glass transition temperature (T_g), and loss factor, tanδ, of the fully cured samples were obtained from a TA instruments Q 800 operating in the three point bending mode at a heating rate of 3°C/min from 30°C to 160°C and an oscillation frequency of 1 Hz as shown in Figure 5. The sample specimens were cut by a diamond cutter in the form of rectangular bars of nominal dimensions 3mm×60mm×12mm. The test was carried out according to ASTM D4065-01 [14].

Fig 4. TGA Setup

Fig 5. DMA Setup

2.4.3 Morphological Characterization

Microstructure of neat and nanocomposite samples was examined under a Field Emission Scanning Electron Microscope (FE-SEM Hitachi S-900) JEOL JSM 5800), pictured in Figure 6. An accelerating voltage was applied to accomplish desired magnification. Micrographs were taken after the flexural tests were carried out.

Fig 6. SEM Setup

3. RESULTS AND DISCUSSIONS

3.1 Flexural Properties

Flexure tests were performed on the NP, 0.1, 0.2, 0.3, and o.4 wt.% CNF-FP nanocomposites and its laminates to evaluate their bulk stiffness and strength and their typical stress-strain behaviors are shown in Figures 7 and 8, respectively. It is clear from these stress-strain curves that all the samples of CNF-FP composites failed immediately reaching to their maximum values showing significant improvement in the mechanical properties up to 0.2 wt% of CNF loading, beyond that there was decreasing trend. Similar trend was found for the CNF-filled nanophased E-glass/polyester composites showing considerable nonlinearity before reaching the maximum stress. However, more or less ductility was observed in each type of laminate sample but no obvious yield point wasfound.

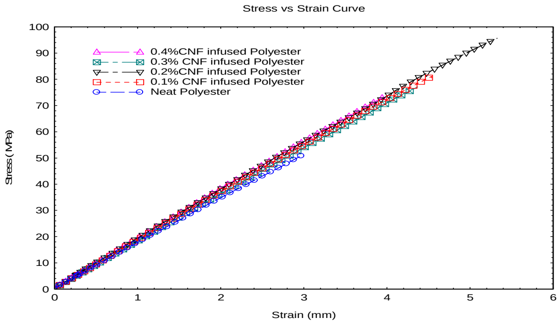

Fig 7. Flexural Stress-Strain Curves of Neat and

Nanophased CNF-FP Composites

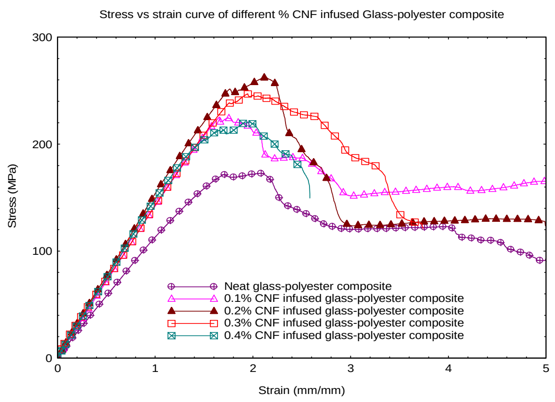

Fig 8. Flexural Stress-Strain Curves of NP and Nanophased CNF-FGRP Composites

Five samples were tested for each condition and the average properties obtained from these tests are listed in Tables 1 and 2. Table 1 shows the properties of the NP and CNF-FP samples loaded up to the 0.4 wt.% CNF with increment of 0.1 wt.%. It is evident that for 0.2 wt.% loading the flexural strength and modulus increased by about 76% and 16%, respectively, as compared to the NP samples. Similar trend was observed for the CNF-FGRP composites in Table 2.

Table 1: Results of CNF-FP with different % CNF

Sample	Flexural Strength (MPa)	% Gain in Strength	Flexural Modulus (GPa)	% Gain in Modulus
NP	51±2	-	3.44±0.21	-
0.1% CNF-FP	81±2	59	3.86±0.03	12.21
0.2% CNF-FP	95± 4	86	4.00±0.15	16.28
0.3% CNF-FP	77± 6	51	3.99±0.07	15.98
0.4% CNF-FP	73±4	43	3.83±0.14	11.34

Table 2: Results of CNF-FGRP composites

GRP	Flexural Strength (MPa)	% Gain in Strength	Flexural Modulus (GPa)	% Gain in Modulus
NP	174±5.8	-	16±0.8	-
0.1% CNF	228±9.4	31%	19±0.5	19%
0.2% CNF	260±4.3	49%	21±1.3	31%
0.3% CNF	248±8.3	43%	20±1.7	25%
0.4% CNF	220±5.2	26%	18±0.1	13%

From the resultant data it was found that the sonication mixing method is better than the mechanical one. 90 minutes sonication time and 0.2 wt.% CNF were explored the optimized conditions for this material system listed in Table 3.

Table 3: Sonication over mechanical mixing method

Sample Type	Flexural Strength (MPa)	Flexural Modulus (GPa)
NP	51±2	3.44±0.21
0.2%CNF-FP-90m-Sonication	95± 4	4.00±0.15
0.2%CNF-FP-90m-Mechanical	62± 6	3.5± 0.1

3.2 Thermal Response

TGA responses of NP and CNF-FP have been shown in Figure 9 as a function of temperature. It is clear from the plots that the decomposition temperature is slightly improved and overall weight loss was less for the 2 wt.% CNF-FP sample compared to all other samples.

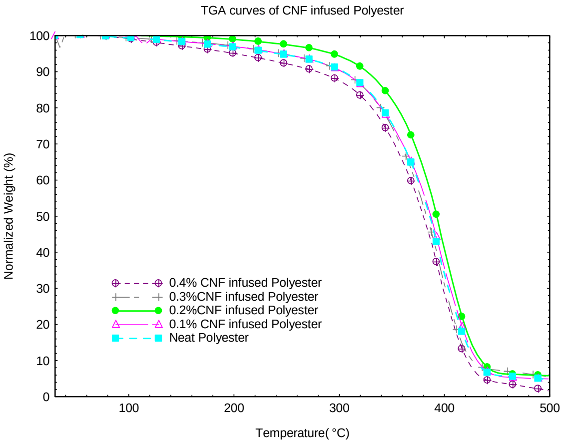

Fig 9. TGA Results of NP and CNF-FP Samples

The storage modulus and loss factor tan δ plotted as functions of temperature from DMA are shown in Figures 10 and 11. It is observed from the analysis that the storage modulus increases and peak height of the loss factor decreases with the addition of CNF. The addition of 0.2 wt% of CNF infused polyester showed the maximum improvement of 20 % in the storage modulus at room temperature. The CNF infusion does not affect the T_g of this material. DMA results are given in Table 4.

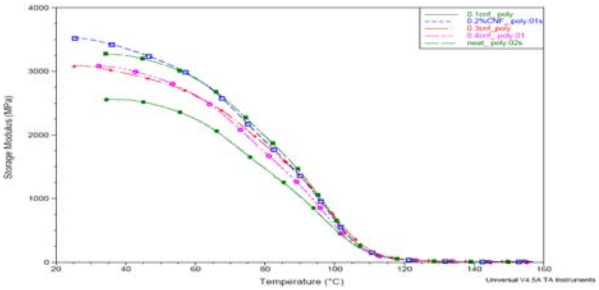

Fig 10. Storage Modulus-Temparature Curve

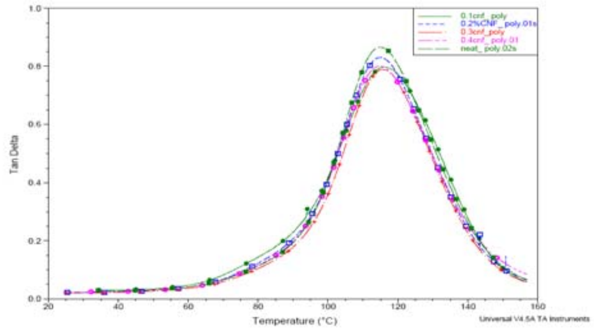

Fig 11. Loss Factor-Temperature Curve

Table 4: DMA results for NP and CNF-FP sample

Sample Type	Storage Modulus (MPa)	Tg (°C)
NP	3272	114.82
0.1%CNF-FP	2557	116.22
0.2%CNF-FP	3936	115.01
0.3%CNF-FP	3078	115.65
0.4%CNF-FP	3082	114.89

3.3 Fracture Surface Analysis

Scanning electron microscopy was performed on the NP, 0.2% CNF-FP, GRP, and 0.2% CNF-FGRP tested samples to study the fracture morphology. The SEM micrographs of the fractured surfaces of NP, CNF-FP, GRP, and CNF-FGRP are illustrated in Figures 12, 13, 14, and 15, respectively.

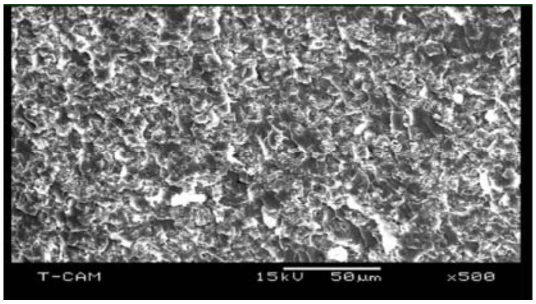

Fig 12. Fracture Surface of NP

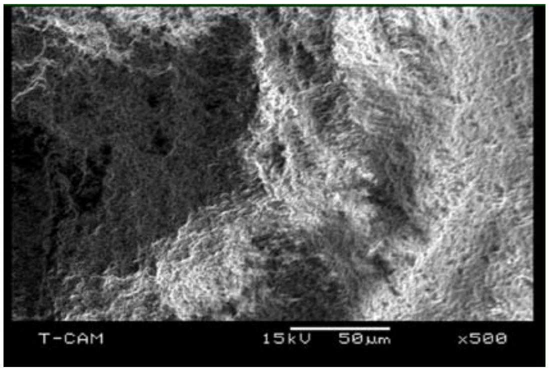

Fig 13. Fracture Surface of 0.2% CNF-FP

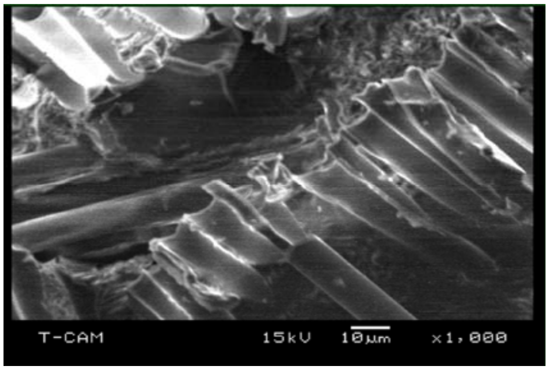

Fig 14. Fracture Surface of GRP Composite

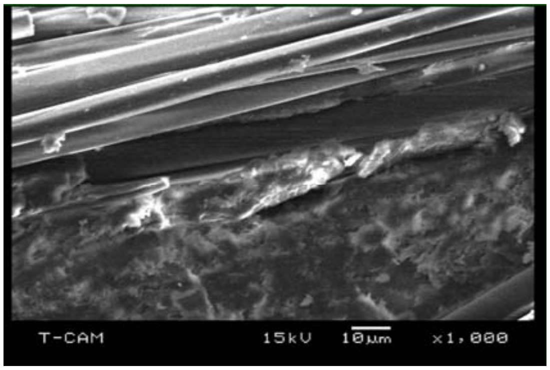

Fig 15. Fracture Surface of CNF-FGRP Composite

It is evident from the CNF-FP fractured surface is rougher compared to the NP fractured surface that gives rise to the mechanical and thermal properties. The rough surface attributes to the higher strength and modulus in the nanophased composites. Comparative analyses of the fractured surfaces of glass reinforced polyester composites and the CNF-filled glass reinforced polyester composites shows that the CNF-FGRP composites shows better adhesion between the fiber and matrix due to the addition of CNF than that of the GRP composites [15]. This better adhesion provides the less damage in the nanophased composites in terms of matrix cracking, fiber breakage, matrix fiber debonding, and delamination.

4. CONCLUSION

A high intensity ultrasonic liquid processor was used to infuse CNFs into polyester matrix which was then mixed with catalyst using a high speed mechanical agitator. The neat, CNF-filled polyester, conventional and nanophased composites samples were prepared and tested under the flexural and thermal loading condition. The fractured surfaces of the failed samples were examined under the SEM. The significant conclusions drawn from the investigation are given below.

1. Sonication mixing method is better than that of the mechanical mixing method to disperse the CNFs uniformly in the polyester.
2. 90 minutes sonication time and 0.2 wt.% CNF are the optimum condition to achieve the maximum mechanical and thermal properties.
3. 0.2% CNF-FP and 90 minutes sonication enhanced the 86% and116% improvement of flexural strength and flexural modulus, respectively.
4. 0.2% CNF-FGRP exhibited the 49% and 31% improvement of flexural strength and flexural modulus, respectively.
5. TGA results showed the addition of CNF has insignificant improvement in the decomposition temperature.
6. DMA results illustrated 0.2 wt.% CNF-FP improved 20% of storage modulus and negligible effect on the T_g.
7. SEM micrographs showed the rougher

fractured surfaces with addition of 0.2 wt.% CNF that attributed to the improved mechanical properties.
8. SEM studies revealed the better adhesion of fiber –matrix in the CNF-FGRP composites due to the uniform dispersion of the CNF.

5. ACKNOWLEDGEMENTS

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7. NOMENCLATURE

Symbol	Meaning
CNF	Carbon nanofiber
NP	Neat polyester
CNF-FP	CNF-filled polyester
GRP	Glass-reinforced polyester
CNF-FGRP	CNF-filled glass-reinforced polyester

8. MAILING ADDRESS

Assistant Prof. Mohammad Kamal Hossain
E-mail: hossainm@tuskegee.edu

Muhammad Enayet Hossain
E-mail: mh0684160@tuskegee.edu

Associate Prof. Mahesh Hosur
E-mail: hosur@tuskegee.edu

Prof. Shaik Jeelani
Director of T-CAM & Ph. D Program in Materials Science and Engineering, and Vice President for Research and Sponsored Program
Center for Advanced Materials (T-CAM),
Tuskegee University
101 Chappie James Center
Tuskegee, AL 36088, USA

E-mail: jeelanis@tuskegee.edu