Research Article

Energy Dissipation and High-Strain Rate Dynamic Response of E-Glass Fiber Composites with Anchored Carbon Nanotubes

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Abstract

This study explores the mechanical properties of an E-glass fabric composite reinforced with anchored multi-walled carbon nanotubes (CNTs). The CNTs were grown on the E-glass fabric using a floating catalyst chemical vapor deposition procedure. The E-glass fabric with attached CNTs was then incorporated into resin based composites and compared to similar composites without CNTs. Long and short beam bending tests, uniaxial compression measurements for energy dissipation, high strain-rate Split-Hopkinson pressure bar measurements, and ballistic performance (V50) tests were performed to characterize the mechanical properties of the CNT composites. The CNT composites showed a reduction in interlaminar shear strength by 25.9 %. They also showed an increase in the specific energy absorption by 106 % at high strain rates and an increase in energy density dissipation by 64.3 % after 5 cycles at quasi-static strain rates. In ballistic V50 tests, the CNT based composites showed a higher V50 value by 11.1 %. Due to their reduced weight and energy dissipation properties, the direct growth of CNTs on E-glass fabrics incorporated into composites have potential defense applications such as blast protection.

Keywords: Glass fiber reinforced polymer (GFRP) composite, carbon nanotube, mechanical properties, split-Hopkinson pressure bar, energy dissipation

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1. INTRODUCTION

Glass fiber reinforced polymer (GFRP) composites have excellent mechanical properties such as high Young's modulus, strength, stiffness, toughness, interlaminar shear strength, and are light weight. Due to their strong in-plane properties, these composites are used in a wide variety of structural applications including aerospace, automotive, civil, and the sporting industry [1-3]. Carbon nanotubes (CNTs) [4] have recently been used to reinforce these polymer based composites typically by improving the load transfer between the glass fiber and the polymer matrix material. The addition of CNTs to polymer based composites is a promising route for further improvement of the composites' mechanical properties due to their high modulus, large buckling and fracture strains, large strength, and low density [5-8]. The addition of CNTs also provides other improved properties of composites such as electrical conductivity, thermal conductivity, wear resistance, and electromagnetic shielding [9-14].

Many studies involving the mechanical properties of composites with incorporated CNTs involve the attempt to improve properties such as interlaminar shear stress (ILSS), toughness, Young's modulus, strength, and energy absorption [1, 11, 15-19]. In various defense and aerospace applications, the energy absorption of composites is important, and studies have been done to increase its capacity. An increase in energy dissipation was measured using both Dynamic Mechanical Analysis (DMA) and quasi-static compressive stress measurements in studies that intercalated separated vertically aligned CNT forests in between fabric layers in a polymer based composite [16]. For composites fabricated by dispersing CNTs in a polymer based resin, the absorbed impact energy increased by 21% [20] compared to the pure composites [21-22]. Using high strain-rate Split-Hopkinson bar measurements, composites with dispersed CNTs in the resin matrix showed an increase in both energy absorption and strength [23-27]. There has also recently been an interest in the ballistic properties of composites incorporating CNTs. By dispersing CNTs in the resin, ballistic properties such as the V50 value have marginally increased by less than 5% and fatigue life has been extended [28-32]. The addition of CNTs to (GFRP) composites for ballistic applications is a promising route since it offers a high hardness from the CNTs to fragment the projectile and a large toughness from the polymer matrix and pull-out to absorb energy [29].

There are a variety of methods that have been used to incorporate CNTs into a composite to improve the composite's mechanical properties. Most of them involve some method of

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4 mixing or dispersing CNTs in the resin and then using this as the matrix element in the
5 composite. This method has some drawbacks including CNT alignment, dispersion, and
6 adhesion of the CNTs in the polymer matrix [10, 33-35]. Other approaches that have been used
7 include the electrophoretic deposition of carbon nanofibers (CNFs) on the surface of carbon
8 fabric [36], transferring pre-grown aligned forests of CNTs to prepreg at room temperature while
9 maintaining CNT alignment [37], and stacking of pre-grown aligned or electrospun CNT forests
10 with fabric sheets [16, 38]. The electrophoretic method lacks CNF alignment, fabric attachment,
11 and has poor attachment to the resin while the other two methods only have CNT coverage on
12 the top fiber layer and lack attachment to the fabric.
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16 A more recent approach is to grow CNTs directly on the fabric material so that the CNT
17 nano-reinforcements are anchored on the fiber surface. This approach has been theoretically
18 shown to improve the transverse properties of the composite [39]. The first experiments were
19 done using a chemical vapor deposition (CVD) technique where CNTs were grown on carbon
20 fibers [40]. This method has the potential to increase the fiber-matrix interfacial adhesion [41],
21 improve the composite interlaminar shear stress (ILSS), and improve the toughness. The CNTs
22 at the fiber/matrix interface also stiffen the matrix material and increase the reinforcement
23 surface area, which both result in improved stress transfer. Since then, CNTs have been grown
24 on a variety of fiber types including ceramic [15, 42-43], carbon [40], and glass fibers [44].
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28 The main focus regarding the mechanical properties of composites fabricated with
29 CNTs grown directly on the fiber surface has been an attempt to improve transverse properties
30 such as ILSS [1, 15, 18, 45] and fracture toughness [15]. The impact of CNTs on the mechanical
31 properties of these composites, including compression energy dissipation, in the through-
32 thickness direction, has not been as well documented. The purpose of this research is to study
33 these properties of polymer based composites with direct CNT growth on the glass fabric
34 reinforcement material. The process used to fabricate the composites can be seen in the flow
35 diagram in Figure 1(a). One set of samples was made incorporating CNTs while the other set of
36 samples contained no CNTs. The CNTs were grown on desized glass fabrics using a floating
37 catalyst CVD method. The composites were fabricated using the hand lay-up method (Figure
38 1(c)) with the glass fabric (GF) scheduling shown in Figure 1(b). The GFRP composite samples
39 were mechanically characterized through long beam bending, ILSS, axial compression, high
40 strain rate Split-Hopkinson bar, and ballistic V50 measurements. The in-plane properties such as
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flexural strength and ILSS decreased with the incorporation of CNTs while the through thickness properties such as energy absorption in axial compression increased.

Figure 1. Schematic of the composite fabrication: (a) process flowchart: steps 5-8 were followed for fabrication of PE composites while steps 1-8 were followed for fabrication of PE-CNT composites, (b) stacking schedule, (c) hand lay-up method, (d) compression molding.

2. MATERIALS AND METHODS

2.1 Glass fabrics and desizing

The GFRP composites were fabricated using two commercially available glass fabrics (Fiber Glast Development Corp., Brookville, OH) with different thread counts and diameters. The control samples were made using only glass fabric type 1 (GF1), which can be seen in Figure 2(a). GF1 is a plain weave fabric with 197 by 157 threads/m, a thickness of 0.72 mm, a weight of 832 g/m², and a measured fiber diameter of $21.3 \pm 1.5 \mu\text{m}$. The CNT based GFRP composites contained standard GF1 sheets and glass fabric type 2 (GF2) sheets, which were used as the substrate for CNT growth. The GF2 sheet, which can be seen in Figure 2(a), is also a plain weave fabric with 629 by 551 threads/m, a thickness of 0.36 mm, a weight density of 339 g/m², and a measured fiber diameter of $8.9 \pm 1.1 \mu\text{m}$. The GF2 material was chosen as the substrate for CNT growth due to the larger surface to volume ratio which should result in a greater density

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4 of anchored CNT growth. Both GF1 and GF2 contain a sizing component which is a coating
5 over the surface of each glass fiber that adds strength and improves the adhesion to the resin
6 system [46-47]. The sizing prevents the attached growth of CNTs on the surface of the glass
7 fabrics. So a desizing process, as described below, was used on GF2 to remove the sizing
8 compound from the fabric surface.
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11 The GF2 sheet was cut to a size of about 38 cm by 38 cm and placed in a container that
12 was filled with a 4% by wt. solution of hydrofluoric acid (KMG Electronics Chemical Inc.,
13 Houston, TX). After a 1 min wetting time, the fabric was gently rolled with a paint roller for 4
14 min to break up and loosen the sizing compound. The exposure to hydrofluoric acid served to
15 both remove the desizing material and slightly etch the glass fiber to prepare its surface for CNT
16 growth. The container was then agitated and the GF2 sheet was removed and rinsed with
17 running tap water for about 5 min. The GF2 sheet was then dried at room temperature for at
18 least 12 hours. The edges were trimmed to eliminate edge fraying which resulted in a fabric with
19 a size of 30 cm by 30 cm.
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Figure 2. Optical and SEM images of CNT growth on desized GF2 sheets; (a) optical image of GF1, GF2 and CNT-GF2 fabrics, (b)-(g) SEM images of CNT growth showing full and partial growth at different magnifications.

2.2 CNT growth

The CNTs were grown on the GF2 substrate using the well-established floating catalyst chemical vapor deposition (FC-CVD) method [48-49]. A solution of 4% by wt. ferrocene (Sigma Aldrich, 98%, St. Louis, MO) in *m*-xylene (Sigma Aldrich, anhydrous $\geq 99\%$, St. Louis, MO) was prepared to implement the floating catalyst fabrication of CNTs. The processing was done in a rectangular steel box (14 in by 13 in by 3 in), mounted on a 3600 W ceramic plate heater (Omega, Stamford, Connecticut), with 3 inlet manifolds supplying the reactants and 3 matching outlet exhaust manifolds and can be seen in Figure 3. One 30 cm by 30 cm sheet of desized GF2 was arranged on each of three racks in the rectangular steel reactor which was heated to the

process temperature in about 2 hr under the flow of 2000 cm³/min of N₂ (S.J. Smith Welding Supply, ultra high purity, Davenport, IA). To start the pyrolysis, the solution was pumped into the reactor using an Ismatec Ecoline metering pump (Wertheim, Germany) through three inlet manifolds, each of which was externally heated to about 350 °C to vaporize the solution. Nitrogen and hydrogen (Specialty Gases of America, ultra high purity 99.999%, Toledo, OH) carried the vapor into the reaction chamber containing the three GF2 sheets at a flow rate of 2000 and 300 cm³/min, respectively. The fabrics were processed for 60 min and a total solution of about 300-400 mL was used for each experiment. The process temperature was set to between 550 and 650 °C. After the process was complete, the ferrocene solution, H₂ gas, and reactor power were turned off so the reactor could cool to room temperature under the flow of N₂ gas.

The CNTs grew over the entire 30 cm by 30 cm area on the desized GF2 substrate. The CNT density varied slightly across the sample area (Figure 2(a)). The slight non-uniformity of the growth profile is a result of the desizing process [17] and the gas flow distribution (including carbon precursor and Fe catalyst) due to the rectangular growth chamber and obstacles such as the GF cloth and metal mesh supporting each fabric disrupting the flow. SEM images of the anchored CNTs are shown at various magnifications in Figures 2(b)-(g). The CNT forest consisted of multi-walled CNTs and grew around the cylindrical surface of the exposed individual glass fibers (Figure 2(c)-(g)). The top and bottom surfaces of the GF2 desized cloth were covered with the CNT forest and CNT growth partially penetrated through the thickness of the fabric. The anchoring of the CNTs to the glass fiber can be seen in Figure 2(f). The average diameter of the CNTs grown on the glass fibers was 52.3 ± 29.4 nm while the average forest height was about 5.4 μm. The average diameter was determined by calculating the average of 180 individual diameter measurements using SEM images from multiple samples. To determine the average CNT forest height, the average diameter of the desized GF2 fiber was subtracted from the average diameter of the GF2-CNT fiber (including CNTs) and divided by 2. A total of 30 individual measurements were used to calculate the average GF2 and GF2-CNT diameter using multiple samples. There were some residual amorphous carbon and Fe catalyst impurities on the fabric, but these were mostly removed with the purifying process described below.

Figure 3. Composite fabrication; (a) large process reactor for CNT growth on GF, (b) inside view of the manifold inlets, (c) (top) PE and (bottom) PE-CNT sample cross sectional view showing the scheduling of GF1 and GF2 sheets.

2.3 Purification of the CNT sheets and functionalization

To purify the GF2-CNT sheets of amorphous carbon and extra catalytic iron particles and to increase the bonding strength of the CNTs to the resin, a purification and functionalization process was carried out on the sheets. The GF2-CNT sheets were placed in a pan filled with 1N nitric acid (HNO_3) (Spectrum Chemical Mfg. Corp, Garden, CA) and agitated using a shake table (Thermolyne Corp, Bigger bill digital, Dubuque, IA) at 3 Hz for 1 hr. The sheet was then placed in tap water and agitated for 4 min. The sheet was then placed in a solution of 10% by wt. oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) (Crystal, Spectrum Chemical Mfg Corp, Gardena, CA) and shaken at 3 Hz for 6 hr. The sheet was then agitated in tap water for 4 min and then dried at room temperature. This process is expected to add carboxyl, hydroxyl, amines, and nitro functional groups to increase bonding to the PE resin. There was a slight black color in the nitric acid and oxalic acid after processing indicating that some CNTs or amorphous carbon has been released from the GF2 surface or that non-anchored CNTs have been removed. The black color on the fabric surface was also slightly dulled after the purification and functionalization process.

2.4 CNT and pure GFRP composite fabrication

Two sets of GFRP composites were fabricated using a combination of the hand lay-up and compression method to ensure proper fiber wetting and uniform distribution of the resin through the fabric layers. The pure composite containing no CNTs was termed “PE” and was the control. The PE composite contained 20 square 30 cm by 30 cm layers of GF1 stacked so that the warp strand was oriented in the same direction for all layers. The CNT based composite was termed “PE-CNT” and contained both the sized GF1 sheets and the desized and processed GF2 sheets with anchored CNTs. These composites were scheduled according to Figure 1(b): on the bottom were five layers of GF1, in the middle were 6 sets of alternating GF2-CNT and GF1 sheets, and on top there were five layers of GF1. Again, all the GF1 warp directions were oriented in the same direction. This configuration was chosen to isolate the effect of intercalating layers of anchored CNTs and to reduce the effect of the weakened GF2 fabrics due to the desizing process. The CNT layers were placed in the middle of the composite so that they would be protected from the initial impact of the load and survive to act as nano-springs to absorb energy.

The resin used in the hand lay-up was unsaturated polyester E15-8082 resin (Fiberglass Supply, Burlington, WA) which is suitable for hand lay-up due to its low viscosity. The resin has a mass density of 1.08 g/cm³, a flexural stress failure point of 78 Mpa, a modulus of 4 GPa, and a strain at failure value of 1.8% [50]. The E43-4704 Catalyst (Methyl Ethyl Ketone Peroxide) (purchased from Fiberglass Supply, Burlington, WA) was used to initiate the polymerization process. Since the polymerization time is a function of catalyst concentration, a 1% by wt. concentration was chosen for the catalyst which was mixed in the resin and stirred for 2 min at 350 rpm using a RW20 digital stirrer (IKA, Wilmington, NC). Using a 1% by wt. catalyst permitted a long enough time (about 23 min) to hand lay-up all layers before polymerization took place.

The resin was then applied to the GF1 and GF2 sheets using the hand lay-up method (Figure 1(c)) and the laminates were stacked according to their respective schedule. Some CNTs were removed during the hand lay-up process, but post-bending SEM images (such as Figure 6) show that a high-density of CNTs remained firmly attached to the fabric. The entire lay-ups were then uniformly axially compressed at about 550-575 kN using a Carver Laborator Press Model 2629 (Carver Inc., Wabash, IN) at room temperature for about 12 hr to pre-cure the resin (Figure 1(d)). After removing the load, the excess resin was trimmed and the composite was post-cured at 86 °C for 1 hr and then at 120 °C for 2 hr as per the manufacturer recommendation in a

temperature controlled oven Model CE3G (Sheldon Mfg. Inc., Cornelius, OR). The composite was then cut into individual samples as required for flexural strength, ILSS, energy dissipation, split-Hopkinson pressure bar, and V50 testing. The average thickness of the PE composite was about 9.3 mm and the average PE-CNT composite thickness was about 12.3 mm (Figure 3(c)). The difference in thickness of the two composites is due to an increase in the effective GF2 fabric thickness resulting from CNT growth and the presence of an extra GF1 layer in the PE-CNT composites. For the PE composites, the resin, GF1, and void volume fraction was 31.07%, 62.92%, and 6.01%, respectively. For the PE-CNT composites, the resin, GF, and the void + CNT volume fraction was 47.37%, 47.61%, and 5.01%. The estimated percent CNT in the PE-CNT composite was 0.88 % by wt. The bulk density of the PE and PE-CNT samples were measured by dividing their mass by their volume. The density of the PE composites was $2017 \pm 12.3 \text{ kg/m}^3$ while the density of the PE-CNT composites was $1732 \pm 11.5 \text{ kg/m}^3$. There was a reduction of 14.1 % in the composite density due to the replacement of six GF1 sheets with GF2 sheets, the desizing process, and the presence of anchored CNTs on the GF2 surface.

2.5 Low strain rate measurements

2.5.1 Flexural properties

The flexural properties were measured in a 3-point bending test following ASTM 790-10 [51]. The PE composite samples were cut using a diamond blade saw to a size of 27.1 mm by 193 mm by 9.45 mm while the PE-CNT composite samples were cut to a size of 27.1 mm by 252 mm by 12.4 mm. The span length of the PE and PE-CNT samples measured in the 3-point bending were 152 mm and 203 mm, respectively, to approximately maintain the span length to thickness ratio of 16:1 according to the ASTM standard. The force vs. displacement measurements were conducted with a MTS servo hydraulic device model 311-11904.98 (Eden Prairie, MN, USA) using a 222.4 kN load cell with a noise level of about 10 N. The samples were center loaded in a 3-point bending configuration as a simply supported beam using cylindrical supports and a loading nose with radii of 5 mm. The cross head motion rate (R) for the PE samples was set to 4.1 mm/min according to the ASTM standard which was calculated using Equation 1:

$$R = \frac{ZL^2}{6d}, \quad (1)$$

$$\sigma_f = \frac{3PL}{2bd^2} \quad (2)$$

$$\varepsilon_f = \frac{6Dd}{L^2} \quad (3)$$

where Z is a strain rate constant of 0.01/min, L is the span length, and d is the sample thickness. The cross head motion rate was maintained at this same value for the PE-CNT bending measurements. The measured force and displacement values were used to calculate flexural stress and strain according to Equations 2 and 3, where σ_f is flexural stress, ε_f is flexural strain, P is the center load, D is the maximum deflection of the center of the beam, and b is the sample width. At least three specimens were tested for each sample configuration and the calculated results are plotted in Figure 4(a). The flexural strength was identified as the maximum flexural stress sustained by the test specimen during the bending test.

2.5.2 Inter laminar shear stress (ILSS)

The ILSS was measured using a 3-point short beam strength test following ASTM D-2344-00 [52]. The measurement was conducted on a MTS servo hydraulic device model 311-11904.98 using a 1.27 mm/min cross head speed. The samples were center loaded in a 3-point bending configuration as a simply supported beam using cylindrical supports with a diameter of 3 mm and a loading nose with a diameter of 6 mm. The sample size was determined according to ASTM 2344-00 where the sample length was 6 times the sample thickness, the width was 2 times the thickness, and the span length was set to 4 times the sample thickness. The average PE and PE-CNT composite sample dimensions were 27.4 mm by 67.8 mm by 9.45 mm and 24.2 mm by 76.7 mm by 12.4 mm with span lengths of 53 mm and 50 mm, respectively. The maximum observed load for each sample was used for calculating the ILSS (short beam strength) which is given by Equation 4:

$$ILSS = \frac{3P_m}{4bd} \quad (4)$$

where P_m is the maximum observed load, b and d are the width and thickness of sample, respectively. The calculated ILSS values are presented in the inset of Figure 4(b).

2.5.3 Axial compression for energy dissipation

The energy dissipation measurements were conducted on a MTS servo hydraulic device model 311-11904.98 in compression mode using a compression tool to ensure flat surfaces and uniform

load distribution. The samples were compressed at a rate of 178 N/s in the through-the-thickness direction for 5 complete cycles while measuring load vs. displacement up to a maximum stress of 100 MPa. All samples were cut to near square shape with average side dimensions of 14.54 mm for the PE composites and 14.3 mm for the PE-CNT composites. The PE composites had a thickness of about 9 mm and the PE-CNT composites had a thickness of about 12 mm. The force limit was adjusted to account for the small variation in the samples lateral dimensions. The total dissipated energy for each cycle was calculated by integrating the force vs. displacement curve for each cycle. The energy density dissipation was found by summing up the area enclosed in the stress vs. strain curve for each cycle presented in Figure 6. No failure or cracks were noticed in any samples measured up to 100 MPa.

2.6 High strain rate split-Hopkinson pressure bar measurements

Split-Hopkinson Pressure bar (SHPB) compression tests have been performed using 6061-T6 Aluminum round bars of 19.05 mm (0.75 inch) diameter. The striker, incident, transmission, and momentum bars used were 0.46 m (18 inch), 3.66 m (144 inch), 2.44 m (96 inch) and 0.46 m (18 inch) long, respectively, and axially aligned on nylon ball bearings to achieve near frictionless translational motion. The square shaped specimens were axially mounted between the incident and transmission bars. A thin layer of glycerin was applied on both contact surfaces of the specimen for proper positioning and to avoid slippage. The average dimensions of the PE and PE-CNT samples measured were 12.4 mm by 12.4 mm by 9.2 mm and 14.7 mm by 14.7 mm by 11.9 mm, respectively.

The striker bar rested on two nylon sleeves inside a cylindrical steel barrel. Compressed air was released at 10-15 psi from a reservoir and axially propelled the striker bar toward the incident bar. An 8 mm diameter and a 0.9 mm thick pulse shaper made of polyurea were axially mounted (with a drop of glycerin) at the impact end of the incident bar for modifying the shape of the incident stress wave. The impact of the striker bar sent a ramped compressive stress wave through the incident bar.

Due to the impedance dissimilarity between incident bar and specimen, a certain portion of the incident stress wave passed through the specimen according to the one-dimensional wave propagation theory, and the remaining part reflected back into the incident bar as a reflected tensile stress wave. Consequently, a certain portion of the stress wave compressed the specimen

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4 in the through-the-thickness direction and reverberated between two end surfaces. The remaining
5 part was transmitted through the transmission bar. The momentum bar received the transmission
6 stress wave without allowing further reflection and was trapped in a putty-clay block installed at
7 the end of the SHPB apparatus. The equilibrium stress state within the specimen has been
8 verified to ensure the validity of the SHPB analysis.
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11 The transient strains of the bars due to the incident, reflected, and transmitted stress
12 waves were obtained from strain gages mounted on incident and transmission bars and gave
13 strain rate and stress in the specimen, respectively. The least time-width of the reflected and
14 transmitted pulses was considered as the duration of the dynamic test event. The strain of the
15 specimen was derived from the time integral of the strain rate. The stress versus strain plot
16 showed the dynamic response of polymer at that strain rate. The area under the stress-strain plot
17 estimated the energy absorption capacity of the specimen per unit volume and after being divided
18 by the specimen mass-density, provided mass-specific energy absorption.
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30 *2.7 Ballistic V50 tests*

31 The V50 value for the samples was measured in accordance with MIL-STD-662F in an indoor
32 range (Oregon Ballistic Laboratories, LLC, Salem, OR) with the muzzle of the test barrel
33 mounted 5.03 m from the target and positioned to produce 0° obliquity impacts. The samples
34 were center mounted in between two faceplates that had square openings with dimensions of
35 3.65 cm by 3.65 cm. The V50 value for a sample is defined as the projectile velocity at which
36 there is a penetration success of 50%. Four infrared light screens, in conjunction with time-
37 based frequency counters, were positioned such that the projectile velocity was measured 2.51 m
38 from the target. Penetrations were determined by examination of a piece of 0.508 mm 2024-T3
39 aluminum mounted 15.24 cm behind and parallel to the test sample. A 17 gr FSP 1-7 projectile
40 was used in conjunction with a 0.223 Rem FRAG/1:12/11" barrel for all tests. All samples were
41 cut to 5.08 cm by 5.08 cm size and the PE composites had an average thickness of 9.27 mm
42 while the PE-CNT composites had an average thickness of 11.48 mm.
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54 *2.8 Scanning electron microscopy (SEM) and failure analysis*

55 Scanning electron microscopy (SEM) images of the CNT anchored GF2 sheets were obtained
56 with a Hitachi S4800 High Resolution SEM with an accelerating voltage of 5 kV and a working
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distance of 8-10 mm. From high magnification images of the CNTs on the GF2 sheets the average CNT diameter was found to be 52.3 ± 29.4 nm with an average height of 5.4 μ m. Fractured PE and PE-CNT samples from the ILSS tests were imaged using a JEOL JSM 6390 SEM (JEOL USA Inc., Peabody, MA) with an accelerating voltage of 5 kV and a working distance of 10 mm. These images were used to analyze the failure modes and failure patterns for each type of sample. To avoid the charging effect, these samples were first sputter coated with Au for 2 min at a current of 45 mA using a Denton Desk-II sputter coater (Denton Vacuum, Moorestown, NJ).

3. RESULTS AND DISCUSSION

Experiments were conducted to characterize the flexural and interlaminar shear strength properties of the PE and PE-CNT composite samples and the results are shown in Figure 4. These samples had both a higher average ultimate strength and modulus than PE-CNT composites with values of 469 MPa and 33.1 GPa, respectively. The PE-CNT composites had a lower mean ultimate strength and modulus with values of 247 MPa and 21.6 GPa, respectively. Thus, the ultimate strength of the CNT coated fiber composites decreased by 47.3 % while the modulus decreased by 34.7 %. The standard deviation of the ultimate strength and modulus for PE composite samples were 13 MPa and 0.46 GPa, while for the PE-CNT samples they were 58 MPa and 4.1 GPa. These results show that the composite fabricated using only sized GF1 sheets are both stronger, have a larger modulus, and have significantly less variation in these parameters. This is not a surprising result since the PE composite is made from sized GF where the sizing material is designed for increased strength and protection during the fabric fabrication process [46-47]. The desized GF2 sheets were introduced to the PE-CNT composite at 6 locations and were interspersed between GF1 layers. The average fiber diameter in the sized GF2 layer was 8.9 ± 1.1 μ m which was decreased by 24 % in the desizing process to 6.8 ± 1.8 μ m leading to a reduction of strength and modulus. The strength and modulus are both expected to decrease in composites when fabricated using desized GF sheets rather than sized sheets. This is due in part to a reduction in fiber diameter and a reduction in the bonding strength between the resin and the glass surface. One study involving a tensile test on a single desized carbon fiber observed a decrease of 29 % in the ultimate tensile strength and a decrease of 50 % in the interfacial shear strength compared to a sized fiber [53]. When CNTs were grown on these

desized fibers using the harsh CVD conditions necessary for good CNT growth (similar to those used in this work), the ultimate tensile strength decreased 30-37% while the interfacial shear strength increased by 11-71 % compared to the plain desized fiber. However, these CNT coated fibers decreased by 50-55 % in the ultimate tensile strength and 15-45 % in the interfacial shear strength compared to a sized fiber [53]. This overall decrease was due to the reduced diameter of the fibers and the defects introduced on the GF fiber surface due to thermal degradation and oxidation effects, which can be reduced by processing at lower temperatures [45]. By optimizing the process conditions for the CNT growth and resizing the fiber after CNT growth, this reduction in strength can be minimized or even reversed.

A decrease in strength was also noticed in the ILSS of the PE-CNT composite samples. The force vs. displacement was measured according to the ASTM short beam test and the results are plotted in Figure 4(b). The maximum force observed in the short beam test was measured to be about 7.1 % higher for the composite samples containing only sized GF1 fabrics while the average value of the displacement where the failure occurred was nearly similar. The ILSS was calculated according to Equation 4 for both the PE and PE-CNT composites. It was found that the average ILSS was higher by 34.9 % for the PE composites. This is in contrast to most studies involving composites with adjacent fiber layers with anchored CNTs, where an increase in ILSS was measured [15, 18, 45]. This was due in part to the desizing and thermal CVD process conditions the GF2 layer was exposed to and the lack of a stitching effect due to non-adjacent CNT layer stacking [15, 40, 54]. However, the average strain at failure was 25.2% higher for the PE-CNT composites. This increase in the strain to failure is consistent with other measured CNT anchored composites [17].

Figure 4. Bending measurements for PE (black) and PE-CNT (red) composites; (a) flexural stress vs. strain data, (b) short beam showing force vs. displacement. (Inset) ILSS values obtained from the short beam measurements.

Further insight into the failure mechanisms can be gained by analyzing the SEM images of the failure sites and comparing them to the images of the unstressed samples, which are presented in Figure 5. Before the bending test, a cross sectional image (Figure 5(a)) of the PE sample reveals good resin penetration in the GF1 fabric. There are few voids and most of the sized GF1 fabric has not cracked after the compression molding. The SEM image of the premeasured PE-CNT composite (Figure 5(b,c)), on the other hand, revealed more voids. This is due to the high concentration of CNTs around the GF which partially obstructs the flow of resin [1]. However, the void % per unit volume actually decreased for the PE-CNT composite which was due to the increased thickness of the composite. The cracks that occur throughout the CNT grown GF2 sheets are due to the compression molding and the reduced GF2 fiber diameter due to desizing and glass etching.

After the short beam test, the SEM images of the PE samples show a clear ILSS failure in the GF1 sheet (Figure 5(d)) which occurs due to a delamination of the sized GF1 fiber from the surround matrix material (Figure 5(g)). The tested PE-CNT composites showed a similar ILSS failure mode except that the failure always occurred in the GF2 layer, while the GF1 layer remained intact as can be seen in Figure 5(e). Many fibers had no resin attached indicating the reduced binding of the resin to the glass fabric surface due to desizing. After failure, CNTs were observed both on the GF2 surface (Figure 5(h) and (i)) and in the resin that was in direct contact with the GF2 surface (Figure 5(f)) showing that the CNTs played a role in the failure. However, in most of the failed samples, GF2 fibers were stripped of the attached CNTs indicating that the CNTs have a stronger bonding strength to the resin than the fibers. This was previously observed [45] in GF composites with anchored CNTs which also showed a reduction in ILSS. This was attributed to defects on the GF surface during CNT synthesis.

Figure 5. SEM images of fracture surfaces; (a) PE composite before bending, (b)-(c) PE-CNT composite before bending showing voids and broken glass fibers in the GF2 layer, (d) and (g) PE composite after bending failure showing delamination in the GF1 layer, (e) PE-CNT after

bending failure showing delamination, which always occurred in the GF2 layer, (f) CNTs embedded in resin after failure (h) and (i) CNTs still attached to GF2 fibers after failure.

The reduction of bending strength and ILSS of the PE-CNT suggests the possibility of new modes of energy dissipation upon sample loading. The energy dissipation of the pure composite and the CNT reinforced composite were measured in a non-failure compression mode in the through-the-thickness direction of the composites. Each cycle was stress limited to 100 MPa and a total of 5 cycles were measured. In Figure 6(a) the stress vs. strain is plotted for the first and second full compression cycles for representative curves for both the PE and the PE-CNT composite. There are two distinct regions in the stress vs. strain graph. At low strains (less than about 0.02) the compressive stress is small, but at higher strains, the stress increases more rapidly. This is due to a densification phenomenon where the resin void volume decreases as the stress increases filling them in with surrounding cured polymer resin. After this hardening process the stress begins to increase at a greater rate because of this added confinement. The first cycles for both the PE and PE-CNT samples show a much larger hysteresis than subsequent cycles. The hysteresis in the stress vs. strain diagram is related to the energy density dissipated per cycle. The area enclosed by the stress vs. strain plot is equal to the energy density dissipated by the composite sample. Since this is larger for the first cycle, more energy is dissipated in the first cycle than in subsequent ones. This is a plastic deformation process and can be attributed to hardening. This also explains the residual strain of about 0.005 observed after the first cycle. The hardening significantly decreases, but is still present, for subsequent cycles.

As a result of the hardening, there is a large hysteresis or energy dissipation in the first cycle for both sample types. The second cycle still shows hysteresis, but the dissipated energy is reduced by about a factor of two. In subsequent cycles the hysteresis is still present, and the average dissipated energy continues to decrease but by less than 11.5 % and 4.6 % on average per cycle over the last 3 cycles for the PE and PE-CNT samples, respectively. Even after the fifth cycle there is still significant dissipated energy, showing that these samples can be cycled many times and still be useful in dissipating energy.

The PE-CNT samples showed higher energy dissipation in all five cycles measured. This can be seen in Figure 6(a) as a greater area enclosed by the stress vs. strain curve. This is the case even after five cycles. A plot of energy density dissipation vs. cycle number is shown in Figure 6(b) for three PE and three PE-CNT samples. Both the average dissipated energy and

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4 average energy density (per unit volume) dissipation was greater for the PE-CNT composites
5 after all cycles. After 5 cycles the average dissipated energy was greater for the PE-CNT
6 composites by 64.3 %. This increase in energy dissipation is due to the presence of CNTs in the
7 composite. In carbon fiber composite experiments both with anchored CNTs [41] and with
8 mixed in CNTs [20], an increase in energy dissipation was observed as a result of the presence of
9 CNTs. They provide additional rupture mechanisms and dissipate energy through fracture
10 energy absorption, inter-tow friction, friction between the CNT and the resin matrix, and plastic
11 deformation [11, 20]. The dissipated energy potential for the PE-CNT samples was reduced by
12 the compression molding step in the fabrication process since some CNTs were damaged. The
13 energy dissipating properties of these samples are expected to increase with an optimization in
14 the compression molding step in the fabrication process. The GF2 fabric is not expected to
15 contribute much to the energy dissipation due to its small fiber sized compared to GF1 which
16 results in less strand movement and less energy dissipation due to friction [55].
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Figure 6. Compression measurements for energy dissipation; (a) representative stress vs. strain data plotted for the first and second cycle for both PE and PE-CNT composites, (Inset) a zoomed in view showing the hysteresis (b) energy density dissipated vs. cycle number for 3 samples each of PE and PE-CNT composites. The dashed lines show the average dissipated energy density for the PE and PE-CNT composites samples, (Inset) energy dissipated vs. cycle number for the PE and PE-CNT composites.

High strain rate compression measurements were conducted using a split-Hopkinson pressure bar to study how growing CNTs directly on the GF surface impacts the energy absorption properties of the resulting composite at high strain rates. To do this, three PE and three PE-CNT samples were measured in compression at strain rates of 110-125 /s and 143-170 /s. Their stress vs. strain values were recorded and are plotted in Figure 7(c). The PE and PE-CNT samples showed a mixed response at low strains. At medium strains, the PE composites

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4 had a larger stress. The PE-CNT samples were able to be compressed to even higher strains
5 while still maintaining a lower stress value than the PE composites. This can be attributed to the
6 greater presence of voids [56] in the PE-CNT samples and the ability of the CNTs to transfer
7 load adding to their energy absorption properties. Despite the lower density of the PE-CNT
8 samples, the specific energy absorption of the PE-CNT samples was 106 % higher than the PE
9 samples. The increase in energy absorption is due to both the higher presence of voids in the PE-
10 CNT samples and the CNTs themselves. Increased energy absorption under high strain rates
11 has been observed in the literature for CNTs mixed in polycarbonate and epoxy resin composites
12 and was found to be a function of CNT loading [24-27]. The CNTs contribute a new mode of
13 energy absorption since the CNTs can be plastically deformed through bending or fracture
14 during the high strain compression and can dissipate energy due to CNT-CNT and CNT-resin
15 friction. Not only was the specific energy greater in the PE-CNT samples but the rate of specific
16 energy absorption was greater by 112 %. Thus the incorporation of CNTs grown on the desized
17 GF2 sheet increases both the specific energy absorption and the rate of specific energy
18 absorption at high strain rates.
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Figure 7. High strain rate Split-Hopkinson pressure bar data; (a) stress vs. strain data for 3 PE and PE-CNT composite samples, (b) average specific energy absorption of the PE and PE-CNT composites, (c) the average rate of specific energy absorption of the PE and PE-CNT composites.

The ballistic properties of the composites were analyzed in accordance with MIL-STD-662F. Both the V50 value and the corresponding damage modes were analyzed. Out of the 8 individual 5.08 cm by 5.08 cm PE samples tested, 5 resulted in partial penetration while 3 resulted in complete penetration. Out of the 8 PE-CNT samples tested, 4 resulted in partial penetration and 4 in complete penetration. This indicates that the V50 data are reliable. An analysis of the optical images of the partial and complete tested PE samples (displayed in Figure 8(a) and (b)) revealed damage due to shear failure (delamination), fracturing, cracking, and shattering. The same damage modes were observed in the PE-CNT samples for both the partial and complete penetration results (Figure 8 (c) and (d)). For the PE samples, the delamination

was significant and occurred in the last approximately 1/3 of the thickness of the sample opposite to the end of projectile entry. The delamination for the PE-CNT samples was also significant and always occurred at the GF2-CNT interface due to a lower ILSS at this interface. Like the PE samples, the delamination often occurred at the opposite end of projectile entry. Unlike the delamination in the PE composites, the delamination in the PE-CNT composites often occurred near the middle of the sample or near the entry plane of the projectile. This indicates that at the GF2-CNT interface there is a reduced toughness in the PE-CNT samples. The V50 data are displayed in Figure 8(e) and show that the PE-CNT composites have a higher V50 value compared to the PE composites by 11.1 %. The greater delamination in the PE-CNT samples further helps to dissipate the energy and stop the projectile. The high value of the CNTs hardness also helps to dissipate the projectile's kinetic energy by projectile fracturing. For improved V50, the CNT layers should be placed near the front of the composite and be perpendicular to the composite face, which was partially satisfied in these samples [29, 31]

Figure 8. V50 testing results; (a)-(b) optical images of representative PE composite samples showing the front side (top) and back side (bottom) of samples after V50 testing with partial (a) and complete (b) penetration, (c)-(d) optical images of representative PE-CNT composite samples showing the front and back sample sides after V50 testing with partial (c) and (d) complete penetration, (e) projectile velocity vs. shot # showing partial and complete penetration data for both PE and PE-CNT samples with dashed lines showing the corresponding V50 values.

4. CONCLUSION

CNTs have been directly grown on GF2 sheets which have been intercalated with plain GF1 sheets and incorporated into a resin based composite. A desizing process was necessary to achieve CNT grown on glass fabric. Long beam bending, short beam bending, uniaxial compression, split-Hopkinson bar, and ballistic V50 measurements were done on both plain composites and CNT-grown GF composites to determine the effect of the anchored CNTs on the composites in-plane and through-thickness properties. It was found that in long beam bending both the ultimate strength and the modulus decreased in the PE-CNT samples by 47.3 % and 34.7 %, respectively. In short beam bending, the ILSS was 34.9 % higher for the PE composites and the failure in the PE-CNT composites always occurred at the GF2-CNT interface. Thus, the in-plane properties of the PE-CNT samples were lower than the PE samples. On the other hand, the energy absorption properties increased in the through-thickness direction. After 5 uniaxial compression cycles at a quasi-static strain rate the PE-CNT composites showed an improved energy density dissipation of 64.3 % compared to the PE composites. At high strain-rates the specific energy absorption of the PE-CNT composite samples was 106 % greater than the PE composite samples while the rate of specific energy absorption was greater by 112 %. This improvement in energy absorption at high strain rates with the incorporation of CNTs translated into improved V50 values which were higher in the PE-CNT samples by 11.1 %. In the V50 tests, the delamination in the PE-CNT samples always occurred at the GF2-CNT interface. Overall, the CNT composites resulted in a decreased of in-plane properties such as ILSS and bending but an increase in through the thickness properties such as energy absorption.

In future work, the force of compression during composite fabrication can be optimized to eliminate voids while not causing unnecessary pre-straining which reduces the mechanical properties of the composite including its capacity for energy absorption. The resin matrix, GF type, and arrangement of GF fabrics within the composite must also be optimized. In order to

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4 achieve a high energy absorption and a high ILSS, the desizing process must be optimized. Too
5 much desizing reduces the strength of the composite while not enough results in poor CNT
6 coverage and thus reduced energy absorption. Controlling the number and placement of the GF1
7 and GF2-CNT layers is another route to explore to achieve an optimization in both the in-plane
8 and through-thickness mechanical properties. A higher number of GF2-CNT layers will most
9 likely result in more energy dissipation but perhaps a reduction in ILSS. A ceramic film may be
10 added to the PE-CNT composites to further increase the composite hardness which would result
11 in even higher V50 values. Overall, the direct growth of CNTs on GF sheets for composites is a
12 promising route for improved energy dissipation of structures at both low and high strain rates.
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23
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34 **Disclaimer**

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36 The names of commercial glass fabrics, polymer resins, and manufacturers are provided for
37 identification purposes only. The results reported herein were derived from a limited set of
38 experimental conditions that may not represent the optimal performance range for all products.
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44 **6. REFERENCES**

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