HIERARCHICAL CARBON NANOTUBES GROWN ON 3D WOVEN GLASS FIBER PREFORMS FOR MULTIFUNCTIONAL STRUCTURAL COMPOSITES BEAMS

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Abstract
Delamination and poor interfacial properties between matrix and reinforcement have been considered as major problems of laminated composites. They also limit their use in aerospace industry when durable, multifunctional and lightweight materials are of recent demand. In this study, mechanically robust and electrically conductive composite beams are manufactured by combining two innovative approaches such as 3D weaving and production of fuzzy fiber architecture of carbon nanotubes (CNTs) onto 3D preforms. 3D weaving enables the manufacturing of delamination-free preforms, while growing vertically aligned CNTs on fibers contributes to the electrical conductivity. Among several studies performed for enhancing the interlaminar properties of laminated composites, this novel approach eliminated the most probable failure as delamination in structural composites and allows to manufacture conductive complex 3D shapes without causing loss of tensile properties. Aligned CNTs (a-CNTs) were first grown by a modified chemical vapor deposition (m-CVD) method onto an I-profile shaped 3D glass fiber woven preforms. Those preforms were then impregnated with epoxy resin by vacuum infusion process (VIP) to form multifunctional 3D I-beam composites. The morphological analysis showed 7.57 μm long CNTs having radially aligned growth on glass fibers. The electrical conductivity of CNTs grown glass fibers measured by 4 point-probe set-up was 4.52×10^{-2} S/cm, which was a remarkable enhancement of as over non-conductive glass fibers with an order of 10^6 S/cm. Failure mechanisms subjected to flexural loading was also noted to explore the contribution of CNTs.

1. Introduction

Laminated composite structures have been widely used in aerospace industry since the major demands of light-weight and robust structures are satisfied. Multi-phased and anisotropic properties of composites feature tailoring the performance of design in many desired ways, however; these properties might also cause some weaknesses such as poor interlaminar and intralaminar performance. These drawbacks emerge premature failures and restrict the use of composites in primary load-bearing structures which form infrastructure. Other components such as skins and panels made of composites also suffer from low impact resistance in such cases of bird strikes and tool drop [1]. Low electrical conductivity of polymer matrix composites becomes an issue due to need of static discharge through airframe [2]. Generic solution to this problem is to use copper mesh panels which brings weight penalties to the overall structure.

Many researchers reported several solutions to those phenomena at the nanoscale such as adding CNTs which both increase electrical conductivity and enhance interfacial shear strength by promoting

delamination toughening. Within this perspective, the common approaches were mostly grounded in tailoring interlayers in composites, such as adding nano-particles in matrix or sizing formula of fibers [3, 4], depositing nano-particles on fibers [5, 6]. So far, CNTs have been the most used nanomaterial since their intrinsic geometry and graphitic structure of sp^2 carbon atoms provides both excellent mechanical and electrical properties to composites structures [7-10]. In other words, as new generation nanomaterials, they play essential role in achieving multifunctional structures in aerospace industry.

Among several methods, 3D weaving is an approach which enables yarn manifestation to improve interlaminar properties and impact response by inserting yarns in through-the-thickness direction. Near-net-shape 3D preforms such as I, T or C profile beams that can be woven at once, which further eliminates the labourius ply stacking step in composite manufacturing. It is important to note that minor complications would be enough to transform a standard weaving loom to a weaving loom capable of 3D weaving [11]. Many studies reported that delamination and impact resistance of 3D orthogonal, interlock woven composites were enhanced with simple prismatic geometries [12-14]; however, apart from weaving no reports have been published on mechanical properties of those 3D woven profile beam structures.

The aim of the study is to investigate multifunctional structural beams by fabricating mechanically durable, electrically conductive I-beam composites where these two aforementioned approaches, CNTs and 3D weaving, were combined to achieve multifunctionality. I-beam shaped preforms were cut from a 3D woven glass fiber rectangular spacer fabric which was woven by slightly modified dobby type weaving loom. First, CNTs were grown onto the strands of these fabrics to optimize the CNTs morphology and evaluate the changes in tensile properties and electrical conductivities. m-CVD method was used for all CNTs synthesis where a-CNTs could be grown onto glass fiber strand with radial conformality. Then, CNTs growth was performed on I-beam preforms and referred as fuzzy fiber CNT 3D preforms. Last, CNTs grown I-beam preforms were impregnated with epoxy resin by VIP to have functional CNTs grown I-beam composites. Electrical conductivity assessment was performed both on CNTs grown strands and preforms and 3-point-bending tests revealed the dominant failure modes in CNTs grown I-beam composites.

2. Experimental

2.1. Weaving of I-beam preforms

3D glass fiber preforms having I-profile cross-sections were extracted from a 40.64 cm wide, 2.8 cm high spacer fabric where all walls were interchanging by continuous ground fabrics at the middle-height [15]. Weaving of the spacer fabric was performed by a modified dobby loom. Two warp beams were used as the fabric has two warp layers in different lengths which enables 3D geometry. Plain weave with warp density of 20/inch, and weft density of 10/inch, was used in which walls consisted interchanging two layers having 10/inch of weft and warp density. Dimensions of extracted I-beam preforms were $28\times40\times120$ mm^3 (Figure 1).

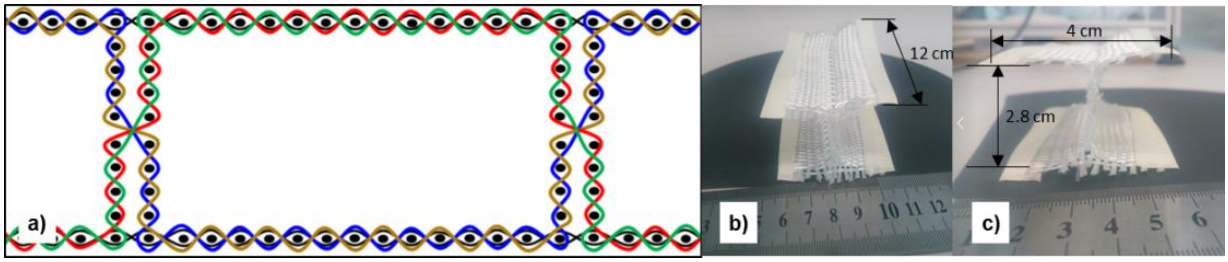

Figure 1. Spacer fabric: (a) weft cross-section representation, (b) and (c) cross-section dimensions.

2.2. Fabrication of functional I beam composites

For CNT growth, first catalyze was coated onto strands and preforms. Catalyst Fe^{+3} ions were coated on glass fibers by immersing fibers into 50 mM Iron (III) Nitrate ($Fe(NO)_3.9H_2O$) and isopropyl alcohol (C_3H_8O, %95) mixture for 5 minutes. The catalysis coating parameters were set for all strands and I-beam preforms.

In m-CVD system, CNT growth was performed in a quartz tube with 48 mm inner diameter, in which temperature and mass flow rates of gasses were controlled by PLC controller. The CNTs growth protocol was as follows: (i) cleaning the tube for 2 min. at ambient temperature with 2000 sccm He, (ii) nucleation for 15 min. with 1600/1000 sccm He/H_2 at 600 and 650°C and (iii) growth for various times (4, 8 and 12 min.) with 400/600/1000 sccm $C_2H_4/H_2/He$ at 600 and 650°C.

First, three (1st, 2nd and 3rd) specimen location in quartz tube and three growth times (4, 8 and 12 min.) were systematically investigated by monitoring the changes in CNTs morphology (see Fig. 2). First, growth temperature was set at 600°C and specimen location effect on the CNT growth was studied. Due to the variation in ethylene decomposition rates; the closer to the outlet of quartz tube, the more ethylene decomposes and the CNT growth onto fibers is expected to be more uniform and have higher coverage. Since, growth time determines the length of CNTs and longer CNTs provide better toughening. [6, 10] A second set of optimization, the effect of CVD growth temperatures of 600 and 650ºC was monitored.

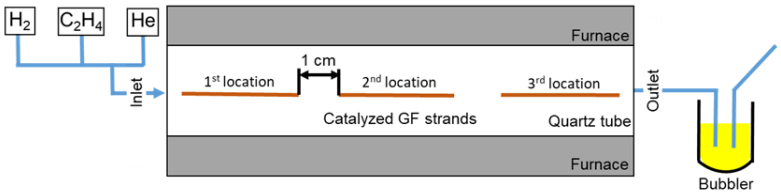

Figure 2: CVD system and glass fiber strand locations.

I-beam composites were fabricated by VIP. To retain the preform shape after VIP, 3D printed and Teflon fabric coated two supporting molds were inserted to fill gaps in preform. Mesh and peel plies were placed on bottom and top of the preform to ease infusion and demolding. Bi-component epoxy resin (Resin: West Systems105 and Hardener: West Systems205) was used at a mixing ratio of 5:1, and cured during 12 hours at room temperature. The web thickness and flange thickness of I-beam composites was 1.19±0.02 mm and 0.88±0.02 mm, respectively and this values were increased to 1.28±0.03 and 0.89±0.01 due to swelling of fabric after CNTs growth [16].

2.3. Characterization

Morphologies of fuzzy CNTs architecture both on glass fiber strands and preforms were evaluated by FEI Quanta FEG 200 branded Scanning Electron Microscopy (SEM).

Tensile tests of neat, catalyzed, CNTs grown and heat exposed strands were performed by SHIMADZU universal test machine with load cell capacity of 1 kN, and each strand bunch contained five specimens. Two different CNTs grown strands were tested with different growth temperatures (600 and 650°C) where other CVD parameters were set as 3rd location and 12 min. growth time. Heated strands were exposed to the same thermal process in CVD without H_2 and C_2H_4 to investigate the effect of heating on tensile properties of glass fibers at 600 and 650°C.

Three-point-bending tests were performed on neat and CNTs grown I-beam composites. For this set of experiment, CVD parameters for CNTs growth were set at 12 min. growth time while preform at 3rd

location was kept at 650°C growth temperature. The span length was 90 cm, 3 cm wide steel tabs were placed between supporting rollers and specimen at loading points to prevent local failure. Testing speed was 1 mm/min. Failure types and maximum forces were recorded for data analysis.

The electrical conductivities of neat and CNTs grown strands were measured by four-point probe measurement system. 28 measurements were taken from each CNTs grown strand and CNT grown preform specimens. Due to negligible fluctuations of conductivity data from neat glass fibers, 14 measurements were used for analysis.

In Table 1, for each characterization, CVD parameters were provided.

Table 1. Characterizations in each specimen types.

Characterization	Specimen Type	CVD Parameters of Interest
SEM	CNTs grown strands	Specimen Location (1st, 2nd and 3rd), Growth Time (4, 8 and 12 min.), Growth Temperature (600 and 650°C)
	CNTs grown I-beam preforms	Growth Temperature (600 and 650°C)
Tensile Tests	Neat, Catalyzed, Heated, CNTs grown strands	Growth Temperature (600 and 650°C)
Electrical Conductivity	Neat, CNTs grown strands, CNTs grown I-beam preforms	Growth Temperature (600 and 650°C)
3-point-bending Test	Neat and CNTs grown I-beam composites	All specimens

3. Results and Discussion

3.1. Morphological Analysis

SEM analysis results showed the successful growth of a-CNTs on fibers, however, to achieve the optimum contribution of stiff CNTs, radially grown CNTs all over fiber surface are required [10]. Hence, CNTs grown on the strands which were placed at the 3rd location revealed the best density and degree of alignment in all growth times (see Fig 3). This could be attributed to increased decomposition rate of carbon source along quartz tube from inlet to outlet. It is noted that CNTs became longer with increasing growth time; while slight increase in length was seen when growth time was doubled from 4 to 8 minutes (2.41 μm to 2.57 μm). In longer growth time of 12 min CNTs length was approximately three times longer (7.57 μm) (Fig. 4). These changes in length due to growth time were in good agreement with study by Yamamoto *et al.* [10].

Until now, 600°C was noted as the lowest temperature in literature to synthesize CNTs onto fibrous substrates [17]. In this study the growth process was performed at this low temperature range where glass fiber sensitivity to high temperatures was also considered. Additionally, 650°C growth temperature was also investigated to monitor the morphology of CNTs on strands and preforms. Overall, the results suggested good alignment and CNTs density over fibers and preforms. However, it is important to note that the initial degradation of glass fibers at high temperatures might decompensate this morphological advantage that enhanced mechanical strength and stability of overall composites [18].

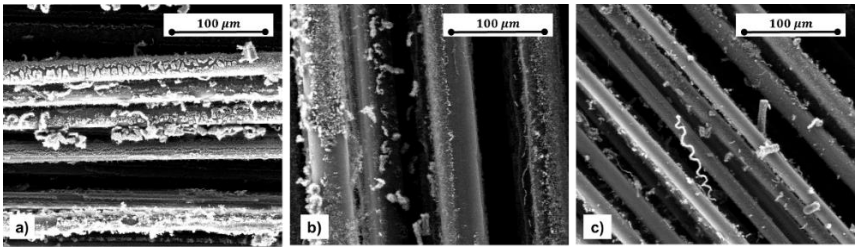

Figure 3: SEM images revealing CNTs areal density on fibers after 4 min. growth time: (a) 3rd location, (b) 2nd location and (c) 1st location

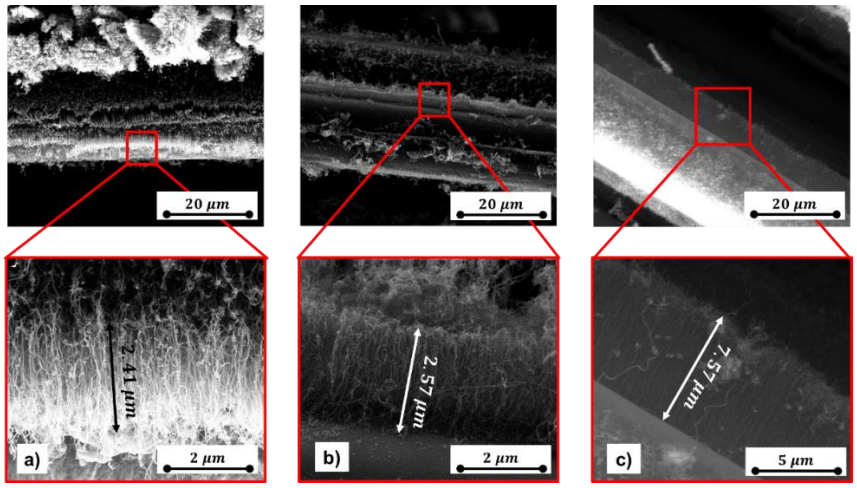

Figure 4: SEM images showing CNTs lengths for different growth times at 3rd location: (a) 4 min., (b) 8 min. and (c) 12 min. at 600°C growth temperature

After the optimization of CNTs growth time and position along tube, the effect of growth temperature was investigated by increasing from 600°C to 650°C. At 650°C, a-CNTs forests were peeled off from surface of glass fibers, as it can be seen in Fig. 5c where five CNTs forests were grown over each other. Regardless to poor adhesion of CNTs onto glass fibers, degree of alignment was improved. But at 650°C, CNTs growth on I-beam preforms revealed different morphologies than the ones on fibers at the same CVD conditions (growth time and location). Rather than randomly oriented CNTs, better degree of alignment and uniform distribution was achieved on fabrics (see Fig 5a and 5b).

3.3. Tensile Test Results

The tensile strength of glass strands was studied to identify the effects of CNTs growth on the fibers and tensile tests showed a significant reduction in terms of strength in a-CNT grown fibers. The main cause was the excessive heat exposure during CVD where sizing material on glass fibers were severely damaged [19]. Heat exposed strands 600°C growth temperature demonstrated 48% decrease in terms of tensile strength compared to neat strands. CNTs growth strands faced 44% reduction at 600°C; slightly stronger than heat-exposed strands, which could be associated to the presence of CNTs

Heated strands at 650°C showed similar trend with 600°C grown CNTs. However, CNTs growth at 650°C caused the strength reduction up to 59%. At this temperature, this decrease in tensile strength indicated the presence of H_2 and C_2H_4 which caused damage over the fiber surface, and resulting peeling off CNTs forests from surface. This damage possibly was associated to H_2 pre-treatment time (15 min.)

at 650°C which was substantially longer than the values reported in literature (2 and 5 min.) [10], and excessive exposure of H_2 reducing the stability of catalyst particles over glass fibers. Tensile strength reduction of around 12% was noted in catalyzed strands indicating that catalysis process had a role due to the removal of sizing in glass fibers as well. Table 2 shows the tensile properties of each processed and unprocessed glass strand.

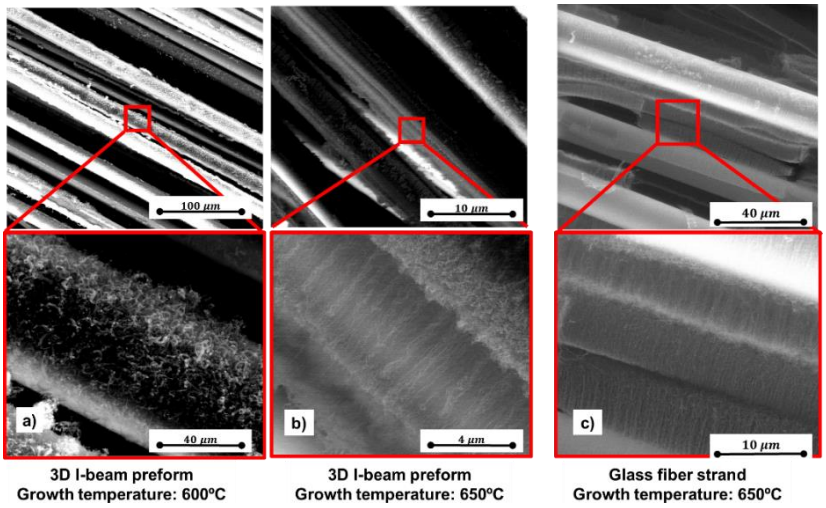

Figure 5: SEM images showing CNTs grown glass fibers in (a and b) fabric level and (c) strand level.

Table 2: Average maximum forces per density for neat and processed glass fiber strands.

Specimen	Neat strands	Catalyzed Strands	Heated strands (600°C)	CNTs grown strands (600°C)	Heated strands (650°C)	CNTs grown strands (650°C)
Force per density (Ncm^3/g)	98.0 ±1.6	85.4 ±1.1	51.1 ±0.8	55.1 ±2.7	52.3 ±0.6	40.0 ±1.2

3.4. Electrical Conductivity Results

Table 3 shows electrical conductivities of neat and CNTs grown fiber strands. Electrical conductivity of CNTs growth on glass fiber strands processed at 600°C growth temperature were six orders of magnitude (2.33×10^{-2} S/cm) higher compared to neat strands (1.49×10^{-8} S/cm). On the other hand, electrical conductivity of strands ripped off from CNTs grown on 3D preforms (8.01×10^{-3} S/cm) was one order of magnitude lower than CNTs growth strands, which pointed out the necessity of additional optimization of CNT growth process if performed on 3D preforms.

CNTs grown strands at 650°C showed slightly lower electrical conductivity than the ones processed at 600°C. While, in fabrics, electrical conductivity was increased one order of magnitude by increased growth temperature to 650°C, which could be interpreted as improved morphology of CNTs (Fig 5).

Table 3. Electrical conductivity results.

Specimen	Neat strands	CNTs grown strands (600°C)	CNTs grown fabric (600°C)	CNTs grown strands (650°C)	CNTs grown fabric (650°C)
Electrical Cond. (S/cm)	1.49×10^{-8} $\pm0.18\times10^{-8}$	2.33×10^{-2} $\pm0.44\times10^{-2}$	8.01×10^{-3} $\pm2.74\times10^{-3}$	6.95×10^{-2} $\pm1.17\times10^{-2}$	4.09×10^{-2} $\pm0.82\times10^{-2}$

3.5. Three-point-bending Test Results

Fiber volume fraction of reference and CNTs grown I-beam composites was calculated as 40%. The failure seen in reference I beams were dominantly due to buckling and shear coupling. The results demonstrated that all CNTs grown I beam composites were failed in buckling mode, which could be related to eliminated shearing effect in CNTs grown I beam composites. He *et al* reported that the enhancement of shear properties due to CNTs presence caused these failure mode changes. [7]. Maximum mean forces of CNTs grown I-beam composites was 5% higher than neat I-beam composites (see Fig. 7). Increase of cross sectional area of CNTs grown I-beam composites also contributed to this enhancement. Tensile strength reduction after CNTs growth did not play any significant role where the failure was complicated by several types.

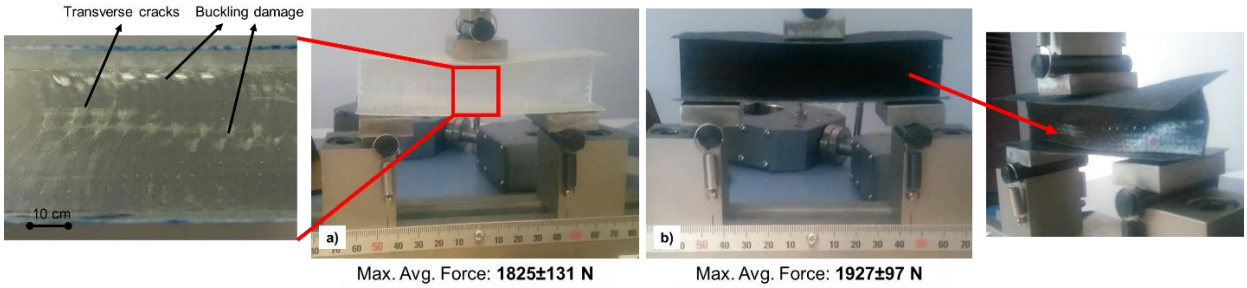

Figure 7: Three-point-bending tests and maximum average forces: (a) reference and (b) CNTs grown I-beam composite.

3. Conclusions

CNTs growth processes both on glass fibers and 3D woven I-beam preforms for fabrication of multifunctional structural composites was systemically investigated in this study. We provided an insight into two-step composite manufacturing by 3D woven preforms and direct growth of CNTs by addressing the changes in morphologies, mechanical and electrical properties. Different CVD parameters such as CNTs growth time, location of specimens in quartz tube and CNTs growth temperature were evaluated to optimize the morphology of CNTs on fibers. The results suggested that optimum growth time was 12 min, and the high degree of vertical alignment and longer CNTs were possible with specimen placement at 3rd location near the outlet. Following the same protocol, effect of temperature was investigated for glass fiber strands and I-beam preforms. Unstable, peeled-off CNTs were monitored in glass fiber strands; however, improved morphology of aligned and uniformly distributed CNTs on I-beam preforms were also seen in glass fabric level. Electrical conductivity measurements showed that CNTs grown strands were six order of magnitude more conductive than neat glass fiber strands. While tensile properties severely were depressed by CNTs growth, maximum forces at three-point-bending tests showed similar behavior in all neat and CNTs growth I-beam composites. CNTs grown I-beam composites dominantly failed by buckling, whereas reference I-beam composites showed the traces of shear triggered transverse cracks and buckling failures.

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