Fabrication and Testing of Three-Dimensionally Reinforced Carbon Nanotube Based Laminated Nanocomposites

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ABSTRACT

In this work, chemical vapor deposition technique has been used to grow vertically aligned arrays of Carbon Nanotubes (CNTs) over the surface of chemically treated 2-D woven cloth and fiber tows. The nanoforest-like fabrics can be used to fabricate 3-D laminated nanocomposites. The presence of vertically aligned CNTs in through-the-thickness direction and in between the adjacent fabric layers of laminated composites is expected to considerably enhance inter-laminar and through-the-thickness properties of the composite laminated structures. To demonstrate the effectiveness of our approach, composite single lap-joint specimens were fabricated for inter-laminar shear strength testing. It is observed that the single lap-joints with carbon cloth insertion layers having CNTs nanoforest can carry considerably higher shear stresses and strains. It is concluded that the adhesion of adjacent carbon fabric layers can considerably be improved due to the presence of vertically aligned arrays of CNTs nanoforests.

Keywords: Carbon Nanotubes, Laminated Composites, Multifunctional Nanocomposites, Material Properties, Inter-laminar Shear strength.

1 INTRODUCTION

Traditional composites have poor interlaminar and through-the-thickness properties. This weakness often leads to interlaminar failures in composites [1]. To overcome this problem, 3-D composites such as 3-D stitching and 3-D braiding have been proposed [2, 3]. The 3-D braided fibers, as raw materials, do not solve general purpose applications since the part thickness should be known in advance. In addition, in 3-D braided materials, the fiber directions are not orthogonal. As a result, the use of 3-D braided fiber architecture is limited to some specific applications and geometries. As far as the stitching is concerned, the thickness should be determined and then performed. While stitching can improve some through-the-thickness properties, it reduces the in-plane properties [4, 5].

It is reported that the addition of certain nanostrutured materials as secondary reinforcement may lead to improvement of the composite materials if a properly processed and optimum amount of nanomaterials is used [6-10]. Owing to their superior material properties CNTs are one of the best candidates to be used as an effective reinforcing material [11-13]. Cao et *al.* [14] and Veedu et *al.* [15] developed a 3-D multifunctional nanocomposite, where a new technique was introduced to grow carbon nanotubes in the perpendicular (through-the-thickness) direction on silicon carbide (SiC) fibers and woven cloths similar to a nano-brush and nano-forest. Using the nano-forest layers, they fabricated a truly 3-D laminated nanocomposite with superior through-the-thickness properties. Moreover, they have introduced multifunctional capabilities in their novel nanocomposite, such as increased mechanical properties as well as manipulation and control of coefficient of thermal expansion, electrical conductivity, thermal conductivity, and structural damping [15, 16]. However, in their work, they only grew CNTs on SiC fibers/cloths and it was not possible to directly grow CNTs on comonly used non-SiC fibers/cloths.

Here in this work, we developed a new techniques to grow radially alligned CNTs on non-SiC fibers (e.g., Glass, Kevlar, and Carbon) and fiber cloths [16]. Once CNTs are grown on fibers and fiber cloths, the same procedures for matrix impregnations, lay-up laminations, and curing, as used in a traditional wet lay-up technique for composites manufacturing [1], can be used to develop 3-D hierarchical nanocomposites with superior through-the-thickness properties and multifunctionality, as demonstrated by Ghasemi-Nejhad and co-workers [14-16]. To demonstrate the effectiveness of our approach, various composite single lap-joint specimens were fabricated for inter-laminar shear strength testing.

2 GROWTH OF CARBON NANOTUBES OVER VARIOUS WOVEN FABRICS

The Chemical Vapor Deposition (CVD) technique is one of the very simple and economical ways of producing CNTs and was introduced in 1993 by Endo et al. [17]. For our research, a CVD growth technique, similar to that introduced by Andrews et al. [18], was chosen due to its simplicity and ability for substantial control over the important growth parameters such as: CNTs length, alignment, and pattern of growth. Depending on their composition, not all substrates are suitable for CNTs growth. Silicon and silicon dioxide based solid substrates are most widely used as substrates in CVD growth of CNTs. However, other types of substrates may also be used if coasted or doped with catalysis, prior to growth process. Several methods (e.g., SiC nanoparticles coating, SiC based pre-ceramic polymer coating, silicon dioxide puttering or chemical treatment) have been used to directly grow CNT arrays over fibrous materials [16]. In this study, chemical treatment with diluted Hydrofluoric (HF) acid was used to directly grow CNTs on different types of fabrics. Aarrays of vertically aligned CNTs were successfully grown on chemically treated Sic, carbon, glass and Kevlar fibers.

Figure 1 shows a photograph of HF treated carbon woven cloths before and after CVD processing. The CVD processing time for the layers from bottom to top was varied with increments of 20 minutes from 0 minutes to 60 minutes, respectively. It can clearly be seen that the CNTs yield for the top layers was much higher than the bottom layers, as one would expect. The size of the carbon woven cloths shown in Fig. 1 was roughly 25 mm by 25 mm. It should be noted that since the optimum growth zone for the growth of CNTs in our current CVD system is only 3.5 cm by 7 cm, the fabrication of larger samples may not be easily possible and require a larger furnace. Figure 2 show the scanning electron micrographs (SEM) of uniform growth of the radially aligned CNTs on chemically treated carbon fiber cloth subjected to approximately 1 hour of the CVD process. The average length of the grown CNTs was measured to be ~ 100 µm. Similar results have been obtained for HF treated SiC, Kevlar, and glass fibers.

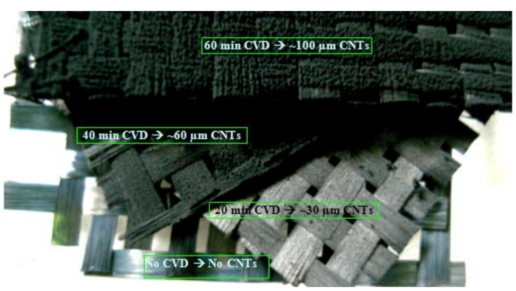

Figure 1: HF treated carbon fiber woven cloths subjected to various CVD processing times, with 20 minutes increments, for the growth of CNTs nano-forests.

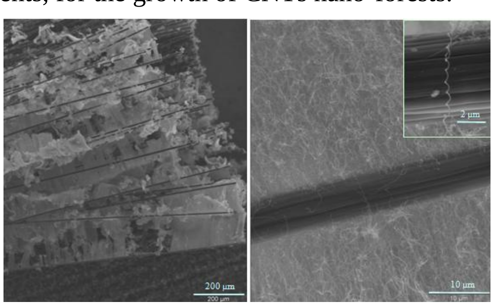

Figure 2: Low (left) and high (right) magnification SEM images of the radially aligned uniform growth of CNTs (Inset: helical CNT) over the HF treated carbon fiber-cloth.

The average diameters of the treated micro-fibers were 6 µm to 20 µm and the diameter and length of the radially grown MWCNTs were approximately 35 nm to 50 nm and 300 µm to 400 µm, respectively. It is observed that the rate of the CNTs growth on SiC fibers, SiC coated non-SiC fibers, and HF treated glass fibers is almost similar (i.e., 300-400 µm/hour) and considerably higher than the growth rate of CNTs over the HF treated Kevlar and carbon fibers (i.e., ~100 µm/hour). These unique structures provide very large chemically-physically available active surfaces which may have potential applications for nanocleaning, painting micro-surfaces, selective chemical absorption and filtration, high efficiency heat dinks and thermal-electrical conductors. In addition, they can be used to substantially enhance mechanical and physical properties of the composite materials. [14, 15]. The use of these CNTs grown fibers/cloths facilitates the fabrication of high performance 3-D laminated nanocomposites with multifunctional capabilities. This will be further discussed in the following sections.

3 SAMPLE FABRICATION & TESTING

In this section of, sample preparations and mechanical single lap-joint shear strength testing based on the ASTM D5868-01 is presented for three different sets, denoted by “A”, “B”, and “C”. Lap joints are widely used in adhesive joints, as they are simpler to make and assemble, and the stress developed in the adhesive is almost always shear [19]. For each set of samples, a layer of carbon woven cloth with or without a CNTs nano-forest on one or both sides, is placed in between two rectangular bars made of carbon fiber laminated composite (see Fig. 3). Next tensile loads were applied to break the lap joints and measure the corresponding shear strength values. The measured shear strengths were in fact the adhesion strengths of middle carbon fabric layers to the adjacent laminae (i.e., the interface between the plain fabrics and the fabrics with CNTs nano-forests).

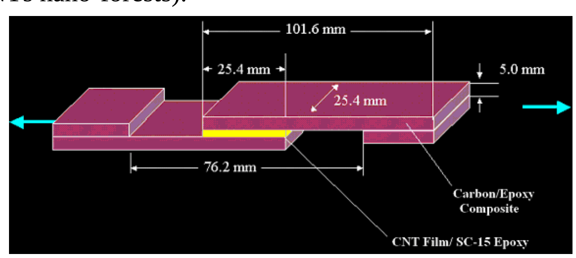

Figure 3: Schematic of the single lap-joint shear strength test based on ASTM D5868-01.

The carbon woven cloth used for set “A” samples is plain in both sides with no CNTs. The set “B” samples have a layer of carbon woven cloth with vertically aligned CNTs nano-forest grown on both sides. Specimens in the set “C” samples have a layer of carbon woven cloth with CNTs nano-forest grown only on one side. These samples are directly used to demonstrate the adhesion enhancement (i.e., higher inter-laminar shear strength) of the carbon fabric layers with vertically aligned through-the-thickness CNTs nano-forests as compared to the plain carbon cloths with no CNTs. The average length of the CNTs grown on carbon fabrics was roughly estimated to be ~ 40 micron, after a 30 minute 30 min CVD process. To manufacture the rectangular carbon fiber/epoxy laminated composite adherends, 8 layers of stain weave (5-harness) carbon prepregs [20] were hand laid-up on a solid aluminum plate followed by a vacuum bagging and an autoclaving technique. Note that a symmetric quasi-isotropic stacking sequence was used and then the manufactured laminated composite was cut to obtain samples with the dimensions suggested by the ASTM standard D5868-01.

To assemble the adherends (i.e., composite laminated bars and carbon plain weaves with or without CNTs nano-forest), a very thin layer of SC-15 epoxy resin & hardener [21] is used as an adhesive in between the adherends, and then the single lap-joint samples were uniformly compressed in the overlapped adhesion area using two solid disks and a C-clamp and then is placed inside a mechanical convection oven followed by a cure cycle according to the manufacturers suggestion [21]. Five samples were prepared for each set (i.e., sets, "A", "B", and "C") as suggested by ASTM D 5868-01. Finally, prepared single lap-joint shear test samples were tested using an Instron testing machine, and then the average values of shear strengths and strains-to-failure for each set of samples were obtained.

4 RESULTS AND DISCUSSIONS

To calculate the shear strength of each sample, the maximum tensile load was simply divided by the overlapping bonded area and to calculate the strain-to-failure value, the axial extension was simply divided by the gauge length of the specimen. The average values of shear strength and strain-to-failure for the set "A" specimens (i.e., single lap-joint samples with bare carbon plain weave cloth) were ***11.62511 MPa*** and ***0.01471***, respectively. It was observed that the fracture of the set "A" specimens had occurred through the adhesive layer and the separation of adherends had occurred within the adhesive bound, suggesting an adhesive failure mode. The bare carbon weave layers were entirely left on one side of the fractured surface without any tear or fiber pullout/distortions (see Fig. 4). It can be seen that the fracture surface is very clean and shiny, meaning that the failure had occurred right at the interface of the carbon fabric layer and surface of the composite laminate, at the adhesive.

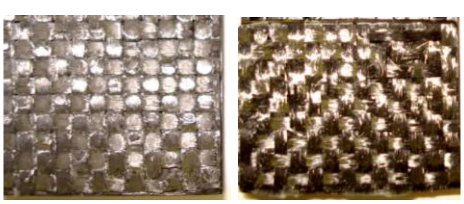

Figure 4: Typical fracture surfaces observed for (left) set "**A**" and (right) set "**B**" specimens, after shear test.

Next, the specimens from set "C" samples (i.e., single lap-joint samples with CNTs nano-forest grown only on one side of the carbon fabric layer) were tested, for which the average values were almost similar to set "A" samples, with no considerable differences. It can be stated that the presence of vertically aligned CNTs perpendicular to the surface of the 2-D carbon weave cloths (i.e., through-the-thickness direction) considerably contributes to a more efficient shear stress load transfer and enhances the interface properties of the laminated composite structures. In other words, additional through-the-thickness vertically aligned CNTs reinforcements improves the adhesion of the adjacent layers, resulting in laminated nanocomposite with much higher inter-laminar shear strength, as well as those properties improvements demonstrated by Veedu et al. [15].

To quantify the inter-laminar shear strength enhancements due to the presence of vertically aligned CNTs nano-forests, set "B" samples were tested similar to sets "A" and "C" samples. The average values of shear strength and strain-to-failure for the set "B" specimens (i.e., single lap-joint samples with vertically aligned CNTs nano-forests grown on both sides of the carbon fabric layer) were ***13.00745 MPa*** and ***0.01709***, respectively. These values are considerably higher than those obtained for sets "A" and "C" samples and show nearly ***12%*** and ***16%*** improvements in shear strength and strain-to-failure, respectively. It should be mentioned that the results from testing different samples were very consistent with standard deviations of less than 3%. Close examination of the fracture surfaces on set "B" samples reveals that the fracture occurred within and through the inserted carbon fabric layer and not at the interface regions (see Fig. 4 - left). It is clearly evident that the carbon fabric is completely torn apart and has remained on both sides of the composite lap joint. The rupture region is within the inserted carbon fabric layer and not the interfaces, suggesting that the inter-laminar shear strength of vertically aligned CNTs nano-forest carbon fabrics is even much higher than the values obtained for set "B" samples.

Therefore, this is a cohesive failure where the adherend has failed before the adhesive, and the fracture occurred through the adherend, which is an ideal type of failure. These observations simply demonstrate that through-the-thickness material properties (e.g., inter-laminar shear strength and strain-to-failure) of laminated composite structures, using vertically aligned 3-D CNTs nano-forest woven fabrics have been substantially improved. However, a more accurate estimate of the inter-laminar shear strength properties enhancements could be obtained, using this test, if the properties of the inserted carbon fabric layers were much stronger in shear. To accurately measure GIC and GIIC properties, DCB and ENF tests [15] have to be carried out. For further verification, SEM images of the fractured surfaces also are obtained for sets "A" and "B" samples, some of which are shown in Figure 6.

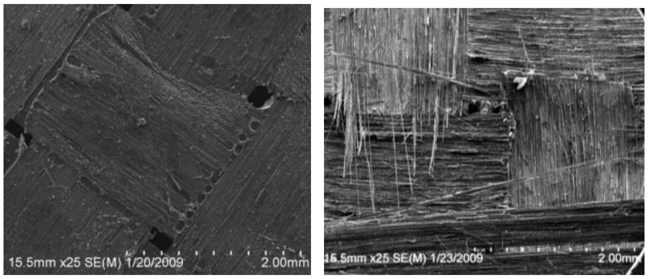

Figure 6: A typical SEM image of the fracture surfaces observed for: (left) set "**A**" and (right) set "**B**" specimens, after single lap-joint shear test.

SEM image in Fig. 6 (left) shows the direct failure of the adhesive layer between the inter-layer and the laminated specimen. This is an evidence for cohesive failure mode in set "A" samples. On the contrary, one can clearly observe the presence of fractured bare carbon fibers in SEM image of Fig. 6 (right) that is a verification of a cohesive failure and thefiber breakage and pull-out can clearly be seen.

5 CONCLUSIONS

Chemical vapor deposition technique have been employed to grow vertically aligned arrays of CNTs perpendicular to the surface of chemically treated 2-D woven cloths and tows of various fibrous materials. The nano-forests like fabrics can then be used to fabricate 3-D reinforced laminated nanocomposites. Due to the presence of aligned CNTs in through-the-thickness direction and in between the adjacent fabric layers of laminated composite, it was expected that the inter-laminar and through-the-thickness properties of composite laminates would be improved, considerably, and the fabricated composite structure would possess multifunctional capabilities. To demonstrate the effectiveness of our approach, composite single lap-joint specimens were fabricated for inter-laminar shear strength testing. Carbon woven cloths with and without CNTs nano-forests were inserted in between the single lap-joints using epoxy adhesive to measure their inter-laminar shear strength improvements. It is observed that single lap-joints with carbon cloth insertion layers having CNTs nano-forest can carry up to 12% higher shear stress and 16% higher strain-to-failure. Fractured surfaces were examined under SEM. The failures of samples with nano-forests insertions were completely cohesive, while the samples with plain carbon woven cloth insertions failed adhesively. This concludes that the adhesion of adjacent carbon fabric layers can be considerably improved due to the presence of vertically aligned CNTs nano-forests in through-the-thickness direction.

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