Effects of vertically aligned carbon nanotubes on shear performance of laminated nanocomposite bonded joints

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Received 3 March 2012
Accepted for publication 9 June 2012
Published 16 July 2012
Online at stacks.iop.org/STAM/13/045002

Abstract
The main objective is to improve the most commonly addressed weakness of the laminated composites (i.e. delamination due to poor interlaminar strength) using carbon nanotubes (CNTs) as reinforcement between the laminae and in the transverse direction. In this work, a chemical vapor deposition technique has been used to grow dense vertically aligned arrays of CNTs over the surface of chemically treated two-dimensionally woven cloth and fiber tows. The nanoforest-like fabrics can be used to fabricate three-dimensionally reinforced laminated nanocomposites. The presence of CNTs aligned normal to the layers and in-between the layers of laminated composites is expected to considerably enhance the properties of the laminates. To demonstrate the effectiveness of our approach, composite single lap-joint specimens were fabricated for interlaminar shear strength testing. It was observed that the single lap-joints with through-the-thickness CNT reinforcement can carry considerably higher shear stresses and strains. Close examination of the test specimens showed that the failure of samples with CNT nanofores was completely cohesive, while the samples without CNT reinforcement failed adhesively. This concludes that the adhesion of adjacent carbon fabric layers can be considerably improved owing to the presence of vertically aligned arrays of CNT nanofores.

Keywords: carbon nanotubes, laminated nanocomposites, 3D reinforcement, shear strength, bonded joints

1. Introduction

The main advantage of composites, in addition to their high specific strength and stiffness, is their ability to be tailored towards a specific loading condition, i.e. placing the load-carrying fibers where the loadings and stresses are. Nearly one-dimensional (1D) fiber materials with their anisotropic properties have been used as the reinforcements, along with a bonding material called the matrix, to manufacture structural composites in which mechanical loads are to be transferred through the embedded fibers. Fibers usually are very strong in the longitudinal direction but weak in the lateral direction. Therefore, when they are used to make structural composites, the final product will have weak through-the-thickness mechanical properties. In addition, when 1D unidirectional composites and/or 2D woven laminated composites are manufactured, the interlaminar properties are controlled by the matrix properties, since the adjacent layers are bonded by the matrix only, yielding poor interlaminar and through-the-thickness properties. This weakness often leads to interlaminar failures (such as delamination) in composites [1]. To overcome this problem, 3D composites such as 3D stitching and 3D braiding have been proposed [2, 3]. The 3D braided fibers, as raw materials, do not solve general purpose applications since the part thickness should be known in advance. In
addition, in 3D braided materials, the fiber directions are not orthogonal. As a result, the use of 3D 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 stitching performed. In this case, the fibers can be orthogonal; however, the post operation of stitching is performed only after the structure is designed to obtain a specific thickness. The stitching provides reinforcing fibers in through-the-thickness direction (i.e. normal to the fabric layers). While stitching can improve some through-the-thickness properties, it may reduce the in-plane properties [4, 5]. Above all, the traditional composites lack rooms for multifunctionality.

The effect of stitching on mechanical performance of laminated composites is a complicated issue that is not fully understood. The stitching effects depend on many factors such as loading type (e.g. static, fatigue, in plane, out of plane, bending and twisting), type of fiber materials, resin, stitching pattern, stitching thread and the stacking sequences [4–6]. Aymerich et al [6] have concluded that the improvement of delamination resistance of statically loaded laminated composites due to stitching does not necessarily translate into a better fatigue performance for all lamination sequences. Dransfield et al [7] have extensively reviewed the advantages and disadvantages of stitching for mechanical performance of laminated composites.

Kuo et al [8] have studied the transverse shear characteristics of 3D woven composites. Their observation suggests that matrix cracking is the main cause of tensile rupture of axial yarns due to loss of shear rigidity, which results in complex damage modes. Finite element modeling of modified double cantilever beam (DCB) tests for 3D orthogonal interlocked fabric composites have shown that coupling effects from z-directional fiber slip, slack absorption, and the fiber failure result in interlaminar fracture toughness improvements [9, 10].

The addition of certain nanostructured materials as secondary reinforcement may yield superior composite materials if an optimum amount of properly processed nanomaterials is used [11–15]. Owing to their remarkable properties, carbon nanotubes (CNTs) are one of the best candidates for such a reinforcing material [16–18]. Cao et al [19] and Veedu et al [20] developed a 3D multifunctional hierarchical 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, yielding structures resembling a nanobrush or nanoforest. Using the nanoforest layers, a truly 3D laminated nanocomposite was fabricated with a superior combination of properties such as fracture toughness $G_{IC}$, $G_{HIC}$, flexural modulus, flexural strength, flexural toughness, damping, coefficient of thermal expansion, through-the-thickness thermal conductivity and through-the-thickness electrical conductivity [20, 21]. These results show the effectiveness of the proposed solution for improvement of the through-the-thickness materials properties and multifunctionality of the laminated composites by means of additional vertically aligned CNT reinforcement over the fiber cloths. However, in the previous work, CNTs were only grown on SiC fibers/cloths and it was not possible to directly grow CNTs on common materials such as glass, Kevlar and carbon.

Preliminary studies by Hsiao et al [22] have shown considerable increase in the average shear strength of adherent in composite adhesive joints just by the use of CNT-reinforced epoxy. Jain et al studied the fatigue life of through-thickness stitched composite single-lap joints [23]. Their experimental results reveal significant improvement due to transverse stitching through the thickness with Kevlar thread in a zigzag pattern. Furthermore, recent investigation by Yurdumakan et al [24] has demonstrated that aligned CNT films can mimic a gecko foot with the help of van der Waals forces from the nanotubes. The reported adhesion forces are 200 times higher than those observed for gecko foot-hairs (i.e. 36 N cm$^{-2}$) [24]. Previous investigations [19–26] have established that strength in nanocomposites can be increased at the nanotube interface owing to nanotube pull-out. This phenomenon explains the increase in shear strength.

In this work, we developed a method to grow radially/vertically aligned multiwalled CNTs (MWCNTs) on non-SiC fibers and fiber cloths [21] using chemical vapor deposition (CVD). CVD is a simple and economical way of producing aligned CNTs that was introduced in 1993 by Endo et al [27]. The CNTs grow perpendicular to the surface of a substrate that is placed inside the quartz tube in an optimum location. Once CNTs are grown on fibers and fiber cloths, the same procedures for matrix impregnations, lay-up laminations, and curing that are employed in a traditional wet lay-up technique for composites manufacturing [1], can be used to develop 3D hierarchical nanocomposites with superior through-the-thickness properties and multifunctionality [19–21]. To demonstrate the effectiveness of our approach, various composite single lap-joint specimens were fabricated for interlaminar shear strength testing. Carbon plain weaves with and without CNT nanofores were inserted between the single lap-joints using epoxy adhesive for the measurement of interlaminar shear strength improvement due to the presence of through-the-thickness aligned CNT nanofores. The addition of CNT nanofores resulted in at least 12% higher shear stress and 16% higher strain-to-failure. The failures of samples with nanofores were completely cohesive while the samples with no CNT reinforcements failed adhesively. This concludes that the adhesion of adjacent carbon fabric layers can be considerably improved by growth of vertically aligned CNT nanofores normal to the layers.

2. Growth of vertically aligned dense arrays of carbon nanotubes on various fabrics

We chose a CVD growth technique [19–21] similar to that introduced by Andrews et al [28], because of its simplicity and ability for substantial control over important growth parameters such as CNT length, alignment, and pattern of growth. Not all substrate materials are suitable for CNT growth. Silicon and silicon dioxide based solid substrates are
most widely used in the CVD growth of CNTs. Figure 1 shows a scanning electron microscopy (SEM) image of CNTs grown on an untreated silicon carbide fabric. Other types of substrates may also be used if coated or doped with catalyst prior to the growth process. In our previous studies, several methods such as SiC-based pre-ceramic polymer coating (see figure 2), silicon dioxide sputtering and chemical treatment, have been used to grow CNT arrays over fibrous materials [21]. Here we applied chemical treatment with diluted HF acid to directly grow CNTs on different types of fabrics and fiber tows.

Fibers are often coated with a very thin layer of a compatible material (i.e. sizing) for protection, ease of handling and improved adhesion to the matrix [29, 30]. Peipetis and Galiotis [29] have used laser Raman microscopy to investigate the stress transfer characteristics of carbon fiber-epoxy systems for carbon fibers with and without sizing. The sized fibers consistently showed higher interfacial shear strengths and mainly exhibited mixed-mode cracking at the interface. The interfacial failure mode for the unsized fibers was fiber/matrix debonding [29]. The CNTs cannot directly grow on most of the as-received commercially available fibers. To overcome this problem, the fiber coatings were removed and functionalized with diluted HF acid. The glass fibers and Kevlar 49 fiber tows were dipped into 49% HF acid diluted with water (1:10 HF: water by weight) and kept for 30 s, while carbon fibers were kept for nearly 1 min. High-magnification SEM images of all fibers before and after chemical treatment with diluted HF acid were examined and, as one would expect, microscopic surface damage was observed for glass fibers only. No damage was observed for Kevlar and carbon fibers, suggesting that a brief (30–60 s) chemical treatment with diluted HF acid does not affect their mechanical integrity. However, reduction in interfacial adhesion strength of chemically treated fibers to matrix material, due to the removal of sizing layer, remains an issue that can be resolved by reapplying the sizing layer after the CVD growth of CNT nanoforests on fibers. We have also treated carbon fibers with concentrated HF acid for an extended period of 30 min and observed no surface damage. Concentrated HF acid is a strong solvent that can dissolve glass fibers within minutes. Therefore, only diluted HF acid should be used for the treatment of glass fibers, and the treatment should be short. Once the treatment was completed, samples were washed with deionized (DI) water and then dried under an enclosed fume hood.

Chemical treatment exposed the main materials of the fibers, and the iron catalyst particles attached to them during the CVD process. Consequently, arrays of vertically aligned CNTs were successfully grown on chemically treated carbon, glass and Kevlar fibers. Figures 3–5 show the growth of CNT arrays on chemically treated glass fabrics, glass fiber tows and Kevlar fiber tows, respectively.

Figure 6 shows an optical image of the chemically treated carbon plain weaves before and after CVD processing. The CVD processing time for the layers from bottom to top was varied with increments of 20 min from 0–60 min, respectively. As expected, the CNT yield for the top layers is much higher than the bottom layers. The size of the carbon plain weaves shown in figure 6 is roughly $25 \times 25 \text{mm}^2$. It should be mentioned that the optimum zone for the growth of CNTs in our CVD system was roughly $3.5 \times 6 \text{cm}^2$ and the fabrication of larger samples required a larger furnace.
Figure 4. (a) Low and (b) high magnification SEM images of radially aligned growth of CNTs over the chemically treated glass fiber tows, after ∼1 h of CVD.

Figure 5. (a) Low and (b) high magnification SEM images of the radially aligned growth of CNTs over the chemically treated Kevlar fiber tows, after ∼1 h of CVD.

Figure 6. Chemically treated carbon fabrics subjected to various CVD processing times for the growth of CNTs nanofores.

Figures 7 and 8 show the SEM images of uniform growth of the radially/vertically aligned CNTs on chemically treated carbon plain weaves subjected to CVD for approximately 1 h. The average length of the grown CNTs was ∼100 μm. Similar results have been obtained for chemically treated Kevlar and glass fibers.

SEM images demonstrate our success in CVD growth of radially/vertically aligned MWCNTs on different microfibers. The average diameter of the examined microfibers was 6–20 μm and the diameter and length of the radially grown MWCNTs were approximately 35–50 nm and 300–400 μm, respectively. The rates of the CNT growth on SiC fibers, SiC-coated non-SiC fibers and acid-treated glass fibers are similar (300–400 μm/h) and are considerably higher than the CNT growth rates on chemically treated Kevlar and carbon fibers (i.e. ∼100 μm/h). These unique structures provide very large chemically and physically available active surfaces that have potential applications for nanocleaning, painting micro-surfaces and capillaries, selective chemical absorption and filtration, heat sinks, and thermal and electrical conductors. In addition, they can be used to considerably enhance mechanical and physical properties of the composite materials [19, 20]. Since the CNTs are radially grown on the fibers, it is expected that they will affect not only mechanical properties (e.g. strength, strain-to-failure, fracture toughness, coefficient of thermal expansion and damping), but also physical properties (e.g. thermal and electrical conductivities) [20] of the traditional laminated composites. As a result, the use of these CNT nanofores should facilitate the fabrication of high-performance 3D laminated nanocomposites with multifunctional capabilities. For further demonstration, CVD-processed chemically treated carbon plain weaves were used to fabricate single lap-joint samples to measure the shear strength. The presence of CNTs aligned normal to the layers and in-between the layers is expected.
Figure 9. Schematic of the single lap-joint shear strength test specimens (based on ASTM D5868-01) with or without CNTs reinforcement.

Figure 10. (a) Carbon/epoxy laminated composite samples manufactured for single lap-joint shear test. Carbon plain weave cloths (b) with and (c) without CNT nanoforests.

to considerably improve the interface properties that will translate into enhancement of the fiber-matrix adhesion.

3. Sample preparation and testing

In this section, sample preparations and mechanical single lap-joint shear strength testing based on the ASTM D5868-01 standard is presented for three sets of samples, A, B, and C. Lap-joints are widely used in adhesive joints, as they are simple to make and assemble, and the stress developed in the adhesive is almost always shear stress [31]. For each set of samples, a layer of carbon plain weave, with or without a CNTs nanoforest on one or both sides, was placed between two rectangular bars. The bars were made of carbon fiber laminated composite fabricated from satin-weave (5-harness) carbon prepregs [32] (see figures 9 and 10). To manufacture the rectangular composite adherends, 8 layers of satin-weave (5-harness) carbon prepreg tapes were hand laid on a polished aluminum plate coated with a thin layer of dry mold release agent. The sample was then vacuum bagged and placed inside an autoclave for curing. The vacuum was applied through the vacuum pump in the bagging system and then a pressure of nearly 690 kPa was applied, while raising the temperature to 180 °C within 30 min. The sample was kept at 180 °C for 2 h, then cooled to room temperature within 30 min, and removed from the autoclave. 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, (see figures 9 and 10).

To assemble the adherends (i.e. composite laminated bars and carbon plain weaves with or without CNT nanoforests), a very thin layer of SC-15 epoxy resin and hardener [33] was used as an adhesive between the adherends. First, the carbon plain weaves were gently soaked in the epoxy resin for nearly 10 min and then placed between the overlap areas of the adherend composite bars that were previously wetted with a thin layer of epoxy resin. Next, the single lap-joint samples were uniformly compressed in the overlapped adhesion area using two solid disks and a C-clamp (see figure 11). Then the samples were placed inside a convection oven followed by a cure cycle, according to the manufacturer’s suggestion [33]. The temperature of the convection oven was increased from the room temperature of 23 to 150 °C at a rate of 1.5 °C min⁻¹. It was then held at 150 °C for nearly 1 h followed by natural cooling.

Five samples were prepared for each set as suggested by ASTM D 5868-01. A 50 kN load cell with a load measurement accuracy of down to 0.2% of the load cell capacity was used. As shown in figures 9 and 10, the carbon plain weave used for set A samples is clean on both sides with no CNTs. The set B samples have a layer of carbon plain weave with vertically aligned CNT nanoforest grown on both sides. Specimens in the set C have a layer of carbon plain weave with CNT nanoforest grown only on one side. These samples were used to demonstrate the adhesion enhancement (i.e. higher interlaminar shear strength) of the carbon plain weave with vertically aligned through-the-thickness CNT nanoforest, as compared to the clean carbon plain weave without CNTs. The
average length of the CNTs grown on carbon fabrics within 30 min was estimated as 40 µm.

It should be mentioned that the surface texture of substrate directly affects the growth direction and uniformity of the CNTs. Owing to this fact, [19] states that the cloth pattern influences the alignment of MWCNTs in the laminate’s thickness direction and this will affect the through-the-thickness properties of the composites. Therefore, due to the uniformity of surface texture in plain weave pattern as compared to the stain weave pattern, the CNT growth on carbon plain weaves is more uniform and better aligned in through-the-thickness direction. This is why a plain weave is used as a middle layer, on which CNTs have a tendency to grow more uniformly and in through-the-thickness direction.

Tensile loads were applied to break the as-prepared single lap-joint shear test samples using an Instron testing machine (see figure 12), yielding the shear strength and strains-to-failure values for each set of samples. The measured shear strengths were in fact the adhesion strengths of middle carbon plain weaves to the adjacent laminae (i.e. the interface between the clean fabrics from the laminated composite bar and the fabrics with or without CNT nanoforests), see figure 9.

The next section of this report presents and compares the results obtained from single lap-joint shear tests and discusses the effects of the additional through-the-thickness CNT nanoforest reinforcement on the interlaminar shear strength of laminated composites.

4. Results and discussions

As mentioned above, five samples were tested for each set to determine average values of shear strength and strain-to-failure. To calculate the shear strength of each sample, the maximum tensile load was divided by the overlapping bonded area, and to calculate the strain-to-failure values, the axial extension was divided by the gauge length of the specimen. Table 1 shows the results for set A specimens. The average values of shear strength and strain-to-failure (i.e. single lap-joint samples with bare carbon plain weaves) are 11.6 MPa and 1.47%, respectively.

The fracture of set A specimens occurred through the adhesive layer and the separation of adherends occurred within the adhesive bound, suggesting an adhesive failure mode. The bare carbon plain weaves were entirely left on one side of the fractured surface without any tear or fiber pullout/distortions (see figure 13). It can be seen that the fracture surface is very clean and shiny, indicating that the failure had occurred right at the interface of the carbon plain weave and surface of the composite laminate, at the adhesive.

There are two dominant mechanisms of failure for adhesively bonded joints, namely adhesive failure and cohesive failure. Adhesive failure is the interfacial failure between the adhesive and one of the adherends, which is indicative of a weak-boundary layer adhesion. On the other hand, cohesive failure is when the fracture results in a layer of adhesive remaining on both adherend surfaces and, more rarely, when the adherend fails before the adhesive with fracture almost contained in the adherend [31]. This later failure is known as cohesive failure of the substrate. It should be mentioned that the ideal type of failure is when cohesive failure occurs through the adhesive or one of the adherends; with this type of failure mode the joining system is strong.

Next, we tested the specimens from set C (i.e. single lap-joint samples with CNT nanoforest grown only on one side of the carbon plain weave), for which the average values were similar to those of set A samples. While assembling the set C samples and prior to the shear strength testing, the sides with CNT nanoforests were marked to examine whether the specimens will break at the bare side or the CNT nanoforest side. Interestingly, fractures occurred on the bare side of the carbon plain weaves where no CNTs were present. The ruptures of lap-joints for set C samples

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**Table 1.** Shear strength and strain-to-failure values for set A single lap-joint composite specimens.

| Sample no. | A-1 | A-2 | A-3 | A-4 | A-5 | Average | Standard deviation |
|------------|-----|-----|-----|-----|-----|---------|-------------------|
| Shear strength (MPa) | 11.8 | 11.6 | 11.5 | 11.7 | 11.6 | 11.6 | 0.1 |
| Strain-to failure (%) | 1.53 | 1.39 | 1.46 | 1.50 | 1.47 | 1.47 | 0.05 |

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**Figure 12.** A single lap-joint composite sample under shear stress due to the application of axial tensile load.

**Figure 13.** A typical fracture surface observed for set A specimens, after single lap-joint shear test.
were within the adhesive layer resulting in adhesive/interface failure. Note that the fracture surfaces were similar to those of set A samples, as shown in figure 13. From the results of testing of set A and C samples alone, it is evident that the interlaminar shear strength of the adhesive bonds between the carbon plain weaves with CNT nanoforests and composite laminates is higher than that of bare carbon plain weaves without CNT reinforcement. Thus the presence of CNTs aligned perpendicular to the surface of the 2D carbon plain weaves (i.e. through-the-thickness direction) considerably contributes to a more efficient shear stress load transfer and enhances the interface properties of the laminated composites. In other words, additional through-the-thickness vertically aligned CNT reinforcement improves the adhesion of the adjacent layers, resulting in laminated nanocomposites with higher interlaminar shear strength. Such reinforcement also enhances other properties as demonstrated by Veedu et al [20].

To quantify the interlaminar shear strength enhancement due to the presence of vertically aligned CNT nanoforests, set B samples were tested similar to set A and C samples and the results are summarized in table 2. The average values of shear strength and strain-to-failure for the set B specimens (i.e. single lap-joint samples with vertically aligned CNT nanoforests grown on both sides of the carbon plain weave) were 13.0 MPa and 1.71%, respectively. These values are considerably higher than those obtained for set A and C samples and show nearly 12 and 16% improvements in shear strength and strain-to-failure, respectively. The results from testing different samples were reasonably consistent with standard deviations shown in the last columns of tables 1 and 2.

| Sample no. | B-1 | B-2 | B-3 | B-4 | B-5 | Average deviation |
|------------|-----|-----|-----|-----|-----|-------------------|
| Shear strength (MPa) | 13.0 | 13.0 | 13.1 | 12.8 | 13.2 | 13.0 |
| Strain-to-failure (%) | 1.81 | 1.90 | 1.73 | 1.61 | 1.49 | 1.71 | 0.08 |

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 figure 14). The carbon plain weave is completely torn apart and has remained on both sides of the composite lap joint. The rupture region is within the inserted carbon plain weave and not the interface, suggesting that the actual interlaminar shear strength between the vertically aligned CNT nanoforest and carbon fabrics is higher than the values calculated 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 demonstrate improved through-the-thickness mechanical properties (e.g. interlaminar shear strength and strain-to-failure) of laminated composites, using vertically aligned 3D CNT nanoforests. However, a more accurate estimate of the interlaminar shear strength properties enhancement could be obtained using this test, if the shear strength was higher for inserted carbon plain weaves than the interface between the CNT nanoforest and carbon-laminated composites, which could result in adhesive failure. To accurately measure the G_\text{IC} and G_\text{ICD} values, DCB and end notch flexure (ENF) tests [20] have to be carried out, which will be a focus of our future work. Please note that the reported results in references [19, 20] are related to silicon carbide fibers reinforced with CNT nanoforests, employing DCB and ENF tests that can accurately evaluate the G_\text{IC} and G_\text{ICD} properties. We expect that DCB and ENF tests on carbon-fiber-based CNT nanoforest nanocomposites will reveal a stronger enhancement of interlaminar properties. For comparison purposes, optical images of the fracture surfaces for typical set A and B samples are shown in figure 15, where the adhesive and cohesive failure modes are clearly evident in panels a and b, respectively. Similarly, side-view optical images of the fractured surfaces for set A and B samples are shown in figure 16, where the insets are close-up images of the respective failed surfaces. Figure 17 shows a close-up image of the fractured surface of a typical set B sample. The weight fractions of the epoxy matrix, carbon fibers, and CNTs for the fabricated samples were difficult to calculate due to the loss of excess resin during the compaction, solidification and sample preparation stages; they were estimated as 33, 65 and 2%, respectively.

For further verification, SEM images of the fractured surfaces were also obtained for set A and B samples, and some of them are shown in figures 18 and 19, respectively. Figure 18 shows the direct failure of the adhesive layer between the interlayer and the laminated specimen. On the contrary, one can clearly observe the presence of fractured bare carbon fibers in figure 19, which reveals a cohesive failure. The surface of the interlayer carbon plain weave in figure 18 does not show any fiber distortion or breakage where the surface is entirely covered with a thin layer of adhesive and where the failure has occurred in a clean shear mode. This is an evidence for adhesive failure mode in set A samples. However, the fiber breakage and pull-out can clearly be seen in figures 16(b), 17 and 19.

Barber et al [25] have used atomic force microscopy to study the effects of chemical treatment/functionailization on interfacial adhesion strength of CNTs to polymer matrix. In their study, functionalized CNTs showed significantly higher adhesion strengths resulting in CNT failure rather than pull-out from the surrounding matrix that is commonly experienced for unmodified CNTs. Ganesan et al [26] used a single-fiber pull-out technique to investigate the interfacial shear strength and interfacial fracture energy of individual MWCNTs embedded in various lengths in an epoxy matrix. These reports suggest that the presence of CNTs in epoxy matrix can considerably improve its load carrying capacity when the interfacial adhesion of CNTs to the matrix is maintained. In other words, CNTs can be used as an additional mechanical reinforcement in traditional structural composites, provided their distribution, orientation and interfacial properties are controlled. We therefore believe...
that the presence of CNTs aligned normal to the layers and in-between the layers in laminated nanocomposites can considerably improve the interfacial adhesion strength between the adjacent layers.

Figure 14. Typical fracture surfaces observed on both sides of the sheared portions of the set B specimens, after single lap-joint shear test.

Figure 15. Typical fracture surfaces observed for (a) set A and (b) set B specimens, after single lap-joint shear test.

Figure 16. Side views of the typical fracture surfaces observed for (a) set A and (b) set B specimens, after single lap-joint shear test. Insets: close-up views of the fracture surfaces.

Figure 17. A close-up view of the typical fracture surfaces observed for set B specimens, after single lap-joint shear test.

Figure 18. A typical SEM image of the fracture surface observed for set A specimens, after single lap-joint shear test.

Figure 19. A typical SEM image of the fracture surfaces observed for set B specimens, after single lap-joint shear test. Inset: close-up view of the fibers fracture.

Note that the carbon plain weaves used as insertion layers in set A samples were not chemically treated and their sizing layer was not removed. However, the carbon plain weaves used in set B and C samples were chemically treated with diluted HF acid to assist the deposition of CNT nanoforests. Therefore, reapplication of sizing layer on CNT nanoforest fabrics prior to bonding is expected to further improve the
interfacial adhesion of CNTs to the adjacent layers. Figure 20 shows the carbon fibers before and after HF treatment. No damage on carbon fibers is observed.

5. Conclusions

Composite materials have a wide range of applications, depending on their composition, shape, size and properties. Owing to their light weight, multifunctional characteristics and high strength, composite materials have been widely used in space and aerospace structures, as well as in sport and automotive industries. The development of nanocomposite materials with improved properties can significantly benefit the applications requiring high-performance materials. Chemical vapor deposition technique has been employed to grow vertically aligned arrays of CNTs perpendicular to the surface of chemically treated 2D fabrics and fiber tows of various fibrous materials. The nanoforest-like fabrics can then be used to fabricate 3D reinforced laminated nanocomposites. Owing to the presence of CNTs aligned normal to the layers and in-between the layers of laminated composites, it was expected that the interlaminar 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 interlaminar shear strength testing. Carbon plain weaves with and without CNT nanoforests were inserted between the single lap-joints using epoxy adhesive to measure the improvement in interlaminar shear strength. Single lap-joints with carbon plain weave insertion layers containing CNT nanoforest have at least 12% higher shear stress and 16% higher strain-to-failure. Fractured surfaces were examined by SEM. The failures of samples with nanoforest insertions were completely cohesive, whereas the samples with plain carbon weave insertions failed adhesively. This concludes that the adhesion of adjacent carbon fabric layers can be considerably improved due to the presence of vertically aligned CNT nanoforests in through-the-thickness direction.

Acknowledgment

The authors acknowledge the Office of Naval Research (ONR) for the financial support under the government grant number of N00014-05-1-0586 for the ADPICAS project.

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