ALIGNED CARBON NANOTUBE REINFORCEMENT OF GRAPHITE/EPOXY PLY INTERFACES

Enrique J. Garcia, A. John Hart, Brian L. Wardle, Alexander H. Slocum, Dong-Jin Shim[1]
Massachusetts Institute of Technology, Cambridge, MA, USA

Keywords: *CNT, Aligned, Interlaminar, Reinforcement, Composites, Graphite, Prepreg, VACNT*

Abstract

A new interlaminar reinforcement for layered composite materials is presented utilizing aligned carbon nanotubes (CNTs) to bridge the matrix-rich region between advanced composite layers (plies). Fabrication of the CNTs and their incorporation via pattern transfer into a graphite/epoxy preimpregnated (prepreg) system to form a hybrid composite are described. The interfaces are characterized via optical and scanning electron microscopy which demonstrates excellent wetting of the aligned CNT forests by the epoxy in the prepreg. A first-order fracture mechanics model with a simple traction law indicates significant toughening via such aligned CNTs. Mode 1 fracture tests of the first-manufactured 'nanostitched' prepreg laminates shows a 160% improvement in critical strain energy release rate. Future work includes more detailed strength and fracture testing, including other modes, multifunctional property characterization and modeling, and refinement of the manufacturing process to create improved nanostitches.

1 Introduction

Composite laminates contain matrix-rich regions at ply interfaces that reduce their overall performance. The thin, unreinforced pure matrix layer that exists between plies has poor mechanical properties (stiffness, strength, fracture toughness) when compared to in-plane properties of the laminate. Delamination and matrix cracking between plies are the dominant modes of damage and therefore responsible for the reduction of properties in the direction normal to the plane. In recent years several different solutions have attempted to overcome this limitation: 3D-braiding, weaving and stitching (e.g., z-pinning) are the most promising solutions to date. All these processes increase to some extent the through-thickness mechanical properties of layered composite materials, but also reduce the laminate's performance in the in-plane directions of the laminate [1]-[8]. A possible method to increase a composite's resistance to delamination without compromising the in-plane properties is the use of carbon nanotubes (CNTs) in the interface between layers that would not only improve the mechanical properties across the interface, but also help reduce crack propagation by bridging the two plies across the interface. This bridging mechanism has been identified previously by others for polymers reinforced with low volume fractions (to avoid the formation of agglomerates [9], [10]) of randomly oriented CNTs, with limited toughness improvement [11]-[12] in a pure polymer matrix (i.e., not at an interface).

The concept of reinforcing the region between plies using nanomaterials had been used in previous studies with limited success. Additional layers of polymer matrix reinforced with randomly oriented carbon nanofibers (CNFs) [13]-[14] and CNTs [15]-[16] have been introduced between plies with no apparent improvement in the properties of the composite material. Other manufacturing methods reported in the literature include placing randomly oriented bulk CNTs in between plies through spraying [17] and electrophoresis [18]. The matrix interlayer region thickness did not increase, and the mechanical results showed an improvement in the interlaminar shear strength that ranged from 4% [17] to 30% [18]. It is also possible to grow the CNTs on the surface of the fibers before applying the matrix, and mechanical results reported in the literature showed improvements from 70% for the interlaminar shear strength of alumina fiber composites [19] to ~350% improvement in critical strain energy release rate (G_{IC}) of silicon carbide (SiC) fiber polymer composites [20]. Although promising, CNT growth on fibers is for the moment not applicable to carbon or glass fibers. Thus, the

[1] Currently, GE Global Research Center, Niskayuna, NY, USA

problem of reinforcing (graphite/epoxy) prepreg or similarly processed composites remains.

The interlaminar hybrid architecture proposed in this work is based on the architecture presented by Wardle and Kim [21], and further developed by Wardle, García, Hart, and Slocum [22]. Vertically-aligned long CNTs are placed between plies of graphite/epoxy prepregs and wet by the epoxy contained in the prepreg during curing. This architecture's main advantage over the previously mentioned approaches is the orientation of the CNTs. In the current architecture, the CNTs are perpendicular to the ply/laminate plane ("z-direction"), reinforcing the matrix in the direction where it is most needed (see Figure 1). The aligned CNTs act as "nano-stitches" between the plies, bridging cracks produced at the matrix-rich interface, and also strengthening and stiffening the interface. Analysis [23], [26] has demonstrated that toughening is possible with CNTs in this configuration.

This work presents the fabrication and testing of a new hybrid multiscale composite material. Forests of long (>20 micron), aligned carbon nanotubes (CNTs) are grown on commercially-available Si wafers and transplanted between layers of graphite/epoxy prepreg. During the curing of the laminate, the epoxy resin from the prepreg layers fully wets the CNTs, creating aligned CNT "nanostitched" composite laminates with enhanced interlaminar properties.

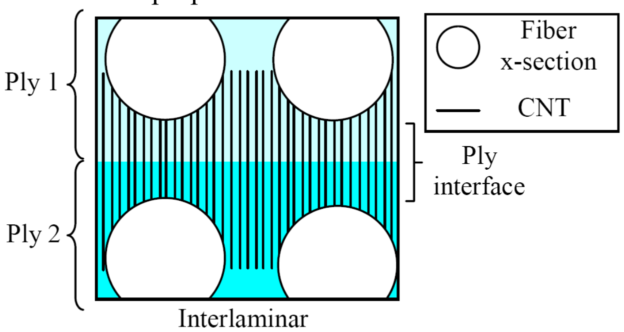

Figure 1: Illustration of interlaminar "nanostitching" using aligned CNTs.

Effective reinforcement of a polymer matrix by the CNTs grown using the CVD process in this work has been demonstrated previously using novel nanocompression techniques on aligned-CNT polymer nanocomposites [24]-[25], and wetting of CNT forests characterized for different off-the-shelf thermoset polymers [19], [25]. The wetting behavior and microstructure of the CNT-reinforced composite laminates is investigated here via optical and scanning electron microscopy (SEM). Interlaminar fracture toughness of the nanoengineered laminates is obtained through tests and compared to that of laminates without CNTs.

2 Analytical Model

An analytical model was developed using fracture mechanics and a "traction law" to compare the effective interlaminar reinforcement of the CNT-bridging (termed "nano-stitching" [21]) with the traditional approach of using fibers to stitch the laminates [2]. Consider a double cantilever beam (DCB) specimen with isotropic properties E and ν and applied moment M. For a composite specimen, E would be associated with the ply modulus in the fiber direction (aligned with x-axis). The crack opening can be described by u(x). A schematic of the model, including the nanostitches bridging the crack, is shown in Figure 2. A simple linear traction law was used to model the pressure applied to close the crack tip by the bridging CNTs. The traction law is linear in the crack coordinate, x, and varies from a maximum at the crack tip (a + Δa) to zero where the CNTs end. An improved model is under development for a traction law linear in crack tip opening displacement (u).

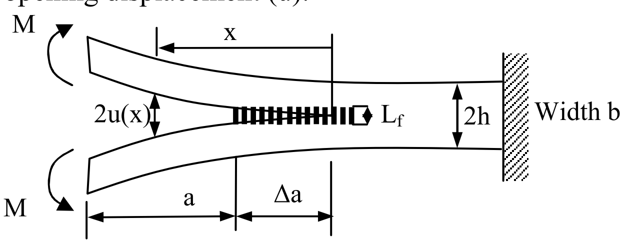

Figure 2: Illustration of the model.

In the model, perfect wetting of the CNTs by the polymer matrix and perfect alignment of the CNTs is assumed. This model is similar to the cohesive zone modeling reported by others for unaligned CNTs [26]. The model here focuses on the effects of bridging fiber (CNT) radius and volume fraction. Applying the principle of superposition, the complete problem can be considered as a sum of two independent problems: the specimen subjected to moment (pure bending), without the bridging fibers and the specimen subjected to the forces/tractions generated by the CNTs. The solution for the fracture toughness is shown in Eq. 1:

$$G_{IC}\big|_{CNT} = E\cdot h\left[\frac{\dfrac{K_0}{E\cdot\sqrt{h}}+\sqrt{3}v_f\left(\dfrac{f}{E}\right)\left(\dfrac{L_f}{h}\right)\left(\dfrac{\Delta a}{h}\right)^2\dfrac{h}{r}}{1+3v_f\left(\dfrac{f}{E}\right)\left(\dfrac{\Delta a}{h}\right)^4\left(\dfrac{h}{r}\right)}\right]^2 \quad (1)$$

where K_0 is the stress intensity factors of the unreinforced composite laminates, v_f is the volume fraction of the stitching fibers (or CNTs), f is the friction coefficient of the CNTs pulling out of the matrix, r is the radius of the stitching fibers, h is half the thickness of the laminate, and Δa_{ss} is the size of the crack of the extension for steady-state bridging, and is obtained from Eq. 2.

$$u_{total}(x = \Delta a_{ss}) = \frac{L_f}{2} \qquad (2)$$

Here, the mechanism of bridging modeled is frictional sliding using a highly conservative friction coefficient (10 MPa) vs. the pullout strength reported for CNTs embedded in a polymer (ranging from 138 MPa obtained through computational simulations [27] to 500 MPa obtained experimentally by Wagner et al. [28]) .

As shown in Figure 3, this model demonstrates that reducing the diameter of the stitching fibers from microns (fibers traditionally used to stitch laminates [2]) to nanometers (CNTs) dramatically increases the resistance of the material to fracture. A small diameter provides a considerably better reinforcement, e.g., for CNTs of diameter 7 nm and a $v_f = 40\%$, the toughening increases by ~100x . The analysis as developed is very sensitive to the assumption for the frictional coefficient, f; if this value is increased to 100 MPa, then the improvement increases to ~900x.

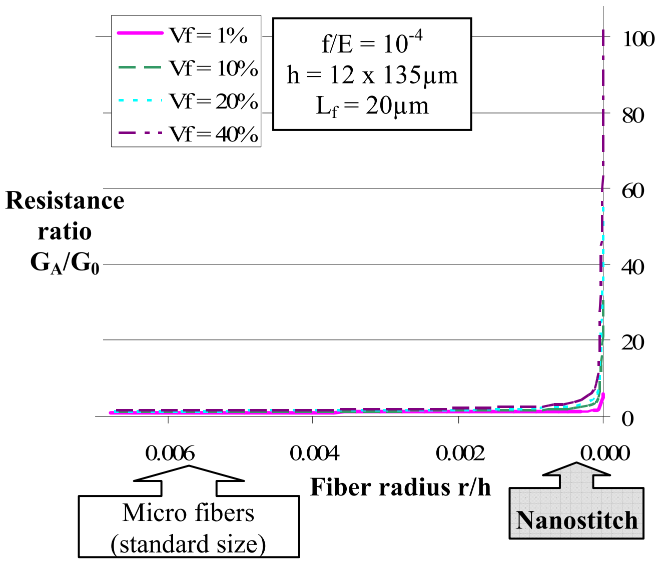

Figure 3: Effect of the radius and volume fraction of the stitching fibers on the fracture toughness increase.

Traditionally, aramid or thermoplastic fibers have been used to bridge the cracks, with diameters in the range of 5 to 10 microns. The process used to stitch these large fibers (as composite fibers or greater) breaks some of the fibers in the composite and also produces matrix-rich regions around the stitched fibers. The mechanical properties of these matrix-rich regions are two orders of magnitude lower than those of the original composite material. This effect is not considered in the model, which means that the effective reinforcement of the traditionally-stitched fibers is even lower than shown in Figure 3. CNTs grown using the present process are on the order of 10 nanometers (3 orders of magnitude below the fibers previously mentioned), which allows a significant toughening, ~100x vs. 2-3x for the traditional (5-10 micron diameter) reinforcing fibers. Models for Mode 2 and 3 toughening have not yet been developed but it is anticipated that the relative improvement will be greater than for Mode 1. Strength of the CNTs themselves is expected to similarly improve the interface strengths.

3 Experimental Methods

The experimental work for this study can be divided into four categories: Growth of carbon nanotubes on silicon substrates, transplantation of the CNTs to the surface of carbon fiber prepreg, tests on the effective wetting of the CNT forest by the epoxy present in the preimpregnated layers, and mechanical testing of nanoengineered composite specimens to determine the reinforcement obtained by the use of aligned CNTs.

3.1 Growth of CNTs on Silicon Substrates

The first step in the construction of the hybrid composite material is growth of forests of aligned CNTs on silicon wafers using a modified thermal chemical vapor deposition (CVD) technique developed at MIT [29]. A continuous catalyst layer was deposited on 6” Si wafers. The catalyst film of 1.2/20 nm Fe/Al_2O_3 is deposited by electron beam evaporation. In this case no pattern was applied to the catalyst, because the desired configuration was a forest of CNTs. The wafers with the catalyst layer were cut into 60x20 mm pieces to fit in the quartz tube furnace (22-mm diameter). CNT growth is performed in a single-zone atmospheric pressure quartz tube furnace (Lindberg). The CNTs obtained are multiwalled CNTs (MWCNTs) with 3 to 5 walls, and an outer diameter of 7-10 nm. The CNTs can be grown to lengths exceeding 3 mm at a rate greater than 2 µm/second. The CNTs grow vertically aligned and perpendicular to the surface of the wafer. The CNTs are easily grown to lengths long enough to fully populate the matrix region between layers in a typical preimpregnated composite laminate. The height for the CNTs (15 to 30 µm) needed for the hybrid architecture should be on the order of the inter-ply matrix region (~10 µm). For this initial study, more stringent conditions were used and CNTs of approximately 150 microns length were grown (see Figure 4). All SEM pictures, such as Figure 4, were taken using an FEI/Philips XL30 FEG SEM.

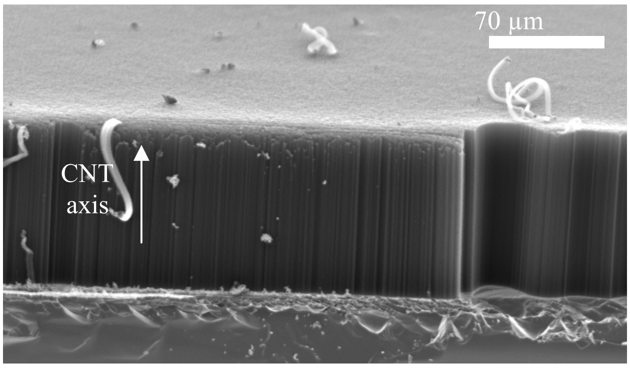

Figure 4: SEM of cross-section of a vertically aligned CNT forest grown using the thermal CVD process.

3.2 Fabrication of Nanoengineered Graphite Fiber/Epoxy Composites Reinforced with Aligned CNTs

Experimental tests were performed to verify the feasibility and scalability of the fabrication process established for the interlaminar hybrid architecture. In this architecture, the CNTs are transplanted from their original substrate and placed in between the plies of a prepreg laminate. The epoxy needed for the wetting of the CNTs during the fabrication process comes from two different layers of prepreg (above and below the forest). The assembly should follow the curing process from the manufacturer, to avoid the flow of epoxy out of the laminate.

The scalability of the fabrication of the interlaminar hybrid architecture to a continuous process relies on an effective transplantation of the CNTs from the silicon substrate where the forests are grown, to the surface of the prepreg plies at room temperature. In order to ensure the future scalability of the process, different purely mechanical transplantation techniques were evaluated to transfer the CNTs to the prepreg prior to curing. The results presented in section 4 will demonstrate the effectiveness of this approach.

3.2.1 Wetting and Microstructural Characterization of the Transplanted CNT Forests

Two tests were used to assess the wetting of the transplanted CNTs in two different configurations: a one-sided nanostitched composite (similar to the configuration presented in the first two sets of tests) and a complete nanostitched architecture comprising two prepreg layers with transplanted CNTs in between.

For the first wetting test of mechanically transplanted CNTs a 20-mm square forest of 150-µm long CNTs was transplanted to a 30 mm x 50 mm IM7/977-3 prepreg strip (single ply). A sheet of non-porous Teflon was placed on top of the assembly, covering it completely. A caul plate with the same dimensions as the prepreg strip (30 mm x 50 mm) was then placed on top of the non-porous Teflon sheet. The assembly was put on a vacuum table and two more layers were added: First, a porous Teflon sheet was used to cover the first assembly completely; second, a sheet of glass fiber cloth was placed on top of the assembly to ensure that vacuum was effectively applied. Finally the whole assembly was closed with a vacuum bag, as shown schematically in Figure 5.

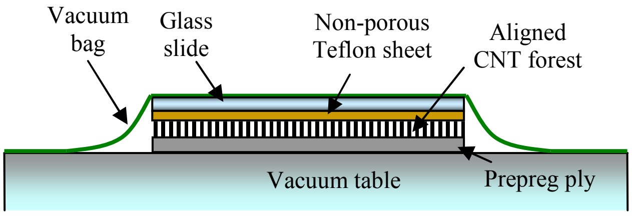

Figure 5: Illustration of the vacuum assisted curing of the one-sided nano-stitched hybrid laminate. The layers on top of the glass slide (porous Teflon and glass fiber cloth) are not included in the scheme for reasons of simplification (not to scale).

The assembly was introduced into an autoclave, vacuum (15 psig) was applied, and the specimens were cured following the manufacturer recommendations (100 psig of total pressure, heat at 5 ºF/min to 355 ºF, hold for 6 h, cool at 5 º/min to 140 ºF and vent pressure, let cool to room temperature). The resulting one-side nano-stitched hybrid composite was diesawed using a DAD-2H/6T disco abrasive system, and analyzed using scanning electron microscopy (using a FEI/Philips XL30 FEG SEM).

The next step was to create a nanostitched laminate, with the CNT forest placed between two laminae of prepreg. An additional prepreg layer was added to the assembly used in the previous set of tests. A square 20-mm forest of 150-µm long CNTs was transplanted to a 20-mm x 20 mm IM7/977-3 prepreg ply. After transplantation, a second single 20 mm x 20 mm prepreg ply was placed in direct contact with the transplanted CNT forest. The rest of the layers were the same used in the previous set of tests, as shown schematically in Figure 6.

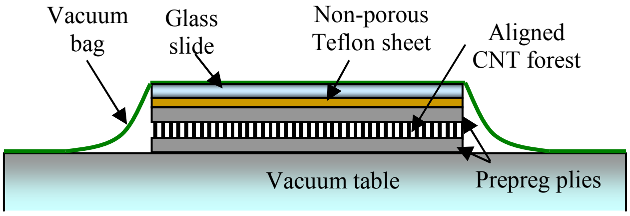

Figure 6: Illustration of the vacuum assisted curing of the two side nano-stitched hybrid laminate (not to scale).

The curing process was the same described previously. The resulting two-side nano-stitched hybrid composite was diesawed (using a DAD-2H/6T disco abrasive system), and the wetting and alignment was analyzed using an FEI/Philips XL30 FEG SEM.

3.3 Mechanical Characterization of the Interlaminar Hybrid Composite

As described in section 3.2, effective transplantation of the CNTs, maintenance of the CNT alignment, and effective wetting of the CNTs are key factor to maximize the effective reinforcement of the interlaminar hybrid architecture. Experiments were performed to compare the mechanical properties of unidirectional prepreg composite laminates with and without the CNT nanostitches.

ASTM Mode I fracture tests [30] are used to assess the interlaminar fracture toughness. A double-cantilever beam (DCB) specimen (as the one shown in Figure 8) contains a precrack, and during the test the crack grows and the fracture toughness is determined.

For the manufacturing of the DCB specimens, 160 x 20 mm strips of 1D IM7/977-3 prepreg were cut and stacked to create two 12-layer laminates. A 90 x 20 mm CNT forest 150 µm-high was transplanted from the silicon substrate to one of the two 12-layer laminates, (three 30 x 20 mm patches of CNT forests), leaving a 50 x 20 mm section not covered by CNTs. A 13-µm sheet of Teflon was placed in that free section. Then the two laminate stacks were assembled together, forming a 24-layer composite laminate with a ~50 mm long precrack in the mid-plane, as shown in Figure 7. This laminate was then placed in a mold on the vacuum table inside the autoclave, and closed under a vacuum bag, as described in section 3.2.1. The curing cycle inside the autoclave followed the recommendations of the manufacturer.

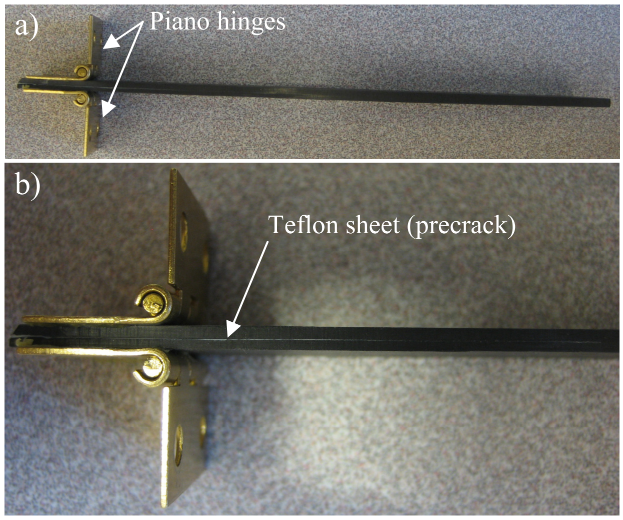

Figure 7: a) CNT/Graphite/Epoxy DCB specimen; b) Closer view of the precrack.

After completing the curing process, piano hinges were glued to the two precracked edges using a 5-min curing epoxy. Lines marking regular distances from the precrack were painted on the specimen, as shown in Figure 8. The specimen was then assembled on a universal tensile test machine. An Instron 8848 MicroTester with a calibrated 2-kN load cell was used to perform the Mode I fracture tests. The microtester can apply and measure static loads ranging from 5 N to 2 kN. The resolution is 1 mN for load and 1 micron for displacement.

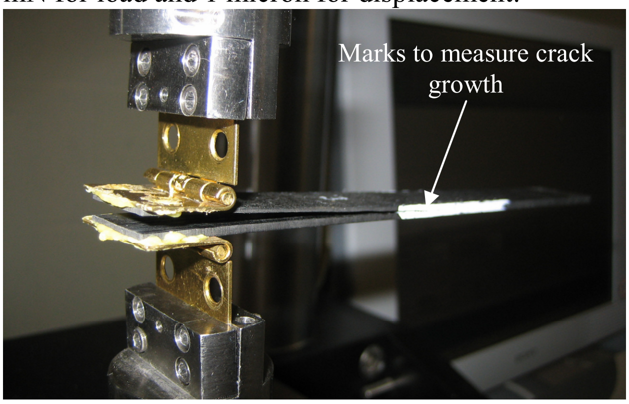

Figure 8: CNT/Graphite/Epoxy DCB specimen mounted in the universal tensile-compression test machine.

The test specimen is placed on the setup such that the 0º fiber direction is along laminate axis of the specimen, and then subjected to a Mode I fracture test (see Figure 8) at a constant crosshead speed of 1 mm/min. The load is applied while the crack opens. The load, displacement, and crack propagation are measured until the crack is grown more than 20 mm [30]. All these three data are used in the calculation of the Mode I toughness of the laminate ply interface. Two unreinforced and one CNT-reinforced specimens were tested.

For the tests the toughness is calculated using the Compliance Calibration Method. The Mode I interlaminar fracture toughness can be calculated from Eq. 2:

$$G_I = \frac{P\delta}{2ba} \cdot n \quad (2)$$

where P is the load, δ is the displacement, b is the thickness of the specimen, a is the delamination length (crack propagation length), and n is the slope obtained from the plot $\log(\delta_i/P_i)$ versus $\log(a_i)$.

R-curves (interlaminar fracture toughness versus delamination length were obtained from the experimental tests. These tests directly measure the reinforcing effectiveness of aligned CNTs in a composite material and explore the mechanisms of this reinforcement (local stiffening of the polymer matrix, and bridging of cracks).

4 Results and Discussion

The two most important factors for the feasibility and scalability of the fabrication process are the transplantation of the CNT forest from its original substrate to the prepreg and wetting of the CNTs by the epoxy in the prepreg. This work contains promising preliminary results that indicate that both transplantation and wetting are possible with CNT alignment perpendicular to the ply/laminate. It is important to note that the results in all three tests were performed with first-generation manufacturing processes, using non-ideal (150-μm vs. "ideal" 20-μm CNTs).

Purely mechanical means of transplantation were developed for transfer of CNT forests to the graphite/epoxy prepreg. Transfer rate, pressure, and geometry were optimized until full transplantation of the CNT forests was achieved (see Figure 9). The transplantation was equally effective for the two different prepreg systems used. The process proved to be repeatable and feasible for a scaled up version.

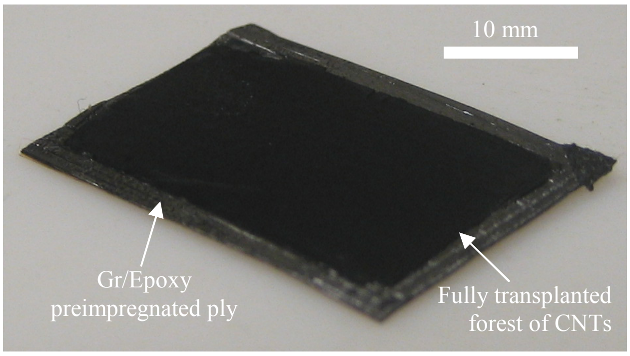

Figure 9: Forest of CNTs fully transplanted to the surface of the prepreg

An example of the results of the transplantation process on the IM7/977-3 prepreg is shown in the SEM pictures in Figure 10 (pre-curing). As shown in Figure 10.a), the interior of the forest is completely stable (note there are no cracks), following the surface of the prepreg, which is an indication of the CNT forest penetrating in the prepreg. The alignment is maintained even at the free edges, as shown in Figure 10.b.

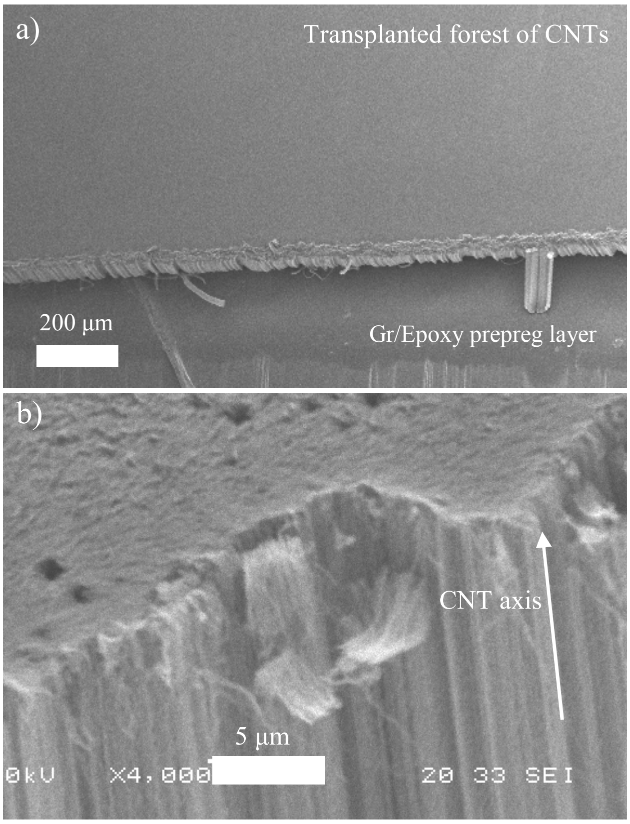

Figure 10: SEMs of a) Transplanted forest of CNTs on the surface of a Graphite/Epoxy preimpregnated ply; b) Closer view of the transplanted CNT forest showing good alignment of the CNTs after the transplantation process.

Once a reliable method to transplant the CNTs to the prepreg had been developed, the next step was to test the wetting of the CNTs by the epoxy contained in the prepreg. It is important to note that the wetting test is more stringent than what is needed to ensure the feasibility of the nano-stitched hybrid architecture (the CNT forests are ~150-μm high instead of the ideal ~10-20 μm). Initially a one-sided architecture was tested. The results obtained from this set of tests shows complete wetting of the CNTs by the epoxy contained in the prepreg. A regular upper surface of the CNT/epoxy with no voids appeared, as shown in Figure 11.a. The pressure in these regions favored the formation of a uniform, fully wet nanocomposite layer. The CNT structure and alignment were well maintained in most cases (see Figure 11.b).

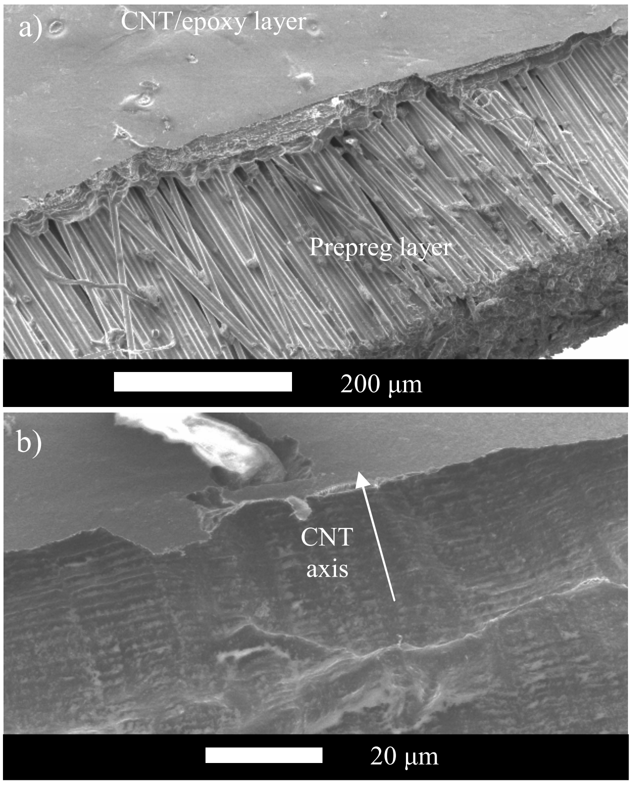

Figure 11: SEMs of a) One-sided nanostitched prepreg showing perfect wetting; b) Closer view of the CNT/epoxy region, showing good alignment of the CNTs after wetting and curing.

In the next set of tests a second layer of prepreg was added to the hybrid laminate on top of the CNT layer. The resulting nano-stitched hybrid composite samples were diesawed (DAD-2H/6T disco abrasive system) in two different directions (perpendicular and parallel to the direction of the graphite fibers) to better assess the wetting and alignment of the CNTS in the interior of the composite. Scanning electron microscopy (FEI/Philips XL30 FEG SEM) was used to study the specimens. Due to the excessive length of the CNTs, a third layer of CNT/epoxy nanocomposite, similar to the one appearing in the previous test, was observed (as expected) in between the two layers of prepreg. As in the previous set of tests, the wetting of the CNT forest between the two prepreg plies was achieved during the curing process, as shown in Figure 12.a) The intermediate layer of CNTs also showed good alignment. No voids are observed in the thick nanocomposite layer (as shown in Figure 12.a). A closer view of the interface between the CNT/epoxy layer and the prepreg plies is shown in Figure 12.a. The nanocomposite layer is completely wet also in this cross section (no voids). The change in color shown is due to the effect of the diesawing process which creates a texture in the composite. As seen in Figure 12.b, the CNTs in the nanocomposite layer penetrate into the prepreg ply ~5-7 μm (in the same order of the carbon fiber diameter), depending on the region.

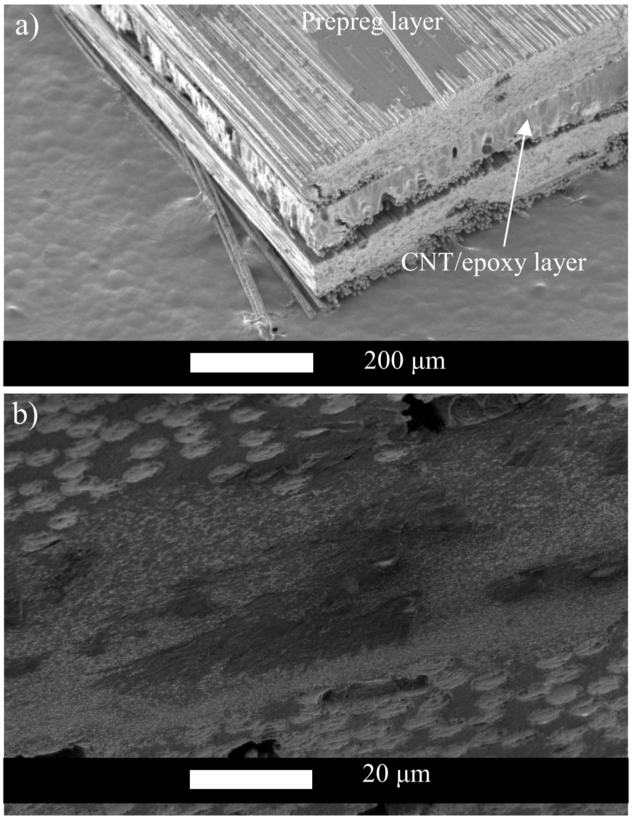

Figure 12: a) Cross-section of the 2-sided nanostitched composite (note the CNT/epoxy layer in between the two layers of prepreg; b) Closer view of the CNT/epoxy layer, showing how the CNTs are effectively penetrating the prepreg ply, acting like nanostitches.

After demonstrating wetting of the aligned CNTs by the prepreg epoxy, mechanical tests were performed on unreinforced and CNT-reinforced specimens. Typical results from the Mode I fracture tests are presented in the form of R-curves in Figure 13.

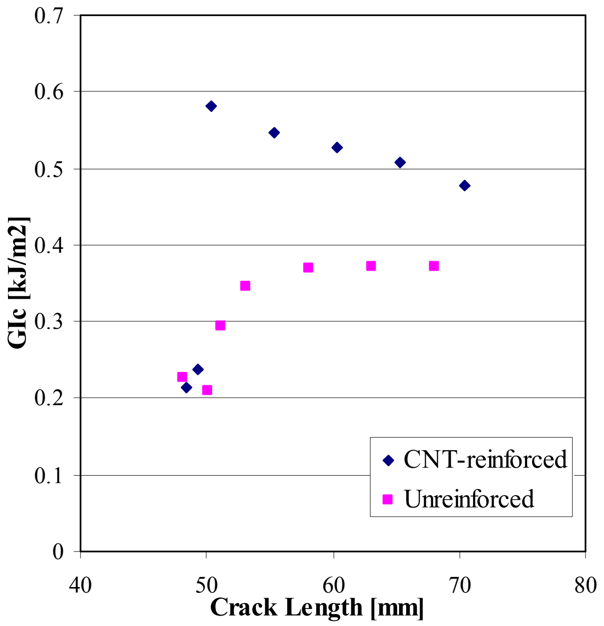

Figure 13: R-curve showing the evolution of the interlaminar fracture toughness while delamination propagates for unreinforced and CNT-reinforced (nanoengineered) composite laminates.

The effective reinforcement from the nanostitch is the increase associated with the toughened response vs. the initiation toughness. The toughening (R-curve) in the unreinforced specimens are due to the well-known 0º fiber bridging ('nesting') mechanism which is an artifact of the ASTM standard test. As the plies in the nanostitched specimen are separated by ~150um (nanostitch ply), there is no toughening contribution from bridging/nesting of the 0º fibers. The origin of the mildly decreasing toughness for the nanostitched interface is still under investigation, but is believed to be associated with increased crack advance in the regions of the nanostitch patch joints. These joints are an artifact of the current manufacturing process where the 60 mm in length of the nanostitched specimen is obtained by placing three 20 mm CNT patches in a row on the laminate (as discussed in the Experimental section 3.3). Future fabrication efforts will use larger, continuous nanostitch patches. The results obtained from the analysis of the R-curves are shown in Table 1.

Table 1. Interlaminar fracture toughness for unreinforced and nanoengineered composites.

	Unreinforced Composite	Nanoengineered Composite	Effective reinforcement
Interlaminar fracture toughness [kJ/m^2]	0.209	0.532	**155%**

Therefore, this hybrid architecture is shown to possess significantly enhanced interlaminar fracture toughness due to the aligned-CNT reinforcement. Aligned CNTs obtained in this study present a considerably more uniform dispersion than CNTs which are grown in bulk and embedded into a polymer matrix using sonication or other dispersion methods used in previous studies. Dzenis et al. [13]-[14] introduced an additional layer of carbon nanofibers (CNFs) between plies of composite material. The CNFs used were randomly oriented in the plane of the laminate and have mechanical properties that are an order of magnitude lower than the CNTs, both limiting factors for the effectiveness of the reinforcement. Gibson [15] introduced a thin film of randomly oriented CNTs between plies, and mechanical tests showed no apparent improvement in the properties of the composite material. In both cases the reinforcement was introduced in the form of an additional layer. Adhikari *et al.*[16] did not obtain any significant reinforcement (less than 2%) in the interlaminar shear strength of laminates by adding a thin layer of randomly oriented single-walled CNTs (SWCNTS)/epoxy between the composite plies Thakre *et al.*[17] dissolved randomly oriented functionalized SWCNTs in ethanol and sprayed the solution on carbon fiber cloth (avoiding the formation of an additional layer), but the interlaminar reinforcement obtained by the randomly was ~4.4% for functionalized CNTs. Bekyarova *et al.*[18] reported an improvement (~30%) for the interlaminar shear strength by using electrophoresis to selectively deposit randomly oriented multi- and single-walled CNTs on woven carbon fabric.

The results presented in this work demonstrate that the effective interlaminar reinforcement that can be obtained by strategically placing aligned CNTs in the interface between laminate plies yields is at least 1 order of magnitude higher than randomly dispersing the CNTs. As shown, the process avoids the formation of aggregates, maximizing the composite mechanical performance. A second possible explanation for the toughness observed is the fracture of a large compliant interlayer (CNTs +

epoxy) between the plies, resulting in plastic toughening of the interface. Due to the particular nature of the CNTs used in this study, it might also be possible to increase the composite multifunctional properties (electrical and thermal conductivities), and possibly damping.

5 Conclusions and Recommendations

Aligned CNT-reinforced hybrid composite laminates offer significant advantages for structural and multifunctional applications relative to laminates reinforced by randomly oriented CNTs embedded into the matrix. The new interlaminar (nanostitched) reinforcement presented in this work has the potential to become a scaled-up solution for the reinforcement of composite materials. The thermal CVD process could allow the continuous growth of CNTs on silicon substrates. The effective transplantation method developed for this study has demonstrated the feasibility of transplanting the CNTs using exclusively mechanical means compatible with the prepreg manufacturing process, addressing the issue of CNT dispersion at the same time. Wetting of the aligned CNTs with the epoxy contained in the prepreg layers has been demonstrated, even under more stringent conditions than required. The interlaminar reinforcement of the hybrid composites was studied by applying a standard Mode I fracture test to unreinforced and aligned CNT-reinforced composite specimens. The hybrid composite showed a 155% increase of the interlaminar G_{IC} with respect to the unreinforced laminate. This result indicates a clear interlaminar strengthening due to the presence of aligned CNTs.

Current studies and future research will be focused on the manufacturing of interlaminar hybrid composites reinforced with shorter CNTs (~20 µm), surface microscopy to determine if pullout is the correct mechanism of bridging as assumed in our model (vs. shear strength, etc), fuller mechanical characterization (Mode II and III tests), and also mechanical characterization of hybrid nanoengineered composite materials with other architectures (CNTs grown on advanced fibers and wet with polymer matrices [19], [31]) built with aligned CNTs, multifunctional property modeling and characterization, and scalability of the CVD process.

References

[1] Poe C., Reeder J. R., and Yuan F. G. "Fracture Behavior of a Stitched Warp-Knit Carbon Fabric Composite," NASA/TM-2001-210868, 2001.

[2] Glaessgen E. H., Raju I. S., and Poe C. C. "Modeling the influence of stitching on delamination growth in stitched warp-knit composite lap joints," *Proceedings of ICCM-12*, Paris, France, Paper No. 449, 1999.

[3] Glaessgen E. H. and Raju I. S. "Three-dimensional effects in the plate element analysis of stitched textile composites," *Proceedings of the 40th AIAA/ASME/ASCE/AHS/ASC Structures, Structural Dynamics, and Materials Conference and Exhibit* St. Louis, Missouri, AIAA-99-1416, 1999.

[4] Stickler P. B., Ramulu M. "Investigation of mechanical behaviour of transverse stitched T-joints with PR520 resin in flexure and tension," *Composite Structures* 52, 307-314, 2001.

[5] Stickler P. B. and Ramulu M. "Parametric analyses of stitched composite T-joints by the finite element method," *Materials and Design* 23, 751–758, 2002.

[6] Stanley L. E. and Adams D. O. "Development and Evaluation of Stitched Sandwich Panels," NASA/CR-2001-211025, 2001.

[7] Krueger R. and O'Brien T. K. "A shell/3d modeling technique for the analysis of delaminated composite laminates," NASA-2000-TM210287, 2000.

[8] Dávila C. G. "Solid-To-Shell Transition Elements for the Computation of Interlaminar Stresses," *Computing Systems in Engineering* 5 2, 193-202, 1994.

[9] Schadler L. S., Giannaris S. C., and Ajayan P. M. "Load transfer in carbon nanotube epoxy composites," *Applied Physics Letters*, Vol. 73, No. 26, pp. 3842-3844, 1998.

[10] Gojny F. H., Wichmann M. H. G., Köpke U., Fiedler B., and Schulte K., "Carbon nanotube-reinforced epoxy-composites: enhanced stiffness and fracture toughness at low nanotube content," *Composites Science and Technology* 64, pp. 2363-2371, 2004.

[11] Qian D., Dickey E. C., Andrews R., Rantell T. "Load transfer and deformation mechanisms in carbon nanotube-polystyrene composites," *Applied Physics Letters*, Vol. 76, No. 20, pp. 2868-2870, 2000.

[12] L. Jin, C. Bower and O. Zhou. "Alignment of carbon nanotubes in a polymer matrix by mechanical stretching," *Applied Physics Letters*, Vol. 73, No 9, pp. 1197-1199, 1998.

[13] Dzenis Y. A. "Spinning Continuous Fibers for Nanotechnology," *Science* 304, pp. 1917-1919, 2004.

[14] Dzenis Y. A. and Larsen G. "Delamination resistant composites prepared by small diameter fiber reinforcement at ply interfaces," U.S. patent pending 6, 265, 333, 2001.

[15] Gibson R. F., Anumandla V., Wu X., and Bettinger D. “Experimental Characterization of Delamination in Unidirectional Carbon/Epoxy Composite Specimens Featuring a Carbon Nanotube-Enhanced Ply Interface,” *Proceedings of the SEM Annual Conference & Exposition on Experimental and Applied Mechanics*, pp. 71-79, 2005.

[16] Adhikari K., Hubert P., Simard B., and Johnston A. “Effect of the Localized Application of SWNT Modified Epoxy on the Interlaminar Shear Strength of Carbon Fiber Laminates,” *Proc. 47th AIAA/ASME/ASCE/AH/ Conference*, Newport, R.I., AIAA-2006-1855-604, 2006.

[17] Thakre P. R., Lagoudas D. C., Zhu J., and Barrera E. V. “Processing and Characterization of Epoxy-SWCNT-Woven Fabric Composites,” *Proc. 47th AIAA/ASME/ASCE/AH/ Conference*, Newport, R.I., , AIAA-2006-1857-212, 2006.

[18] Bekyarova E., Thostenson E. T., Yu A., Kim H., Gao J., Tang J., Hahn H. T., Chou T. W., Itkis M. E., and Haddon R. C. “Multiscale Carbon Nanotube-Carbon Fiber Reinforcement for Advanced Epoxy Composites,” *Langmuir*, 23(7) pp. 3970-3974, 2007.

[19] García E. J., Hart A. J., Wardle B. L., and Slocum A. H. “Aligned Carbon Nanotube Reinforcement of Woven Composite Ply Interfaces”. *Proc. 47th AIAA/ASME/ASCE/AH/ Conference*, Newport, R.I., AIAA-2006-1857-212, 2006.

[20] Veedu V. P., Cao A., Li X., Ma K., Soldano C., Kar S., Ajayan P. M., and Ghasemi-Nejhad M. “Multifunctional composites using reinforced laminae with carbon-nanotube forests”. *Nature Materials*, Vol. 5, pp. 457-462 Letters, 2006.

[21] Wardle B. L. and Kim S. G. “Nano-engineered material architectures: Ultra-tough hybrid nanocomposite system,” MIT TLO Case 11260, 2005.

[22] García E. J., Hart A. J., Wardle B. L., and Slocum A. H. “Production of Reinforced Composite Materials and Aligned Carbon Nanotubes,” MIT TLO Case 12029, 2005.

[23] García E. J. “Characterization of Composites with Aligned Carbon Nanotubes as Reinforcement”. Doctoral Thesis, Dept. of Mechanical Eng., U. Zaragoza, Spain, Nov. 2006.

[24] García E. J., Hart A. J., Wardle B. L., and Slocum A. H. “Fabrication and Nanocompression Testing of Aligned CNT/Polymer Nanocomposites,” *Advanced Materials*, to be published. DOI: 10.1002/adma.200700143, 2007.

[25] García E. J., Hart A. J., Wardle B. L., and Slocum A. H. “Fabrication of Composite Microstructures by Capillarity-Driven Wetting of Aligned Carbon Nanotubes with Polymers,” *Nanotechnology*, 18, 165602, 2007.

[26] Riddick J. C., Frankland S. J. V., and Gates T. S. “Multiscale Analysis of Delamination of Carbon Fiber–Epoxy Laminates with Carbon Nanotubes,” *Proc. 47th AIAA/ASME/ASCE/AH/ Conference*, Newport, R.I., AIAA-2006-1676, 2006.

[27] Wong M, Paramsothy M, Xu XJ, Ren Y, Li S, Liao K. “Physical interactions at carbon nanotube–polymer interface,” *Polymer* 44, 25, pp.7757–64, 2004.

[28] Wagner HD, Lourie O, Feldman Y, Tenne R. “Stress-induced fragmentation of multiwall carbon nanotubes in a polymer matrix,” *Applied Physics Letters* 72, 2, pp. 188–90, 1998.

[29] Hart A. J., and Slocum A. H. “Flow-mediated nucleation and rapid growth of millimeter-scale, aligned, carbon nanotube structures from a thin film catalyst”. *J. Physical Chemistry B*, Vol. 110, no.16, pp. 8250-8257, 2006.

[30] ASTM D 5528-01. "Standard Test Method for Mode I Interlaminar Fracture Toughness of Unidirectional Fiber-Reinforced Polymer Matrix Composites". ASTM International.

[31] García E. J., Hart A. J., Wardle B. L., and Slocum A. H. “Aligned Carbon Nanotube Reinforcement of Ply Interfaces in Woven Composites”. *Proc. 48th AIAA/ASME/ASCE/AH/ Conference*, Waikiki, HI, USA, 2007.