Nano-engineered Composites Reinforced with Aligned Carbon Nanotubes (CNTs)

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ABSTRACT

We present the implementation of aligned carbon nanotubes (CNTs) as a method to enhance properties of traditional advanced composites. The hybrid composites are 3-dimensional architectures of aligned CNTs, and existing advanced fibers and polymeric resins creating nano-engineered composites. Our work to date has focused on interlaminar strength and toughness, and electrical and thermal conductivities of two laminate-level architectures. The first approach utilizes aligned CNT forests placed between ply layers perpendicular to the fiber direction to create "nano-stitches". The second approach involves growing the CNTs directly on woven alumina fibers, so that the CNTs extend radially outward from every fiber forming "fuzzy fibers". Three standard processing routes for are reviewed: nano-stitching of graphite/epoxy prepreg, nano-stitching of graphite/epoxy cloth in a resin-infusion process, and hand layup of fuzzy fiber ceramic cloth.

Keywords: carbon nanotube, nanocomposite, composite, laminate

1 INTRODUCTION

Ever since the initial investigation of carbon nanotubes [1, 2], the multi-functional properties of CNTs have inspired research not only into their mechanical attributes, such as tensile stiffness and strength, but also into their electrical and thermal properties as well. Numerous researchers have confirmed the high tensile stiffness and strength of CNTs [3]. Other theoretical and experimental observations on CNTs include tunable electrical conductivities (from semiconducting to metallic), excellent thermal conductivity, minimal thermal expansion, and low density [4].

These exceptional properties are only beneficial if they can be implemented at engineering-relevant lengthscales. Successful examples in engineering applications include micro-probes and data storage elements [5], and are generally limited to micro and nano-scale applications. This stems from the difficulties inherent in fabricating with nanoscale constituents, scaling production to useable levels, and other issues that arise during integration. Recently, our group has implemented CNTs into macroscopic structures such as aerospace composites, where minimizing weight is a great priority [6, 7]. Laminate mechanical, electrical, and thermal properties could be significantly enhanced by CNT implementation without significant weight addition. Two main approaches to incorporating CNTs in a macro scale have been explored in this work. Embedding VA-CNTs in the interply region focuses on enhancement in interlaminar properties. Another, more aggressive method to implement CNTs is by growing them directly on all fibers, including the ones inside the weaves, providing both interlaminar and intralaminar reinforcement. This paper summarizes work to date fabricating and testing both nano-engineered composite architectures.

2 EXPERIMENTAL APPROACH

2.1 Design of Nano-engineered Composites

The two main architectures developed for introducing aligned carbon nanotube into traditional composites are shown in Fig. 1 [6, 7]. In the first architecture, aligned carbon nanotube forests are introduced between ply layers perpendicular to the fiber direction to create "nano-stitches". Vertically aligned CNT forests are grown on a flat substrate using chemical vapor deposition (CVD) as described below. The CNTs are placed between layers of either carbon/epoxy prepreg or dry carbon weave and cured with conventional methods. The resin-rich region between traditional composite plies is a source of weak interlaminar properties. This particular approach allows the carbon nanotubes to effectively reinforce this region facilitating load transfer between plies. Such stitching has been shown to have substantial (>100%) improvement in critical Mode I and II strain-energy release rates. The second, fuzzy fiber architecture, addresses similar interlaminar weaknesses, but incorporates CNT forests that are radially grown on the fiber surfaces. By spanning both the region between fibers and the interply region, CNTs grown on adjacent fibers can form mechanical connections and electrical/thermal conductive pathways throughout the structure.

2.2 CNT Growth

Multi-walled carbon nanotubes to be implemented into nano-engineered composites mentioned above are grown with a modified chemical vapor deposition (CVD) method developed at MIT [8, 9]. The substrate is first coated with a

catalyst precursor, then is treated with heat and a reduction gas. This pre-conditions the catalyst into nano-particles, which nucleate CNTs when a gaseous carbon source is introduced. Our existing setup consists of an atmospheric pressure quartz tube furnace (Lindberg, 22 mm inner diameter, 300 mm heated length).

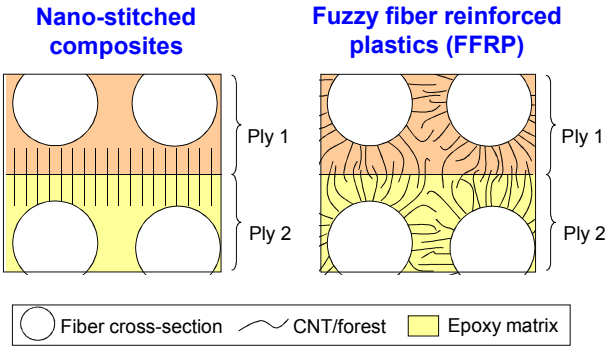

Figure 1: Illustration of idealized micro-structure of the nano-engineered composites reinforced with CNTs (after [6] and [7]). Not to scale.

2.3 FFRP Fabrication

The FFRP fabrication process (Fig. 2) involves growth of aligned CNTs on woven cloth, and then hand layup and curing with thermoset epoxy resin. Alumina (Al_2O_3) fiber cloth was selected as an advanced fiber substrate, as Al_2O_3 can regulate surface diffusion of an iron (Fe) catalyst, and also since Al_2O_3 composites are used in some demanding applications like armor [10]. As-obtained cloth (McMaster-Carr) is cut into swatches, soaked in a solution of iron nitrate dissolved in 2-propanol, and subsequently dried by hanging vertically in ambient air. The samples are placed in the quartz tube furnace. After purging the furnace with helium (Airgas), the furnace is heated up to 750 ^{o}C, at which temperature the Fe layer is pre-conditioned with hydrogen (H_2, Airgas, UHP grade), and then CNTs are grown with ethylene (C2H4) gas. The grown CNTs show radial alignment, uniform distribution, and high density as revealed in scanning electron microscopy (SEM, JOEL 5910 and FEI/Philips XL30) images, which fulfill the desired micro-structure in Fig. 1. The grown CNTs are measured to have 7-8 walls with an inner diameter of ~9.7 nm (standard deviation of 1.8 nm) and an outer diameter of ~17.1 nm (standard deviation of 3.3 nm) averaged over 30 CNTs when inspected under transmission electron microscope (TEM, JOEL 2011). With these diameters, the CNT density grown on the fibers is calculated as ~0.8 mg/mm^3, based on 1.4 mg/mm^3 density of 1-nm-diameter SWCNT [11], and an assumed wall thickness of 0.34 nm (interlayer spacing of graphite). Each cloth sample is weighed with a microbalance (Sartorius) after catalyst coating and after CNT growth. The catalyst mass change during the CNT growth is not considered. Since decomposition of organic elements in the catalyst layer is likely, the estimated CNT mass yield is a conservative value.

After CNT growth, Al_2O_3 cloth layers with CNTs are embedded in epoxy to fabricate the nano-engineered composites based on the traditional lay-up method of dry fibers. First, epoxy (West Systems) is poured into cork dams (I G. Marston) on a guaranteed non-porous teflon (GNPT) covered vacuum table. Cloth plies with CNTs are placed in the pool of epoxy. Enough time is allowed for the epoxy to wet the fibers and CNTs, facilitated by the strong capillary forces generated by the aligned CNTs small spacing [12, 13]. When wetting on the top cloth surface is observed, extra epoxy is poured, and a new cloth was applied on the top. This process is repeated until all the plies are assembled. After introducing cure materials, samples are sealed in with a vacuum bag and cured under vacuum (~88 kPa below the atmospheric pressure) at ~60 °C to draw out voids and enhance the curing process. Cured composites are trimmed using a carbide-grit blade on a water-assisted cutting wheel.

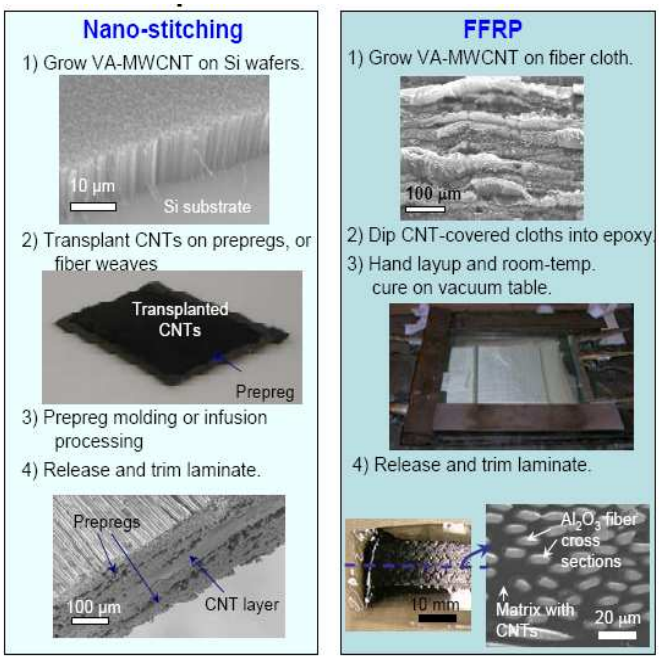

Figure 2: Fabrication and characterization of two nano-engineering architectures

2.4 Nano-stitched Composite Fabrication

The following section describes two different methods of fabricating the nano-stitched composite architecture based on standard prepreg and infusion manufacturing techniques for advanced composites.

2.4.1. Prepreg Method

Chemical Vapor Deposition (CVD) on the nano-stitched composites employs the same catalyst (Fe), reduction gas (H_2), and carbon source gas (C_2H_4) as FFRP

fabrication [8, 9]. The main differences, however, are the substrate, catalyst deposition method, and the growth method. Silicon substrates are e-beam deposited first with 10 nm Al_2O_3 layer as a diffusion barrier, and then with 1 nm Fe catalyst layer on top. These wafers are cut into pieces and are placed inside the quartz tube furnace mentioned above. In this growth method, the H_2 gas is introduced from the start of temperature ramp. The average CNTs diameter produced is ~8 nm, with an aligned-CNT volume fraction of 1%.

The CNT forests are transplanted onto the surface of a prepreg ply with the following method. First, unidirectional prepreg (Cytec IM7/977-3 or Hexcel AS4/8552) is cut and placed on a metal cylinder with the tacky prepreg surface exposed. Then, with pressure, the cylinder is rolled over a CNT-forest-covered Si wafer. As the prepreg contacts the forest, CNTs adhere to the ply, and are removed from the Si wafers. SEM has confirmed that the CNT alignment is maintained during the transplantation process. All of the layers above and below the CNT forest are laid up and cured following the recommended standard method of the material supplier. In our case, the curing cycle is the following: 1 atm of vacuum, 7 atm of total pressure, heating ramp of 2.8 ^oC/min until 180 ^oC, hold for 2.5 h, cooled to 60 ^oC at 2.8 ^oC/min, and then left until room temperature.

2.4.2. Infusion Method

The CNTs for this application are grown following the same method as the prepreg method described above. The length of the CNT forests is ~100 μm, similar to the ply spacing between the woven carbon cloths. After growth, CNT forests are extracted from the substrate using a razor blade. The laminates are prepared with the delaminated CNT forests sandwiched by carbon fiber (CF) woven cloth (Tenax-J G40-800 24K EP03) layers. A stainless steel plate is used as a mold. Teflon mesh flow media sheets are placed on the top and the bottom of the assembled laminates. The entire assembly is enclosed in a vacuum bag and connected to a vacuum pump on one side, with a opening on the opposite side for resin (Hexcel RTM6) introduction. After moving the setup in a heating chamber, RTM6 is heated up to 90 ^oC to achieve a viscosity appropriate for infusion processing. The curing cycle is the following: hold at 160 ^oC for 1h and hold at 180 ^oC for 2h.

3 RESULTS

In the following section, we review the composite quality and laminate-level property enhancement as observed by standard testing.

3.1 FFRP Composites

The fabricated FFRP composites are inspected under an optical microscope (Axiotech) for micron-scale void fraction and scanning electron microscope (SEM, JOEL 5910) for epoxy wetting of CNTs. Wetting of fibers and CNTs is overall successful, with void fractions estimated at <1% for both baseline (no CNTs) and FFRP laminates. TEM imaging of the composite cross sections is in progress to inspect micro-structure morphology of CNTs (alignment, bonding to the fibers) inside the hybrid composite.

Ignoring void fractions, Al_2O_3 weight fraction is evaluated from the conservative measured CNT weight, the measured composite weight, and Al_2O_3 cloth area density. With a composite thickness set by the cork dam height, the Al_2O_3 weight fraction is estimated as ~60%, while the CNT weight fraction varied from ~0.05 to 5 % depending on the growth time. Epoxy weight fraction also varied accordingly.

These hybrid woven composites reinforced by aligned CNTs have been measured for property enhancement. The shear strength was measured by three point bending with short span following the ASTM standard D 2344-00, and ~31% improvement in interlaminar shear strength was observed with ~1 wt% of CNT fraction [7]. The samples were also tested for electrical conductivities with four probes, and the side planes of the samples were coated with silver paint (Structures Probe Inc.). DC electrical conductivity showed $x10^6$-10^8 increase with ~0.5-3 wt% CNT fraction [7]. AC impedance was also acquired by applying an AC test signal with 10 mV over the frequency range of 10 Hz–40 MHz [14]. While the baseline composites without CNTs, consisting of dielectric epoxy/alumina sandwiched by conductive silver plates, exhibited resistive and capacitive behavior, the nano-engineered composites with ~2-7 wt% CNT fraction showed behavior dominated by a small resistance. Thermal property measurements are in progress with the laser-flash method.

3.2 Nano-stitched Composites

3.2.1. Prepreg

Fabricated prepreg samples reinforced with CNTs were tested for Mode I and II interlaminar fracture toughness with an Instron 1332 testing machine, following ASTM standard 471 and the 4ENF method, respectively [7]. Two kinds of specimens were produced of standard size following the manufacturing procedure described above: 24 layer carbon fiber (CF) epoxy prepreg, and 24 layer CF/epoxy/CNT prepreg, with a layer of CNTs at the mid-plane.

The fracture surface was inspected by SEM (JOEL). CNTs have been observed on both sides of the crack, indicating a bridging-type toughening of the interface due to the aligned-CNT nanostitches in the z-direction. Surface or functionalization treatments could improve toughness of the CNTs due to bridging/pullout.

3.2.2. Infusion

Samples were fabricated by sandwiching a 1cm x 3cm forest of CNTs between 5 layers of carbon fiber cloth on top and bottom, producing a 10 CF layers plus 1 CNT/epoxy layer composite. This infusion process was a demonstration of the technique only to this point in time. Although the CNTs are oriented transversely to the resin flow, they remain aligned as evidenced in SEM imaging. No significant differences are observed in the position of the CNT forests. The low viscosity of the resin and the capillary effects of the CNTs resulted in wetting of the forests. No air voids were been observed in the nanostitched center CNT/epoxy layer.

4 CONCLUSIONS

Two nano-engineered composite architectures reinforced with carbon nanotubes have been designed to enhance the multi-functional properties of aerospace structural composites. These two composites were successfully fabricated to achieve the designed nano/micro-structure in laminates suitable for standard mechanical and other testing. Electrical and fracture properties have been tested to demonstrate improved performance with the inclusion of vertically aligned carbon nanotubes. Future work on these architectures will include further optimization of the fabrication processes and a more complete (and expanded, e.g., in-plane laminate strength) characterization of the enhanced multi-functional properties.

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