# VACUUM ASSISTED INFUSION OF HYBRID ALIGNED CARBON NANOTUBE-FIBER COMPOSITES FOR MECHANICAL REINFORCEMENT

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**The effect of aligned carbon nanotube (CNT) content on the manufacturing of fiber-reinforced plastic (FRP) laminates is determined in this paper. Aligned carbon nanotubes (CNTs) are introduced on advanced fiber weaves through *in situ* chemical vapor deposition growth, allowing three-dimensional reinforcement. Extending radially off the fiber surfaces both inside and outside the tow in a fuzzy fiber (FF) architecture, the aligned CNTs are positioned across the interlaminar and intralaminar matrix regions to provide mechanical reinforcement. The impact of length of the aligned CNTs on the manufacturability of fuzzy fiber reinforced plastics (FFRP) is explored through a modified vacuum assisted resin infusion setup. Quantification of laminate permeability revealed less than a 10x decrease in permeability of laminates with the longest CNTs, even though the surface area increased over 20x. Results indicate that infusion processing of large FFRP laminates with an unmodified aerospace-grade resin can be accomplished with standard infusion setups.**

**Keywords**: *carbon nanotubes, hybrid composite, infusion, permeability, fracture toughness*

## 1 Introduction

Fiber reinforced plastics (FRPs) are widely used in aerospace and other demanding applications because of their outstanding mass-specific properties. While in-plane strength and stiffness can allow structural weight savings over traditional aluminum parts, performance is oftentimes limited by the interlaminar region perpendicular to the planar direction of the fibers. The properties in this region are matrix dominated and weak in both strength and toughness, leading to failure modes including delamination. To address weaknesses in the interlaminar region, several approaches have been developed to reinforce the through-thickness direction of the laminate, including Z-pinning, stitching, and 3-D weaving [1]. While effective at improving interlaminar properties, these approaches can result in a significant reduction in in-plane properties of the laminate. The insertion of the hundreds of micron diameter through-thickness direction reinforcements damages the micron diameter in-plane fibers and additionally causes loss of fiber volume fraction in the in-plane directions.

However, CNTs can provide nano-scale reinforcement in the interlaminar region with no drop in in-plane properties. Many approaches to incorporate CNTs at ply interfaces in composite laminates have been explored, including depositing CNTs on surfaces of advanced fibers or mixing CNTs in polymer matrices before infiltration [2-4]. The potential for mechanical property enhancement has yet to be fully harnessed as difficulties in implementation such as control over orientation and large increases in matrix viscosity limit improvements at the laminate level. These challenges can be overcome by the implementation of a fuzzy fiber reinforced plastic (FFRP) architecture [4].

Radially aligned CNTs are grown *in situ* on alumina ceramic fibers (hereafter called ‘fuzzy fibers’) creating a hierarchical architecture of micro- and nano-scale fibers [5-7] as shown in Figure 1. This alumina fiber FFRP system is a model architecture for studying laminate-level property enhancement due to aligned CNTs, because the alumina fibers have been shown to be unaffected by CNT growth [8]. While the aligned CNT morphology on ‘fuzzy fibers have proven to strengthen interlaminar properties and assist forest wetting by capillarity [9], questions still exist about the effect of the CNTs on manufacturability due to the added surface area of the aligned CNTs. This paper studies the impact of the CNT length on laminate permeability and describes the vacuum assisted infusion process developed to manufacture large, uniform FFRP laminates.

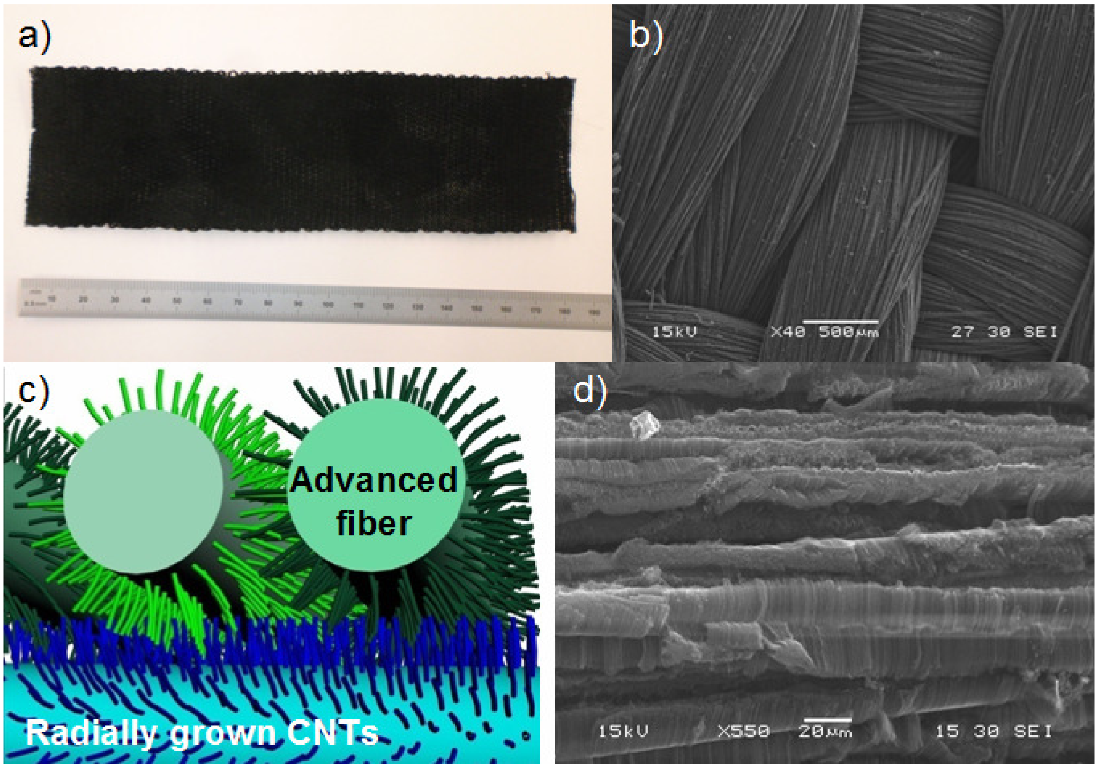

**Figure 1. Aligned CNTs on the surface of fibers in a woven alumina cloth ‘fuzzy fiber’ ply. a) Optical image of FF ply, b) SEM image of fuzzy tows, c) Artistic rendition of FF architecture [9], and d) Mohawk morphology [7] of radially aligned CNTs.**

## 2 Experimental

In situ growth of aligned CNTs on fibers to form fuzzy fiber (FF) cloth is described, followed by the procedures for infusion-processing of the FF cloth into FFRP.

### 2.1 Fuzzy Ply Preparation

The growth of aligned CNTs is accomplished by chemical vapor deposition on 2”x6” plies of alumina ceramic cloth (Cotronics) [7,10], which serves as a useful model fiber system for investigating laminate-level properties as it tolerates the CNT growth process well and retains its tensile properties [8]. The cloth is dipped in a 50 mM solution of iron nitrate in isopropanol, distributing catalyst to all fiber surfaces including inside the tow. Once the cloth has been dried overnight, it is placed in a 2” (5 cm) diameter quartz tube furnace and treated with a hydrogen conditioning process while the temperature is ramped to 650$^{o}$C followed by CNT growth under ethylene. The CNTs area aligned radially outward from the fiber surface in a ‘mohawk’ morphology [7] (see Figure 1), with average lengths of 6, 19, and 26 μm for growth times of 1, 3, and 5 minutes, respectively. BET nitrogen adsorption on similar samples was used to measure the surface area of both baseline (without CNTs) and 5 minute-growth plies indicating a 20x increase of surface area [6]. This result was compared to an approximate calculation of surface area increase using the weight gain of the cloth after CVD and the average CNT diameter and density which yielded an 80x increase of surface area.

### 2.2 Infusion Processing

FFRP and baseline specimens are manufactured by vacuum assisted resin infusion (VARI) using unmodified RTM6 epoxy (Hexcel) [10], an advanced engineering epoxy designed with low viscosity and long working times for resin transfer molding. Similar to a typical industrial infusion process, vacuum distribution mesh sheets and spiral tubes are used to draw epoxy along the laminate stack in the thickness direction, as shown in Figure 2a. The laminate is layered with porous Teflon peel ply and distribution mesh sheets and is sandwiched by steel plates to ensure a flat surface. The 50.8 mm (2 inch) wide top plate is the same width as the laminate allowing the vacuum bag to conform to the top plate and the edges of the laminate, minimizing epoxy flow ‘racetracking’ around the laminate edges that could lead to reduced specimen quality. Fiberglass laminate spacers assist in keeping the plates parallel. Once the laminate and plates are wrapped in vacuum bagging, the infusion setup is placed under vacuum and heated to 150°C (300°F) for two hours. Then the temperature is reduced to 90°C, at which the RTM6 epoxy is melted and degassed to remove trapped air and slowly drawn into the laminate. The inlet and outlet of the infusion table is then closed off and cured at 180°C, according to the manufacturer's recommendations.

Exploratory permeability tests have been performed in order to determine the feasibility of infusion on a large scale. A similar setup to the typical infusion described above is employed but the mesh sheets are removed to isolate the FFRP permeability (see Figure 2b) in the plane of the laminate (perpendicular to the typical flow of resin in VARI). The steel plate is replaced by a glass plate to allow visual tracking of the epoxy flow front. Each laminate consisted of six plies that were clamped between the steel and glass plates in an attempt to maintain a consistent channel volume. For each of the permeability tests, a constant pressure differential was maintained between the inlet and outlet tubes. The flow front position was recorded over time such that the in-plane permeability of each laminate could be calculated via Darcy's law.

$$\frac{dx}{dt} = \frac{K}{\eta \cdot \left(1 - v_f\right)} \cdot \left(\frac{dP}{dx}\right) \qquad (1)$$

## 3 Results and Discussion

Darcy's law describes the flow of a Newtonian fluid through porous media and was later expanded to other fluids and complex geometries by Kozeny and Ergun, among others [11,12]. One form of Darcy's law is represented in Equation 1 where x = distance traveled (see Figure 1b), t = time, K = permeability, $\eta$ = dynamic viscosity, $v_f$ = volume fraction of dry fibers, and P = pressure. In Darcy's law, the flow rate of the epoxy is quantified as dx/dt and is inversely proportional to the porosity of the fiber mat, where porosity is $(1-v_f)$ in baseline laminates. In all of these permeability tests, the porosity and the total fiber volume fraction (fiber + nanofiber) are held approximately constant.

For each sample including the baselines, as the infusion progressed, the velocity of the flow front slowed as more epoxy needed to be pulled through more of the laminate. This was expected and follows Darcy's law, where the velocity of the flow front is directly proportional to the gradient of the pressure (dP/dx) across the sample. The permeability (K) change represents the effect on the flow from the addition of CNTs, namely the change in fiber preform geometry with the addition of nanoscale fibers. Similar relations like the Kozeny-Carman equation present theoretical means of estimating permeability, which establish that permeability scales with fiber surface area. With a known pressure gradient, the results from flow front velocity measurements shown in Figure 3a allow calculation of the in-plane permeability, shown in Figure 3b, for these initial tests. As the CNT volume fraction and surface area increased, infusion rates slowed and permeability reduced. The permeability changes by less than a factor of 10 between the baseline and 5 min laminates, even though the surface area calculated by the BET adsorption and geometry estimates between a 20x to 80x increase in surface area.

Accurate permeability testing relies on the fluid flow being throttled by the laminate, allowing the

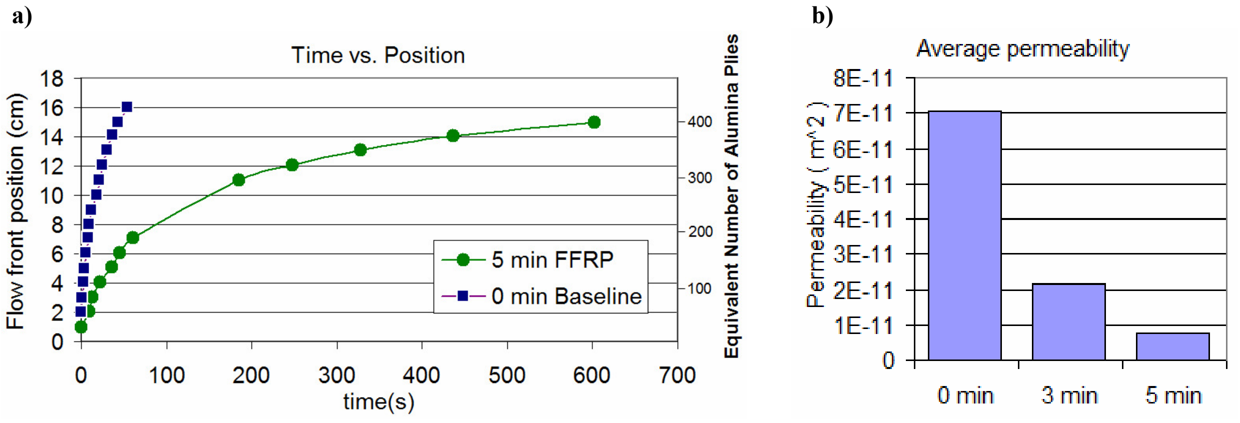

**Figure 3. Preliminary permeability results. a) Exemplary flow front position tracking over time for sample tests, and b) Average permeability calculated for increasing CNT lengths (as controlled by increasing CVD growth time).**

velocity of the fluid to be determined only by the resistance of the laminate. If the epoxy flows too quickly during an infusion however, voids are trapped at the flow front as the locally inhomogeneous woven cloth leads to local flow velocity variation. Once the flow progresses into the laminate and the velocity slows down, these voids are eventually filled in or carried out with the epoxy. For this reason, in the normal infusion process, the flow of epoxy must be throttled by a valve or other means to slow the flow front velocity for quality sample production. In these permeability tests, quality samples were achieved only by flowing excess epoxy to wash voids out of the laminates.

MicroCT scans and optical images taken of similar laminates reveal no evidence of internal voids, indicating that epoxy wet all of the CNT forests. More investigation must be done to quantify the assistance of capillary action between the aligned CNTs for wicking the epoxy into the forests [13,14]. The permeability explored here is properly the in-plane permeability, giving us an indirect idea of the effect of CNTs on the transverse flow that is experienced in the laminate during standard infusion processes. Since the standard process has a mesh sheet that is used to quickly transport epoxy along the laminate surface, these permeability results can approximately reveal maximum laminate thicknesses for each CNT loading that allows epoxy to permeate into the middle of the sample before the surface flow front reaches the resin outlet. Based on the results in Figure 3, 10 cm (4") thick laminates can be feasibly processed, a thickness that is far greater than most laminates used in aerospace and other applications.

Understanding the effect of CNTs on fuzzy fiber permeability allows the design of infusion systems for new polymer matrices. For example, the viscosity of some recyclable reactive thermoplastics is approximately 4 times lower than the RTM6 epoxy used in this work. With fuzzy fiber plies of the same permeability as above, infusion can be performed 4x as fast. This is critical for large part manufacturing of thermoplastic parts made by reactive processing with limited time (on the order of 15 minutes) before the precursors have polymerized into more a viscous state [15].

The standard infusion process (with mesh sheets to assist resin flow) was implemented to manufacture laminates for mechanical property assessment (pictured in Figure 4). As improvement of interlaminar properties is the goal, fracture toughness will be assessed by determining the strain energy release rate, G, and the critical stress intensity, $K_c$.

## 4 Conclusions

In conclusion, the manufacturability of FFRP laminates was investigated by studying the effect of CNT length on laminate permeability. The permeability test setup here includes no mesh sheet to transport epoxy along the laminate surface in order to isolate the 1-D (in-plane) permeability. In the future, as thicker laminates are made, the permeability of the laminate will become more critical for manufacturing quality. Isolating permeability through long specimens can reveal maximum laminate thicknesses for each CNT loading that allows epoxy to permeate into the middle of the sample before the surface flow front reaches the resin outlet. Mechanical testing of laminates is planned to determine the length of CNTs needed to most effectively improve mechanical and other laminate properties. With successful implementation of a pervasive network of

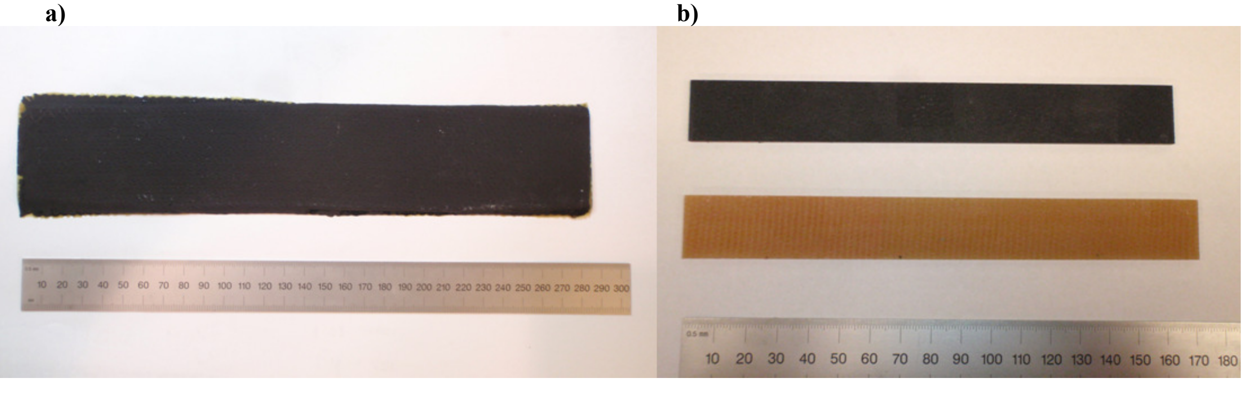

**Figure 4. FFRP laminates a) Large area manufacturing of 28 cm x 5 cm (11" x 2") laminates, and b) Double cantilevered beam laminates for Mode I fracture toughness assessment.**

CNTs for mechanical reinforcement, multifunctional capabilities can be enabled, such as structural health monitoring (SHM) and non-destructive evaluation that take advantage of the conductivity of CNTs to improve damage detection [16-18].

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