

# Long Carbon Nanotubes Grown on the Surface of Fibers for Hybrid Composites

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Hybrid composite architectures employing traditional advanced composites and carbon nanotubes offer significant potential mechanical and multifunctional performance benefits. The architecture investigated here is composed of aligned fibers with carbon nanotubes grown radially on their surface. A novel process for rapidly growing dense, long, high-quality, aligned carbon-nanotube forests is employed. Two fundamental issues related to realizing hybrid composite architectures are investigated experimentally: wetting of the carbon nanotubes by thermoset polymers and retention of mechanical (stiffness and strength) properties of the fibers after the carbon-nanotube growth process. Wetting of carbon-nanotube forests by two commercial polymers (including a highly viscous epoxy) is demonstrated at rates conducive to creating a fully dispersed carbon-nanotube/matrix region around the fibers in a typical composite. Single-fiber tension tests indicate no mechanical degradation for alumina fibers undergoing the carbon-nanotube growth process. Results indicate that hybrid carbon-nanotube/composite architectures are feasible, and future work focuses on mechanical and multifunctional property characterization of other hybrid architectures and scaling to a continuous carbon-nanotube growth process.

## I. Introduction

CARBON nanotubes (CNTs) have been the focus of considerable research since Iijima [1] confirmed their structure in 1991. In addition to the exceptional electronic and thermal properties associated with CNTs, they have also been reported to possess exceptional mechanical properties: for example, an extensional modulus of approximately 1 TPa and fracture strength of approximately 130 GPa for multiwalled CNTs (MWCNTs) [2]. Exploiting such electrothermomechanical properties toward the development of macroscopic structural materials has been the subject of considerable research.

The most direct structural application for CNTs is as reinforcement for traditional composite materials, and most of the work in this direction has focused on dispersing and aligning CNTs (both single- and multiwalled CNTs) in polymeric matrices to reinforce the matrix. The four main processing factors that influence the mechanical properties of the final composite are dispersion and alignment of the CNTs within the matrix, adhesion between the CNTs and matrix, and the CNT length. All have been formidable challenges to the realization of aligned-CNT composites. Dispersion is important because CNTs tend to agglomerate when dispersed in a polymeric resin. These aggregates are not well adhered to the polymer and can also act as stress concentrators, reducing the final performance of the composite [3]. Alignment of the CNTs is needed to increase the effectiveness of the reinforcement; for example, a molecular dynamics model developed by Odegard et al. [4] showed that Young's modulus of a CNT/polyimide composite can be increased by a factor of 3 when the CNTs are oriented parallel to the direction of

the load. The formation of aggregates reduces the effective area of contact between the nanotubes and the polymer, hence reducing the adhesion between the two materials. CNT aggregates also reduce the aspect ratio of the reinforcement, lowering the reinforcing effect, and can further act as inclusions (dry entangled CNTs with no epoxy binding the aggregate together) that reduce the strength of the reinforced polymer. Aggregates are a further difficulty for single- and double-walled CNTs because such CNTs can be held tightly in hexagonally packed bundles/ropes. The two most commonly used methods to embed CNTs into a polymer matrix, sonication [5] and calendaring [6], do not completely prevent the formation of aggregates and usually damage the CNTs. Using these methods, moderate improvements in matrix mechanical properties are typically observed due to the low CNT volume fractions and generally poor dispersion and alignment. Beyond a certain volume fraction (usually around 3%), no further improvements in the composite mechanical properties are achieved using the methods previously mentioned. At higher volume fractions with these methods, dispersion and alignment deteriorate significantly. Good dispersion, alignment, and adhesion are completely necessary to take full advantage of the mechanical properties of the CNTs.

Others have used chemical vapor deposition (CVD) processes to grow densely packed carpets, or forests, of well-aligned carbon nanotubes, which can be wet by polymer solutions [7] to create aligned-CNT composite films. This avoids most of the problems associated with mixing CNTs and polymers. One process used to impregnate the CNTs relies on dissolving the polymer using a low-viscosity solvent. Although this process is perfectly valid for microfabrication, it is not considered to be feasible for large-scale applications, which necessitate large substrate areas and rapid processing. CNT/polymer composites that have been developed so far can improve the mechanical properties of the matrix and open a whole range of multifunctional applications for nanocomposite thin films. However, in terms of structural applications, these CNT/polymer composites cannot compete with traditional continuous-fiber composite materials.

The combination of CNTs, polymer matrices, and advanced fibers to create so-called hybrid composites is seen as a practical approach to deriving structural/multifunctional benefits from CNTs. Perhaps the most promising results to date are related to the improvement in the fiber/matrix interface by growing CNTs on the surface of the fibers. Several studies have shown that growing carbon nanotubes on the surfaces of fibers by CVD methods [8] significantly increases the surface area over which to transfer load (e.g., from 1.77 to 17.2 m<sup>2</sup>/g

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after growing 500-nm-long CNTs on the surface of the fibers [9]), yielding an increase in interfacial shear strength (15% measured improvement with the CNTs previously mentioned [9]). Other mechanisms for the increase in strength might be mechanical interlocking of the CNTs with the polymer and/or the neighboring fibers and a reduction in stress gradients in which the CNTs may be seen as an interlayer of intermediate modulus between the stiff advanced fiber and the compliant matrix. Although mechanistically interesting, the CNT lengths obtained to date vary from 200 nm to 1–2  $\mu\text{m}$  [9,10], and due to the limited length of the CNTs, the reinforcement of the matrix is limited only to the vicinity of the fiber.

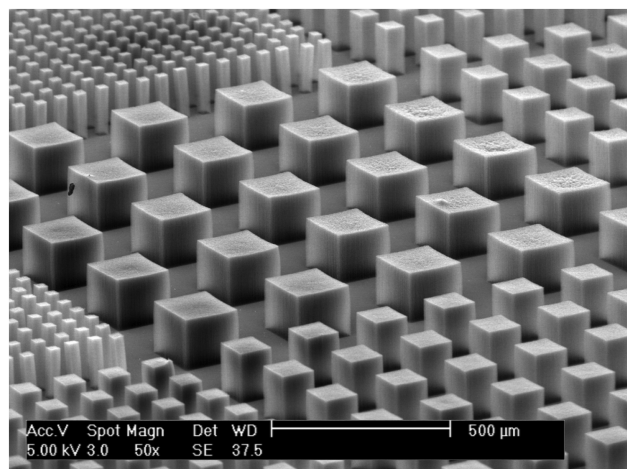
The purpose of this work is to explore the feasibility and scalability of different architectures of hybrid CNT/traditional composites using aligned long MWCNTs grown on fiber surfaces on which the CNT length is on the order of the fiber diameter or greater. Although the process used in this work allows the fast growth of 1-mm-long aligned CNTs, CNT lengths were limited to 30  $\mu\text{m}$ . This value is an order of magnitude longer than previous studies and is approximately the maximum envisioned length for CNT growth on fibers for matrix reinforcement; interlaminar layers and distance between fiber tows are typically on the order of 10–20  $\mu\text{m}$  for existing advanced composites, including the woven alumina cloth 11- $\mu\text{m}$ -diam fibers at 65% volume fraction. Thus, the 30- $\mu\text{m}$  CNTs are the maximum length envisioned for the hybrid composite architectures, consistent with the final goal of creating macroscale hybrid composite architectures. Using the maximum envisioned CNT length is thought to maximize the difficulty of wetting and to also impact the fiber properties after CNT growth. From the different possible architectures under development, the focus of the work herein is the growth of long aligned CNTs on fibers on which the CNT-coated fibers are then impregnated by a polymer to create hybrid composites.

## II. Approach

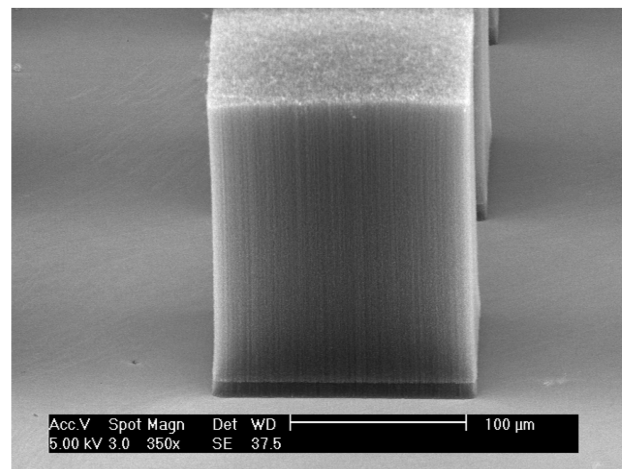
Effective use of CNTs in a composite material demands well-aligned CNTs that are also well dispersed in the matrix. The growth of the CNTs on the surface of the fiber allows a dense, controlled distribution of the CNTs in the matrix. The thermal CVD method used in this work [11] yields considerably longer CNTs than the studies mentioned in the Introduction. Because of this capability, the reinforcement of the matrix is not limited to the vicinity of the fiber/matrix interface. The CNT lengths are greater than the fiber diameters and long enough to fully populate the matrix region between fibers and across ply interfaces in a typical aligned-fiber advanced composite ply. CNT weight fractions (approximately the volume fraction) obtained in this study (approximately 5%) for CNTs in a matrix are higher than those obtained embedding CNTs into a polymer matrix using sonication or other methods of dispersion. No additional dispersion step is needed when the CNTs are grown directly on the fiber surface. An effective reinforcement of the entire matrix is envisioned using this method, provided that the wetting of the fibers and the CNTs with a polymer is possible.

Two important aspects of CNT hybrid composites that have not been addressed by prior work are the wetting of the carbon nanotubes with off-the-shelf polymers (typical of those used in advanced composites) and the possible degradation of the mechanical properties of the fibers subjected to the process for growing CNTs, a process that requires high temperatures and the fiber being exposed to chemicals. CNTs grown in this work form a dense and aligned forest on the fiber. Because of the density of the forest, wetting by the matrix is a concern. Results on the wetting of CNTs using two different polymer matrices at room temperature are presented: wetting of well-aligned dense pillars of CNTs by a viscous room-temperature 20-min-curing conductive epoxy resin, as well as an epoxy solution with lower viscosity (SU-8). These polymers were chosen for their viscosities at room temperature relative to the viscosity of aerospace-grade thermosets at their processing temperature: SU-8 is equivalent in viscosity, whereas the conductive epoxy is highly viscous (approximately 1000 times greater than the relevant aerospace epoxies) and is considered an extreme test of

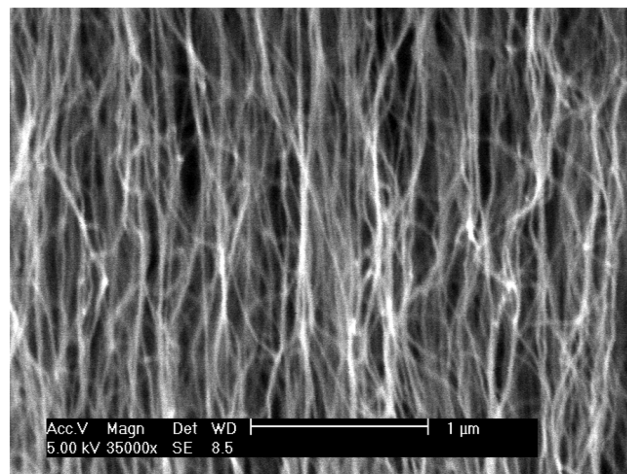
wetting. In the specific CNT growth process used in this work, the catalyst is known to diffuse into the alumina substrate (here, the fiber), likely causing a change in surface characteristics that may lead to embrittlement of the fibers and therefore property degradation. Long (30- $\mu\text{m}$ ) MWCNTs were grown on commercially available alumina fibers to study the effect on fiber properties. The basic mechanical properties (elastic modulus and strength) of the fibers in



a)



b)



c)

**Fig. 1** SEMs of a) CNT pillars grown on a patterned catalyst on silicon substrate (scale bar is 100  $\mu\text{m}$ ), b) a single pillar, and c) alignment of the CNTs.



each step of the process were determined by single-fiber tensile tests and compared to assess degradation due to the CNT growth process.

### III. Experimental Methods

The experimental work for this study can be divided into three categories: Growth of carbon nanotubes on silicon wafers and fibers, tests on the effective wetting of CNTs by epoxy resins, and mechanical testing of fibers in each step of the process to assess any degradation of properties.

#### A. Growth of CNTs on Silicon Wafers and Fibers

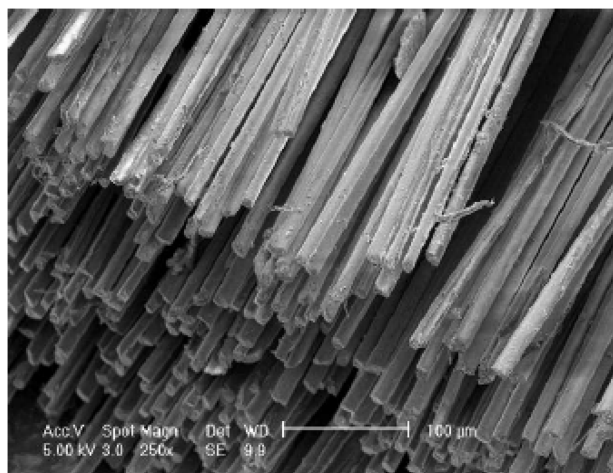
CNTs are grown in two different configurations: dense pillars of long CNTs (up to 1 mm) grown on silicon wafers to test the effective wetting of two epoxy resins with different viscosities and forests of CNTs (approximately 30  $\mu\text{m}$  long) grown on the surface of alumina fibers.

CNT pillars are patterned CNT forests grown on silicon substrates [12] such as those shown in Figs. 1a and 1b. Catalyst patterns are fabricated by liftoff of a 1- $\mu\text{m}$  layer of image-reversal photoresist (AZ-5214E); the photoresist is patterned by photolithography, catalyst is deposited over the entire wafer surface, and then the areas of catalyst on photoresist are removed by soaking in acetone for 5 min, with mild sonication. The catalyst film of 1.2/20-nm Fe/Al<sub>2</sub>O<sub>3</sub> is deposited by electron-beam evaporation in a single pump-down cycle using a Temescal VES-2550 with a FDC-8000

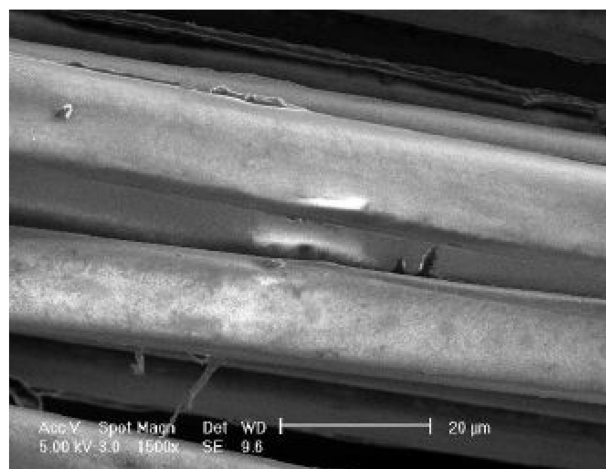
film deposition controller. The film thickness is measured during deposition using a quartz crystal monitor and later confirmed by Rutherford backscattering spectrometry [13]. The substrates are plain (100) 6-in. silicon wafers (*p*-type, 1–10  $\Omega \cdot \text{cm}$ , Silicon Quest International), which were cleaned using a standard “piranha” (3:1 H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>) solution.

CNT growth is performed in a single-zone atmospheric pressure quartz tube furnace (Lindberg) with an inside diameter of 22 mm and a 30-cm-long heating zone, using flows of Ar (99.999%, Airgas), C<sub>2</sub>H<sub>4</sub> (99.5%, Airgas), and H<sub>2</sub> (99.999%, BOC). The furnace temperature is ramped to the setpoint temperature (750°C) in 30 min and held for an additional 15 min under 400 sccm of Ar. The flows of Ar and H<sub>2</sub> used during growth are typically established 1 min before introducing C<sub>2</sub>H<sub>4</sub>, then the C<sub>2</sub>H<sub>4</sub>/H<sub>2</sub>/Ar mixture is maintained for the growth period. The typical growth rate of the current system is 60  $\mu\text{m}/\text{min}$ , and the growth time is chosen to give the desired CNT-forest thickness. Finally, the H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub> flows are discontinued, and 400 sccm of Ar is maintained for 10 more minutes to displace the reactant gases from the tube, before being reduced to a trickle while the furnace cools to below 100°C. The multiwalled nanotubes grown using this method have a diameter of approximately 10 nm (two–three concentric CNTs), with spacing between CNTs of around 50 nm [14]. The pillars show a good alignment of the CNTs, as seen in Figs. 1b and 1c.

CNT forests are also grown on alumina fibers cut from a commercially available (McMaster-Carr) aluminum oxide (Al<sub>2</sub>O<sub>3</sub>)

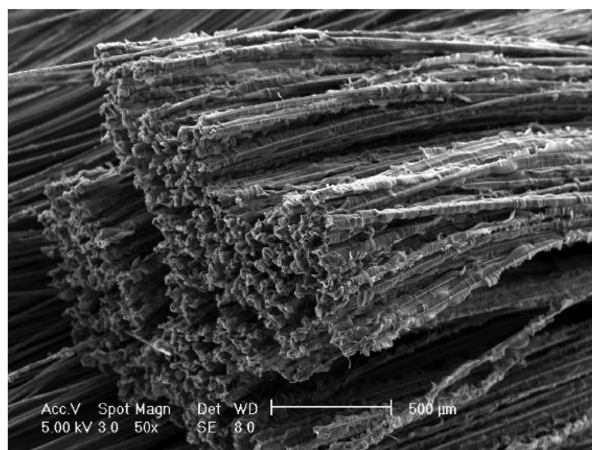


a)

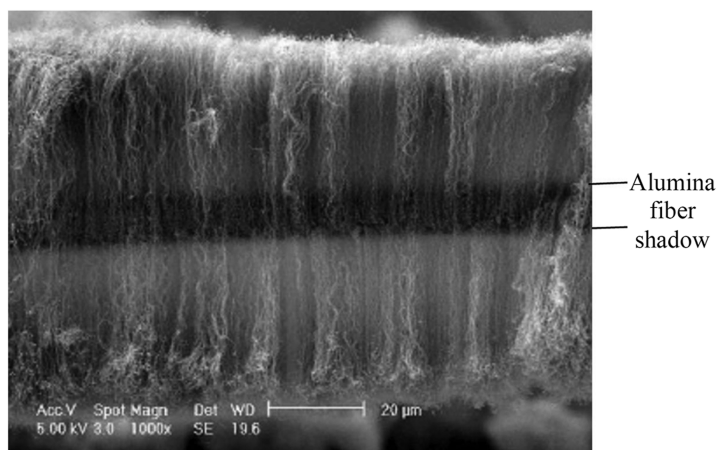


b)

Fig. 2 SEMs of a) pure alumina fibers and b) close-up of pure alumina fibers.

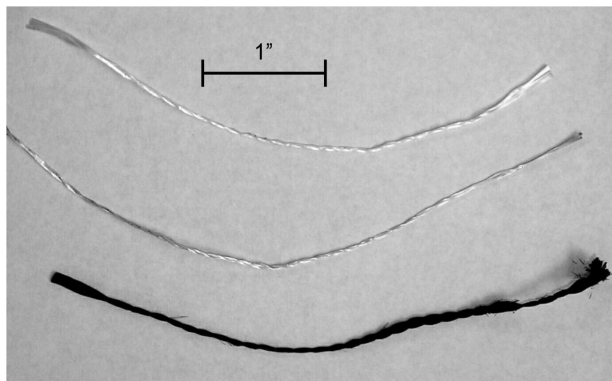


a)



b)

Fig. 3 SEMs of a) alumina fibers with CNTs grown on their surfaces and b) alumina fiber (shadow behind CNTs) with well-aligned 30- $\mu\text{m}$ -long CNTs grown on its surface.



**Fig. 4** Bundles of pure alumina fibers, fibers soaked in a catalyst, and fibers with CNTs grown on their surfaces (top to bottom).

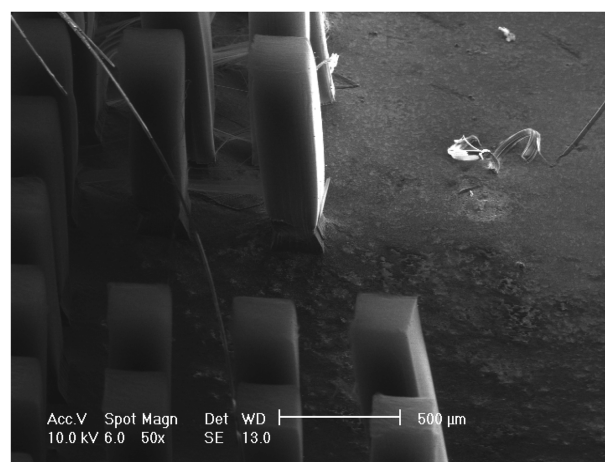
fiber cloth. Each tow in the weave consists of several hundred fibers, each approximately  $11\ \mu\text{m}$  in diameter with a high volume fraction (approximately 65%), as shown in Figs. 2a and 2b. The strands are soaked for 5 min in a 10-mmol solution of  $\text{Fe}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$  dissolved (by stirring and sonication) in isopropanol and allowed to dry in ambient air. The CNT growth process is then the same as that described for the CNT pillars. A strand of alumina fibers after the CNT growth process is shown in Fig. 3a. The typical rate for this process is about  $2\ \mu\text{m}/\text{min}$ , and the final length of the aligned CNTs is around  $30\ \mu\text{m}$ , as seen in Fig. 3b. The CNT long axis is oriented

perpendicularly to the fiber surface. The pictures were taken using an FEI/Philips XL30 field-emission-gun scanning electron microscope. These CNTs are slightly larger at approximately  $15\ \text{nm}$  in diameter and are spaced slightly further apart (at approximately  $130\ \text{nm}$ ) than the CNTs grown on Si.

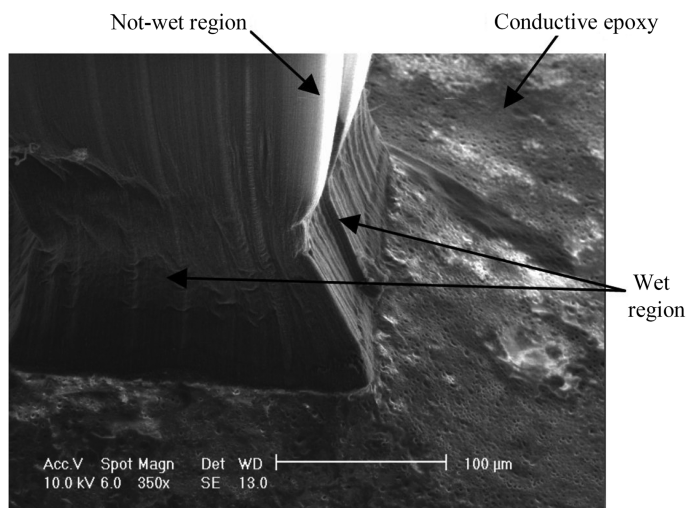
#### B. Wetting of CNTs with Conductive Epoxy and SU-8

The effectiveness of the wetting of the CNT forests was explored for three different sets of CNTs on Si wafers using a high-viscosity conductive epoxy and a low-viscosity UV-curing epoxy. SU-8 is used extensively in microfabrication, and the conductive epoxy has been used to form electrodes on CNT pillars for electrical-property testing [15]. Note that the polymers are unmodified (i.e., no solvents were used) and the CNTs are as grown (i.e., not functionalized or otherwise treated).

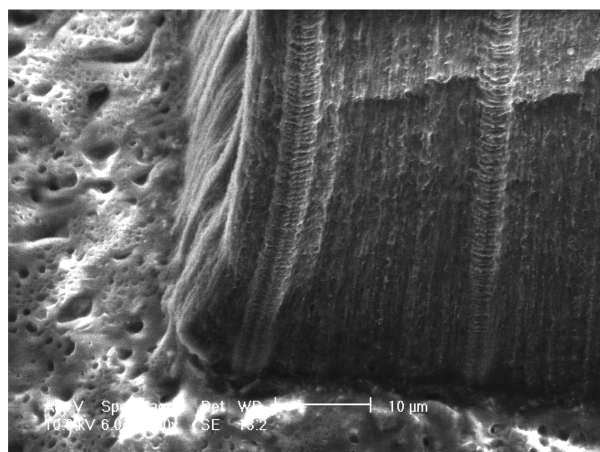
In the first set of tests, a bicomponent, room-temperature, 20-min conductive epoxy (Loctite Hysol 1C, which contains  $1\text{-}\mu\text{m}$  silver particles) was used. This epoxy has high viscosity ( $200,000\text{--}500,000\ \text{cP}$ ) that increases rapidly from the moment it is applied, due to its fast curing path at room temperature. This is considered an extreme wetting test for a polymer, given the high viscosity and the  $1\text{-}\mu\text{m}$  embedded silver particles that are filtered by the CNTs spaced less than  $0.01\ \mu\text{m}$  apart. The bicomponent epoxy was mixed and a thin layer (approximately  $30\ \mu\text{m}$ ) was applied on quartz glass using a razor blade. Square dies ( $15 \times 15\ \text{mm}$ ) containing 1-mm-long,  $200\text{-}\mu\text{m}$ -wide square CNT pillars were put on top of the epoxy layer, and a weight of  $100\ \text{g}$  was placed on top of the assembly. The



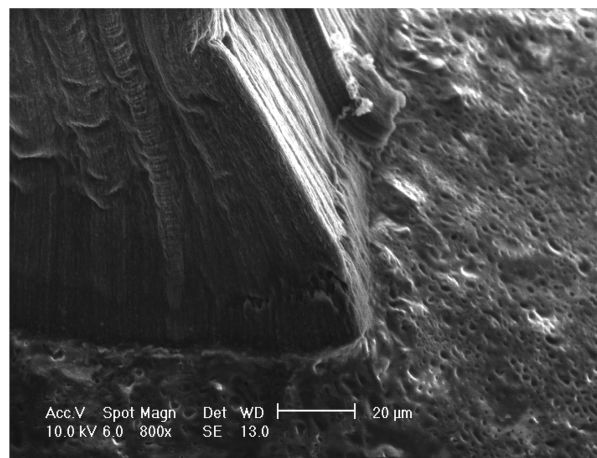
a)



b)



c)



d)

**Fig. 5** SEMs of a) 1-mm-high CNT pillars wet by conductive epoxy, b) close-up of the wet region at the base of the pillar, and c–d) closer views of the wet region at the pillar base.

assembly was cured for 24 h, and the two substrates were separated by mechanical means. The CNT pillars were effectively transplanted from the original wafer to the glass containing the epoxy layer, and wetting was characterized by SEM imaging. For the second set of tests, a thicker layer (approximately  $200\text{ }\mu\text{m}$ ) of the conductive epoxy was applied to quartz glass using the technique previously described. The  $200\text{-}\mu\text{m}$ -wide square CNT pillars for this set of tests were  $200\text{ }\mu\text{m}$  long. As in the first set of tests, the Si die with CNTs was placed on top of the epoxy layer and a  $100\text{-g}$  weight was put on top of the assembly. After 24 h, the two substrates were separated using mechanical means. A disco abrasive system (DAD-2H/6T diesaw) was used to section the substrates. SEM was used to take pictures of the cross sections of the pillars.

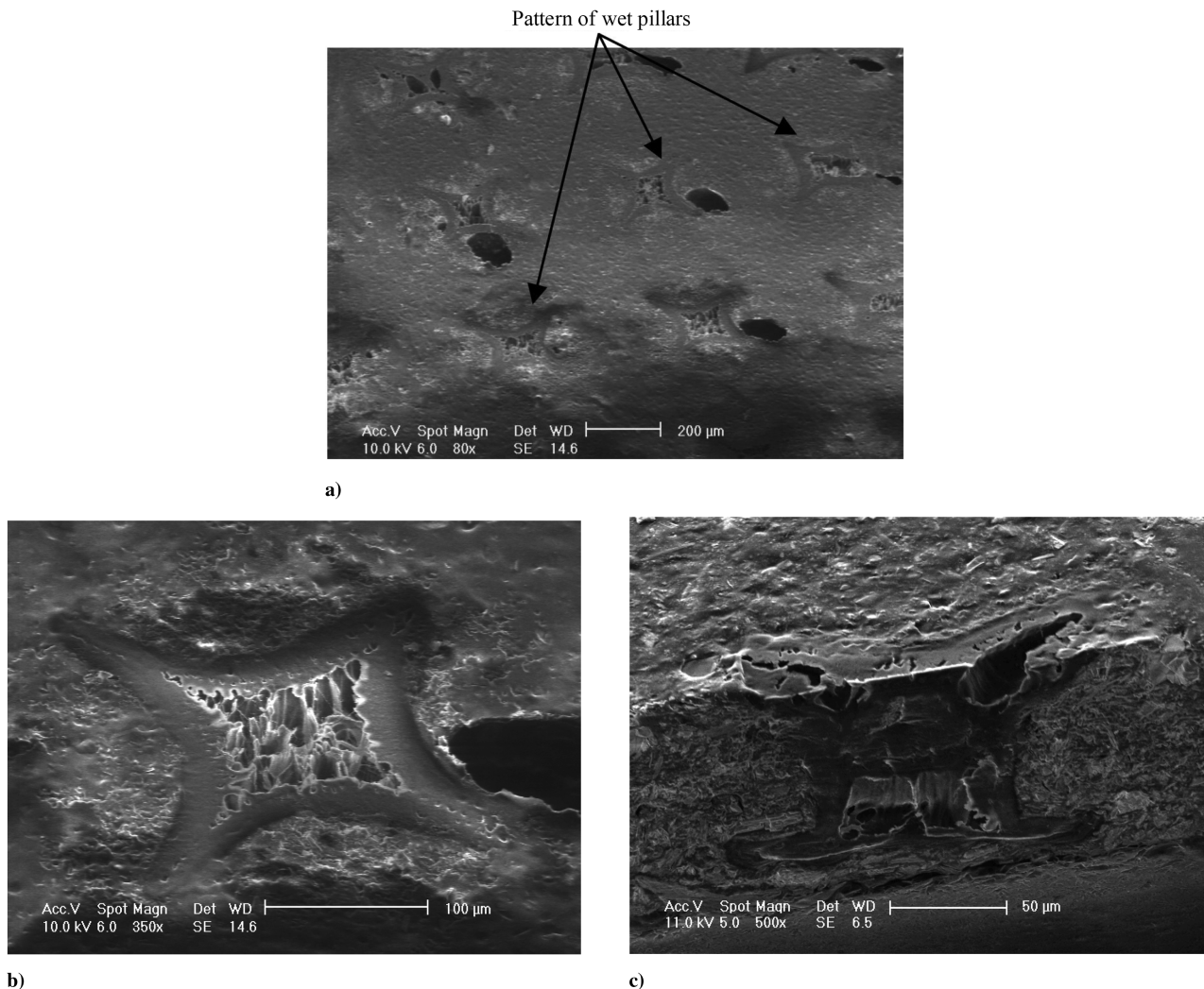
The third set of tests used a low-viscosity UV-curing epoxy solution (Microchem SU-8 2005), typically used in micro-fabrication. Because of its low viscosity, the SU-8 is usually applied by spin-coating. A Headway spinner was used in this experimental work. A  $2\text{-ml}$  drop of SU-8 was put on the wafer containing the  $100\text{-}\mu\text{m}$ -high CNT pattern. A very thin layer ( $5\text{ }\mu\text{m}$ ) of SU-8 was created by setting the spinner at  $3000\text{ rpm}$  for  $45\text{ s}$ . SU-8 was allowed to wet the CNT pillars for  $3\text{ min}$  at room temperature before the assembly was prebaked at  $65^\circ\text{C}$  for  $1\text{ min}$  and at  $95^\circ\text{C}$  for  $3\text{ min}$  using standard hotplates (following the SU-8 standard process). A Karl Suss MJB3 mask aligner was then used to expose the wafer to UV light (wavelength of  $320\text{ nm}$ ) for  $1\text{ min}$  and cure the epoxy resin. The wafer was postbaked at  $65^\circ\text{C}$  for  $1\text{ min}$  and at  $95^\circ\text{C}$  for  $2\text{ min}$  to minimize residual stresses due to the curing process. SEM pictures were taken to assess the wetting for this kind of epoxy. Also in this set

of tests, the CNT patterns were cross-sectioned using diesaw and SEM pictures were taken. Results for all three set of tests are given in Sec. IV.A.

### C. Tensile Tests of Single Fibers

Experiments were performed to compare the mechanical properties of the alumina fibers with and without CNT forests grown on the surface. A standard static tensile test [16] was applied to single fibers at different steps of the process (as-received fibers, fiber soaked in catalyst, and fibers after the CNT growth process) to measure the modulus and strength. These tests served to examine whether the mechanical properties of the fibers are affected by the CVD process used to grow the CNTs. Previous work on the growth of CNTs on fibers does not report results on this important issue.

An Instron 8848 MicroTester with a calibrated  $10\text{-N}$  load cell was used to perform the tensile tests. The microtester can apply and measure static loads ranging from  $5\text{ N}$  to  $2\text{ kN}$ . The resolution is  $1\text{ mN}$  for load and  $1\text{ }\mu\text{m}$  for displacement. Single fibers in this work failed at approximately  $200\text{-mN}$  and  $600\text{-}\mu\text{m}$  displacements. The single fibers were carefully separated from bundles such as those shown in Fig. 4 and mounted with epoxy on cardboard tabs, following the procedures in [16]. Fiber length in the tests was approximately  $50\text{ mm}$ . The tabs were then mounted on the machine and the tensile tests were performed at the recommended displacement rate of  $8\text{ }\mu\text{m/s}$ . Load-displacement graphs were obtained for 10 samples of the pure alumina fiber, 6 of the alumina fiber wet with catalyst, and 10



**Fig. 6** SEMs of wet pillars: a) nanocomposite film made of CNT pillars wet by conductive epoxy, b) close-up of a wet pillar, and c) cross section of a wet pillar.

of the final alumina fibers with CNTs grown on their surface. The load-displacement data were transformed into stress-strain plots to obtain fiber longitudinal modulus and strength. A nominal fiber area of  $95 \mu\text{m}^2$  (diameter of  $11 \mu\text{m}$ ) was used. Fiber strength is inherently associated with flaws in the fibers and is characterized here using the mean  $\bar{x}$  and standard deviation  $S$ . These approximations are employed in the data reported here. Results for these tests are presented in Sec. IV.B.

#### IV. Results and Discussion

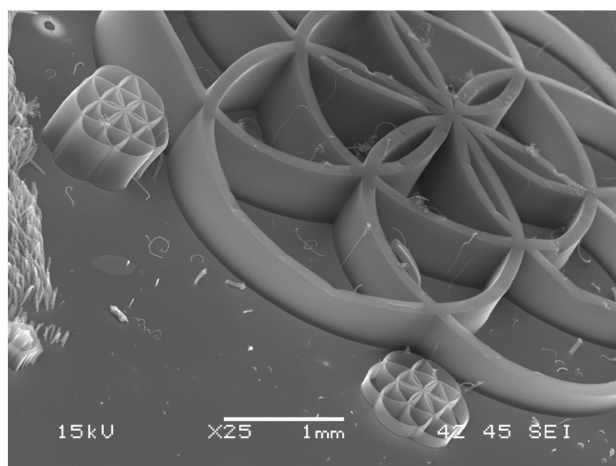
The two main issues addressed in this work are wetting of aligned CNTs using different epoxy resins and the study of the mechanical properties of the fibers throughout the CNT growth process.

##### A. Wetting of CNTs with Epoxy Resins

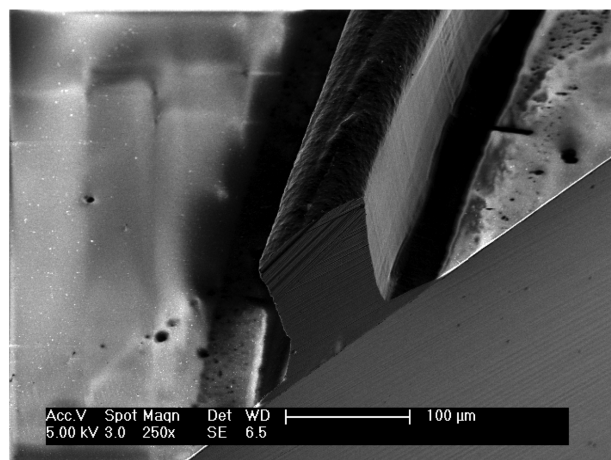
As mentioned in Sec. III.B, three sets of tests explored wetting of the long CNT forests grown on a silicon substrate. The first wetting test used 1-mm-long CNTs with a high-viscosity conductive epoxy resin. As mentioned previously, the epoxy resin cures in 20 min at room temperature, which means that its viscosity increases rapidly until it solidifies. Even with those conditions adverse to wetting, the capillarity effect [16] of the CNTs is strong enough to pull the high-viscosity epoxy resin into the CNT pillars before solidifying. An angled view of the glass substrate (on which the epoxy layer was originally placed) with a pattern of transplanted CNT pillars is shown

in Fig. 5a. The pillars were integrally separated from their original silicon substrate and firmly attached to this glass substrate by adhesion to the epoxy. The epoxy penetrated approximately  $80 \mu\text{m}$  into the pillars, as shown in Fig. 5b, in which contraction due to the capillarity effect can be noted. The contrast change in the SEM images indicates the depth of penetration, in which the darker areas are filled with epoxy. This has been observed in other work in which cross-sectional SEMs were taken that showed the contracted region does correspond to epoxy penetration and further showed that the  $1\text{-}\mu\text{m}$  silver particles in the epoxy are filtered out by the aligned CNTs spaced approximately  $0.01 \mu\text{m}$  apart [17]. The deformation of the pillars at their bases is attributed to the contraction of the epoxy resin during curing (5–6%) and/or contraction due to the capillary forces pulling the epoxy into the porous CNT pillar. A close-up of two of the corners of one pillar is shown in Figs. 5c and 5d. The CNTs show good alignment even after the contraction. The  $1\text{-}\mu\text{m}$  silver particles in the conductive epoxy would restrict the epoxy flow into the pillars, further increasing the difficulty of wetting the CNTs by this viscous epoxy.

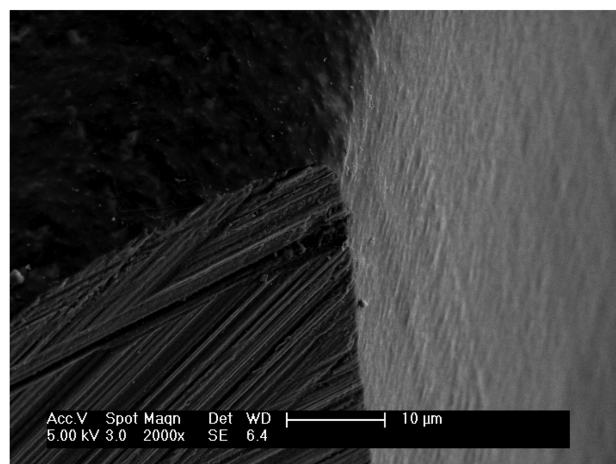
The second wetting test was performed on a pattern of  $200\text{-}\mu\text{m}$ -long CNT pillars (shown in Fig. 1a) using the high-viscosity conductive epoxy used in the previous test. The epoxy layer was as thick as the CNT pillars. When the two substrates were separated by mechanical means, all the pillars were transplanted onto the glass substrate, as in the previous test. Because of the thickness of the epoxy layer, a nanocomposite film was formed by an epoxy layer containing highly contracted wet CNT pillars, as shown in Fig. 6a. The picture shows the surface of the film that was originally adhered



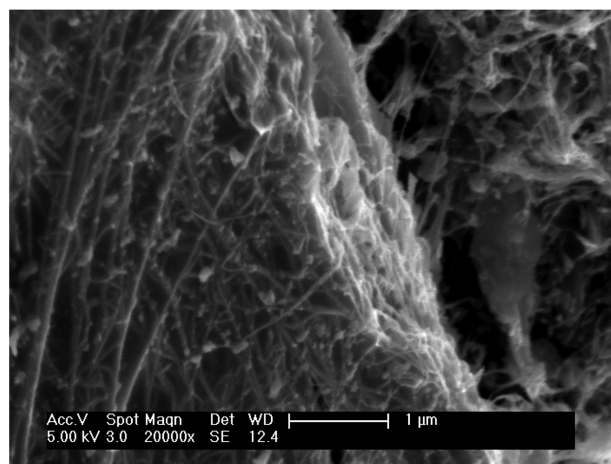
a)



b)



c)



d)

Fig. 7 SEMs of a) dry CNT pattern, b) cross section of the CNT/SU-8 feature showing good wetting, c) close-up of the top region of the cross section, and d) wetting of the CNTs.

**Table 1** Experimental results for pure alumina fibers, fibers soaked with a catalyst, and fibers after the CNT growth process at 750°C

|                              | Tensile strength, GPa |                    | Young's modulus, GPa |                    | Strain to failure, % |                    |
|------------------------------|-----------------------|--------------------|----------------------|--------------------|----------------------|--------------------|
|                              | Mean                  | Standard deviation | Mean                 | Standard deviation | Mean                 | Standard deviation |
| Pure alumina fiber           | 2.19                  | 0.19               | 135                  | 6.38               | 1.63                 | 0.13               |
| Alumina soaked in a catalyst | 2.30                  | 0.21               | 138                  | 12.6               | 1.73                 | 0.06               |
| Alumina fibers with CNTs     | 2.28                  | 0.09               | 134                  | 11.3               | 1.63                 | 0.16               |

to the silicon substrate on which the CNTs were grown. The effect of the contraction of the epoxy during curing is clearer in this test. In Fig. 6b, the free surface of a CNT pillar is shown (the side on which the CNTs were attached to their original silicon wafer). For this viscous epoxy, significant contraction is noted. The voids that can be seen in the center of the pillar in Fig. 6b and in the cross section shown in Fig. 6c support this interpretation. The 200- $\mu\text{m}$ -long CNT pillars shown in Fig. 6c were completely wet by the epoxy, from top to bottom. Given the height of the epoxy layer (similar to the CNT pillar height), epoxy may penetrate through the end of the pillar (as in the first set of tests) and also through the pillar sides. Although the pillar is wet from top to bottom, it does not appear to be wet near the center region at the top; this is consistent with the 80- $\mu\text{m}$ -high wetting obtained in the first tests.

For the third set of tests, a commercial low-viscosity (52 cP, similar to resin-transfer-molding-grade epoxies) epoxy (Microchem SU-8 2005) was used on different patterns of 100- $\mu\text{m}$ -high CNTs (the pattern shown in Fig. 7a and 200- $\mu\text{m}$ -wide square CNT pillars). As described in Sec. III.B, the SU-8 was applied directly to the wafer containing the CNT features. After curing, the wafer was diesawed to assess the wetting. A cross section of one of the features is shown in Fig. 7b. The wetting in the CNT forests is complete, forming a nanocomposite feature with no voids, as seen in the closer view in Fig. 7c. The alignment of the CNTs is maintained. The ridges of the foreground of Fig. 7c are due to the abrasive sectioning method. SEMs at similar magnifications confirm that there are no microscale voids in the nanocomposites. An even closer view of the wetting of the CNTs is shown in Fig. 7d. The wetting results shown in Fig. 7d are very similar to SEMs at similar magnification for fully wet nanocomposite thin films [7].

### B. Tensile Tests of Single Fibers

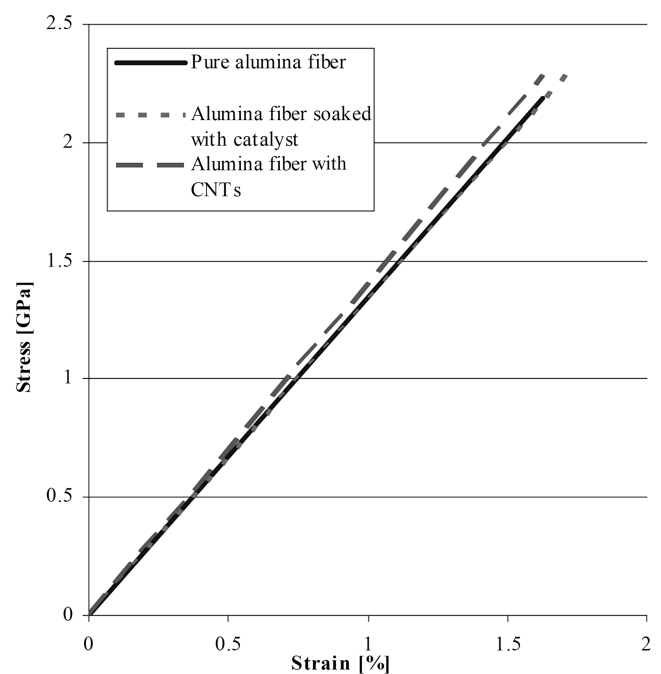
One of the most promising architectures for hybrid composites envisions carbon nanotubes grown directly on the surface of fibers. For this architecture to be feasible, the mechanical properties of the fibers should be maintained during the CNT growth process. Tensile tests were applied to fibers in each step of the process to assess whether the fibers were degraded, as described in Sec. III.C. The results for these 26 tests, summarized in Table 1, show that basic mechanical properties are maintained throughout the CNT growth process. Typical stress-strain curves for the alumina fibers at the different stages of the process are shown in Fig. 8. No important deviation of the properties was detected, indicating that neither the catalyst treatment nor subsequent growth process affects the fiber properties in the case of the alumina fibers. This is important when the composite properties are assessed to elucidate the root cause of either improvement or degradation of ply- and laminate-level properties when such composites can be fabricated. A similar investigation of carbon nanofibers grown on the surface of carbon fibers reported significant degradation of fiber properties related to the metal catalyst reduction step, but also found that this effect could be mitigated by changing catalysis parameters [17].

### C. Discussion

The feasibility of hybrid composite materials strongly depends on the two factors studied in this work: wetting of the carbon nanotubes with commercial polymers and retention of the mechanical properties of the fibers. The results from the two sets of tests that used the high-viscosity conductive epoxy clearly show that the capillarity effect can help in the wetting of CNTs even in the most adverse (i.e.,

highly viscous) conditions. This finding may be particularly interesting for manufacturing processes such as resin-infusion or resin-transfer molding, in which wetting of the fiber is often a limiting factor. The resins generally used in these processes have a lower viscosity and volume contraction than the conductive epoxy used for this test. The relevant viscosity test is the SU-8 wetting performed here in the third set of tests. Therefore, good wetting is likely for polymer resins used commercially to fabricate advanced composites, because SU-8 fully wets the CNT forests grown in this work. Results also show that the mechanical properties of the alumina fibers are maintained after the CNT growth, supporting the viability of hybrid composites based on this process.

The uniquely long CNTs created by the growth process used in this work show promise for enhancing load transfer between the polymer matrix and the fiber with in situ grown CNTs. In addition to the increase in the surface area and the stiffening of the polymer in the interface region, new reinforcement mechanisms should appear due to the length of the CNTs; aligned CNTs from different fibers can overlap one another and produce a further reinforcement of the matrix through bridging. The entanglement between CNTs grown on different fibers would also increase the load transfer between fibers and will likely help suppress or bridge matrix cracks that appear: effectively, toughening the composite. This last bridging mechanism has been reported in the literature for CNTs in resins (no fibers present), but was limited due to very low weight fractions (lower than 5% to avoid the formation of agglomerates [18]) of CNTs somewhat dispersed in a polymer matrix [19,20]. An important advantage of the current method arises from the fact that CNTs are grown in situ on the fiber surface, likely avoiding issues related to the dispersion of the CNTs in the matrix.



**Fig. 8** Typical single-fiber stress-strain curves of the pure alumina fibers, fibers soaked with a catalyst, and fibers after the CNT growth process.

## V. Conclusions

The thermal CVD process reported in this work yields dense forests of well-aligned long CNTs with a growth rate approaching 100  $\mu\text{m}/\text{min}$ . This work also provided insight into two important aspects related to hybrid composites that had not been addressed previously: wetting of CNTs using advanced thermoset polymers and under adverse (viscous) conditions and stability of the mechanical properties of the fibers (alumina) after CNT growth. Both sets of findings support the viability of the hybrid composite architecture, but there remain important questions to be answered.

Future studies will address the wetting of fiber tows and fiber cloths covered with CNTs to further investigate the feasibility of the process described in Sec. III.A to create hybrid composites. Once the wetting is demonstrated for these architectures, mechanical tests will be applied to specimens of these hybrid composites to determine the mechanical effects of the CNTs. Mode-I fracture and three-point bending tests are envisioned as the most critical tests to apply. In parallel to those mechanical tests, the scalability of the CNT growth process should also be pursued. A scaled-up version of the CNT fabrication process that would be compatible with commercial production processes and rates is envisioned.

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