HIGH VOLUME FRACTION CARBON NANOTUBE COMPOSITES FOR AEROSPACE APPLICATIONS

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ABSTRACT

Reported nanoscale mechanical properties of carbon nanotubes (CNTs) suggest that their use may enable the fabrication of significantly lighter structures for use in space applications. To be useful in the fabrication of large structures, however, their attractive nanoscale properties must be retained as they are scaled up to bulk materials and converted into practically useful forms. Advances in CNT production have significantly increased the quantities available for use in manufacturing processes, but challenges remain with the retention of nanoscale properties in larger assemblies of CNTs. This work summarizes recent progress in producing carbon nanotube composites with tensile properties approaching those of carbon fiber reinforced polymer composites. These advances were achieved in nanocomposites with CNT content of ~70% by weight. The processing methods explored to yield these CNT composite properties will be discussed, as will the characterization and test methods that were developed to provide insight into the factors that contribute to the enhanced tensile properties. Technology maturation was guided by parallel advancements in computational modeling tools that aided in the interpretation of experimental data.

1. INTRODUCTION

Mechanical properties for materials typically used for lightweight aerospace structures are shown in Figure 1 [1]. Data points for IM7 and M46J are representative of carbon fiber tensile properties. While these fibers exhibit excellent tensile properties, the carbon fiber reinforced polymer (CFRP) composites produced from them have much lower mechanical properties. This knockdown in properties prevents the full realization of carbon fiber's potential to enable structural weight savings. Plotted on the same graph, the nanoscale tensile properties of individual CNTs are so much higher than those of carbon fibers that despite anticipated knockdowns in mechanical performance of the structural composites produced from them, significant mass reductions of structural components constructed from these composites were deemed to be a promising goal. If realized, these weight savings can enable more affordable space exploration.

Exploiting carbon fiber strength in composites has been an area of interest for several decades, especially in aerospace applications where lightweight structures are paramount [2]. With the advent of CNTs, this need for mass efficiency drove some of the extraordinary attention paid to the potential for these nanofillers to yield composites with mechanical properties that are competitive with those of CFRPs. Until recently, much of the work reported in the literature have been devoted to property enhancements possible with low loadings of CNTs in engineering polymer matrices such as epoxies and polyimides. Dispersing more than a few percent of CNTs in polymer matrices is challenging due to increased viscosities that result from adding these high surface area nanofillers to the polymer matrix. Several approaches to overcome this processing difficulty have been documented [2-5]. Although investigations of lightly doped polymer matrices have yielded some understanding of processing approaches that can improve the nanotube/matrix interface to enhance load transfer, it is evident that significantly more than 5-10% CNT doping will be necessary to attain the desired mechanical properties.

An alternate approach to increase CNT content is to take advantage of assemblies of CNTs such as sheets or buckypapers [6-9] and yarns [10-13]. Laboratory scale mechanical tests of bismaleimide (BMI) matrix composites containing ~60% by weight of aligned CNT sheets yielded composites with tensile strength near parity with and Young's modulus exceeding those of unidirectional CFRPs [7,8]. These results were consistent with the findings of Koziol et al. [11], where lessons from polymer processing were used to support the analyses of mechanical test data for CNT fibers. It was noted that chain alignment and packing were critical to achieving high fiber strength and stiffness. For spun CNT fiber, Mora et al. [12] showed that composite stiffness was directly related to CNT fiber volume fraction; high fiber volumes were required to achieve composite tensile properties consistent with CFRP properties. Likewise, tensile properties approaching those of CFRPs were obtained for high volume fraction CNT composites fabricated from mechanically stretched, aligned CNT sheets [7-9] and yarns [13].
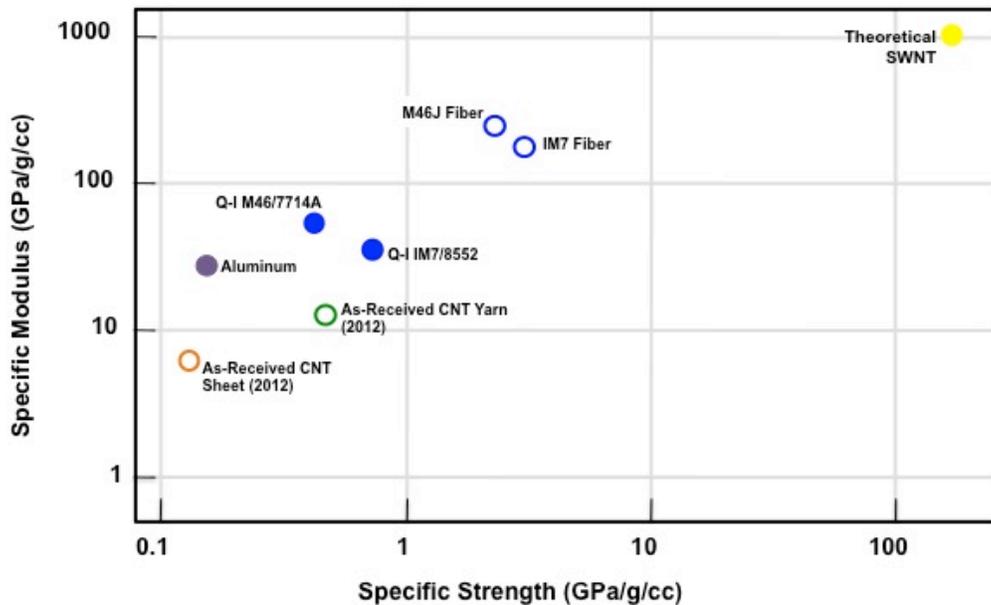
Figure 1. Comparison of nanoscale and bulk tensile properties of materials used for aerospace structures [1]. Properties of CNT sheet and yarn shown are from materials received in 2012.

The commercial availability of bulk CNT sheets and yarns [14] permitted further study of the scalability of findings previously reported in literature. As shown in Figure 1, specific tensile properties of these materials were significantly lower than those of carbon fibers. The work reported here is the culmination of a three-year effort to develop high volume fraction CNT composites with tensile properties competitive with CFRPs. The objective was to develop post-processing methods for commercially available CNT reinforcement to afford CNT composites possessing at least 1.6 GPa/g/cc specific strength (SS) and 80 GPa/g/cc specific modulus (SM), approximately double the quasi-isotropic IM7/8552 properties reported in Ref. 1 which were used as the basis for setting these goals. These properties represent ~540% and ~1700% improvements in SS and SM respectively, relative to the starting bulk CNT properties.

2. EXPERIMENTAL

2.1 Materials

CNT materials used in this study were either acetone condensed, randomly aligned CNT sheets or highly densified CNT yarn obtained from Nanocomp Technologies, Inc., Merrimack, New Hampshire, USA. Composites were fabricated by infiltrating these CNT reinforcements with either BMI (RM-3010, Renegade Materials Corp., Miamisburg, Ohio, USA) or epoxy (API-60, Applied Poleramic, Inc., Benicia, CA, USA) resins. Resin solutions were prepared with either toluene or methyl ethyl ketone (MEK) used as-received from Sigma-Aldrich.

2.2 CNT Composite Processing

As-received, randomly aligned CNT sheets were stretched mechanically using the apparatus depicted in Figure 2 [15]. The system allows continuous processing of highly aligned CNT tape (slit sheets) that can subsequently be infused with the desired resin using a single piece of equipment. The spool of randomly aligned CNT tape is initially mounted on the spindle attached to motor X, while the take-up spool of the stretched tape is mounted on the spindle attached to motor Y. Motor Y is attached to motor Z to allow for lateral translation of the take-up spool. Stretching is achieved by setting the ratio of rotational speed for motors X and Y. The tape is incrementally stretched by cycling the tape back and forth between the two spools until the desired stretch ratio is achieved at which point resin is applied to produce solution impregnated tape.
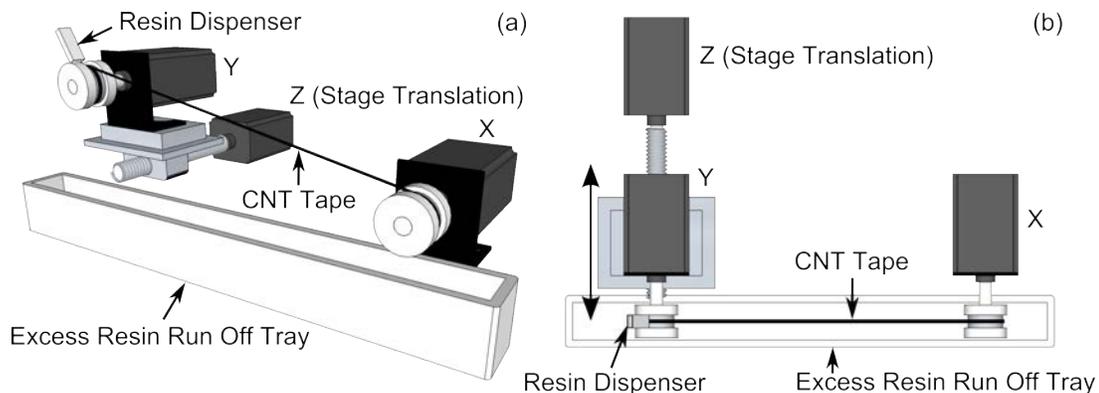
Figure 2. Schematic for continuous tape stretcher and winder: a. isometric view and b. top view.

As-received CNT yarns were already highly aligned and densified, thus reducing the post-processing steps required to obtain high volume fraction composites. Equipment used to solution infiltrate the yarn is shown in Figure 3. The apparatus is designed to infiltrate CNT yarn as it passes through the resin bath and is wound around the substrate of interest. Winding is conducted under applied tension up to a maximum tension of 45 N. Resin metering is achieved with a doctor blade. Lateral placement of the solution impregnated yarn is controlled by yarn guides which consisted of payout eyes with diameters of around 300 μm.
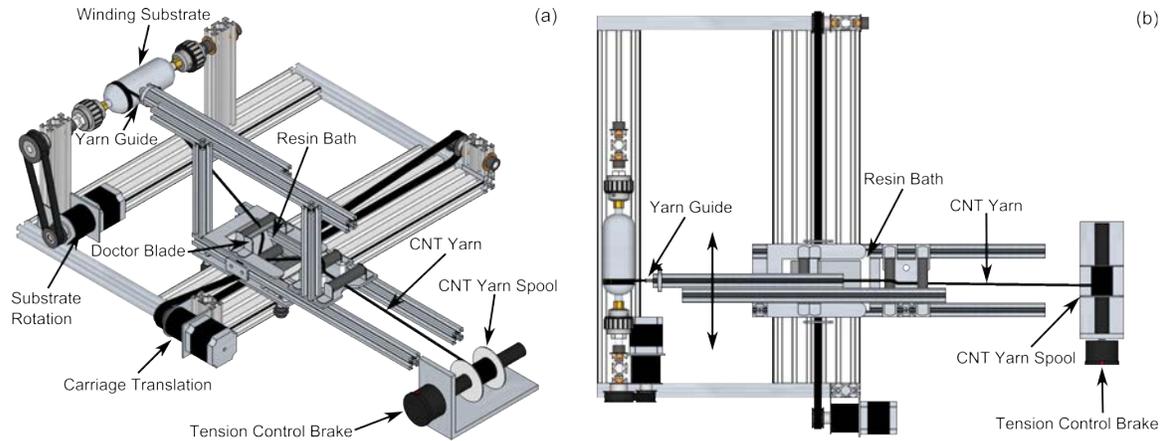
Figure 3. Schematic for yarn composite processing: a. isometric view and b. top view.

2.3 Characterization

2.3.1 Mechanical Testing

Room temperature measurements of the tensile properties of the CNT composites were carried out on a MTS-858 test stand equipped with pneumatic grips and a laser extensometer. This provided more accurate modulus data of the materials because errors associated with sample slippage in the grip were eliminated. The thickness of films was determined with a profilometer-type instrument (Mitutoyo Corp., Model ID-S112PE) and confirmed by microscopic measurements. All mechanical data were normalized by the density of the specimen, which was determined by measuring the area, thickness and weight of the CNT sheet composite. For CNT yarn composites, linear density was used. Tensile test methods were based on modified ASTM standards D882 for tensile properties of plastic sheeting, D638 for tensile properties of plastics and D1708 for tensile properties of microtensile specimens of plastics. Gage length was 10 mm. Crosshead speed was 10 mm/min for pristine CNTs and 0.5 mm/min for the CNT composites. At least five specimens were tested to obtain specific strengths and moduli. Young's modulus was determined by linear regression of the slope in the region between 10-30% of the ultimate load with the strain recorded using a laser extensometer [16].

2.3.2 Imaging

Field emission scanning electron microscopy (FE-SEM) was conducted on a Hitachi Model S-5200 microscope. Computed tomography (CT) scans of CFRPs and CNT composites were

obtained using a Nikon Metrology microfocus x-ray CT system with 5 µm resolution and magnification of up to 160x. It is equipped with a Perkin-Elmer 16 bit amorphous silicon digital detector with a 2000 × 2000 pixel array.

2.4 Molecular Modeling

Molecular simulation of CNT composites was carried out using the ReaxFF reactive force field as implemented in LAMMPS, an open source molecular dynamics program. This tool was used to evaluate the specific tensile properties of model CNT/amorphous carbon matrix composites to determine how these mechanical properties are influenced by the arrangement of the CNTs in the composite [17].

RESULTS AND DISCUSSION

Figure 4 summarizes the progress in materials development over the course of three years. Included in the graph are data points generated by molecular modeling, showing the mechanical properties of CNT/amorphous carbon composites [17]. These results indicate that model composite systems wherein CNTs are bound by amorphous carbon have properties higher than those exhibited by state of the art CFRPs, suggesting that the project objective of at least double the SS and SM of CFRPs is theoretically possible.

In contrast to CFRPs, where tensile composite properties are typically lower than those of the reinforcing carbon fiber tensile properties used as reinforcement, CNT composite properties tended to be greater than those of the CNT reinforcement. This trend is illustrated in Figure 4 by the higher SS and SM of CNT sheet composite (2012) relative to the as-received CNT sheet (2012) from which it was derived. The randomly aligned CNT sheets had SS of ~150 MPa/g/cc and SM of ~6 GPa/g/cc. The best high volume CNT (~70% wt) composite properties obtained from these lots of sheets were ~400 MPa/g/cc SS and ~20 GPa/g/cc SM -- ~167% and 233%
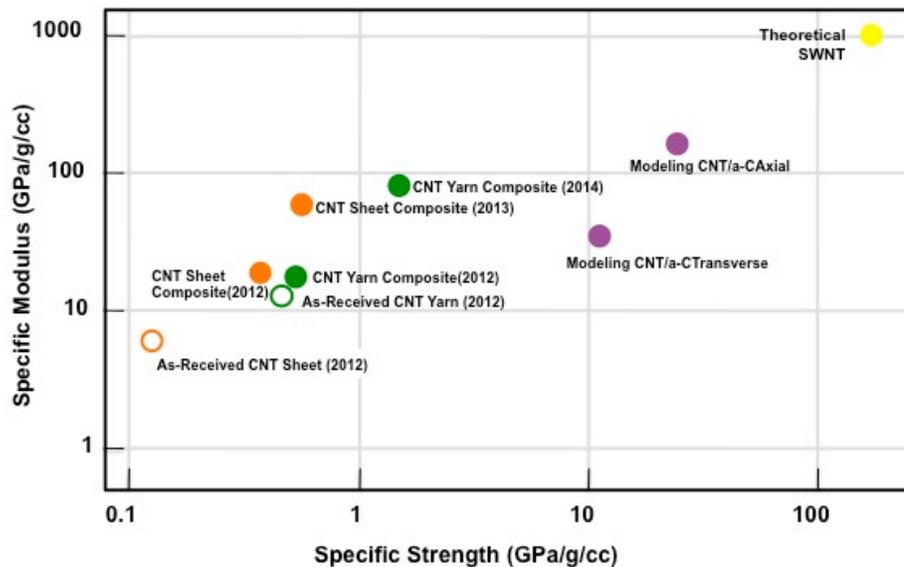
Figure 4: CNT tape and yarn composite properties obtained experimentally and predicted mechanical properties of model CNT/amorphous carbon composites.

increases in SS and SM relative to the as-received CNT sheet, respectively, following post-processing steps in induce alignment in the CNT reinforcement. While this represents a substantial gain in mechanical properties, it is still far from the goals for the project. Better quality starting CNT sheets obtained from the vendor (SS ~ 250 MPa/g/cc and 6 GPa/g/cc SM) yielded CNT composite properties in 2013 of 610 GPa/g/cc SS and 70 GPa/g/cc SM. The dramatic increase in SM was achieved by combining mechanical stretching to align the CNT bundles in the CNT sheet with resistive heating assisted resin infusion to promote wetting of the CNT bundles and improve interfacial adhesion between the fiber and the matrix [9]. Despite near doubling of the CNT composite SM relative to the CFRP SM used as the benchmark for this work, the highest SS attained was still less than 40% of the way to the goal of 1.6 GPa/g/cc.

High resolution SEM imaging of the CNT composites produced from randomly aligned and stretched CNT sheets revealed that the improved tensile properties, especially SM, were a result of significantly enhanced alignment and packing of the CNT bundles following mechanical stretching. This is supported by the micrographs shown in Figure 5 a-d. In particular, Figures 5b and 5d illustrate the benefit of mechanical stretching to densify the CNT bundles to enhance load transfer. This is consistent with the observations that CNT alignment and packing contribute to enhanced composite tensile properties [8,12,13].
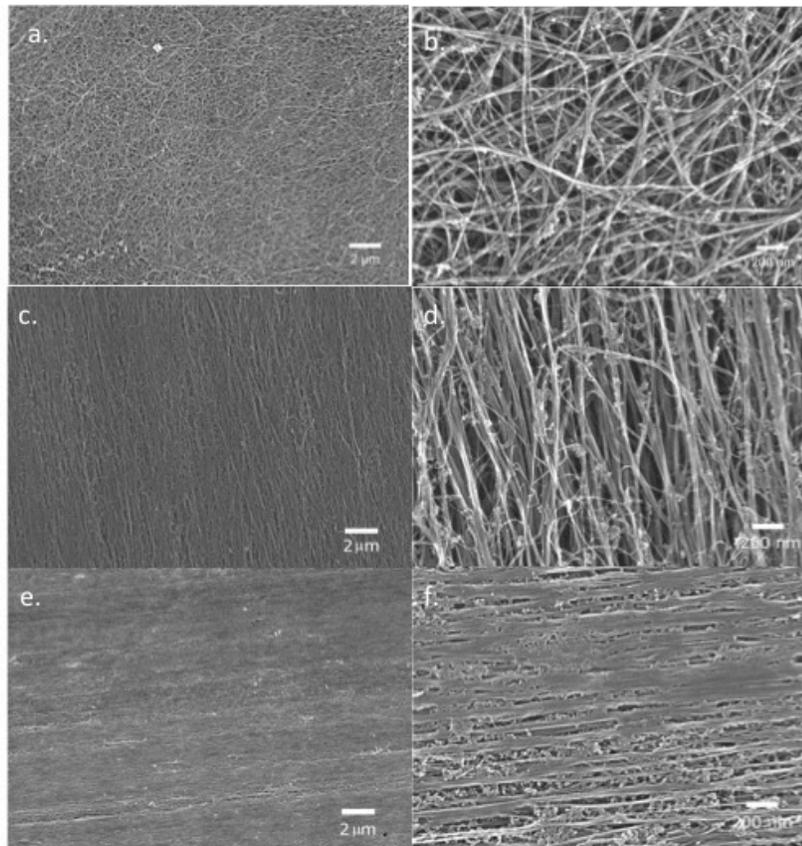
Figure 5: Comparison of sheet and yarn alignment: a, b. As-received, randomly aligned sheet, c, d. Stretched, aligned sheet, e,f. As-received, highly densified yarn.

While methods were being developed to maximize the properties of CNT sheet composite, parallel efforts to improve CNT yarn properties were being undertaken. By 2014, CNT yarns with mechanical properties yielding CNT composites with SS of 1.7 GPa/g/cc and SM of 90 GPa/g/cc became available. The project objective was reached with a material where CNT bundles were even more aligned and densely packed than was possible in 40% mechanically stretched CNT sheets. This improvement is visible in Figures 5c to 5f, where enhanced densification is visible especially at higher magnifications in Figures 5d and 5f.

As shown in Figure 6, the best combination of SS and SM achieved for CNT yarn composites are almost as high as the tensile properties of unidirectional IM7/8552 composite which has reported literature values of SS = 1.7 GPa/g/cc and SM = 104 GPa/g/cc [18]. Although significant progress has been made in understanding how CNTs might be a viable alternative lightweight structural material, near parity with state of the art CFRP will not be sufficient to justify displacing this technology, especially if quantifiable benefits for such replacement are not credibly significant.
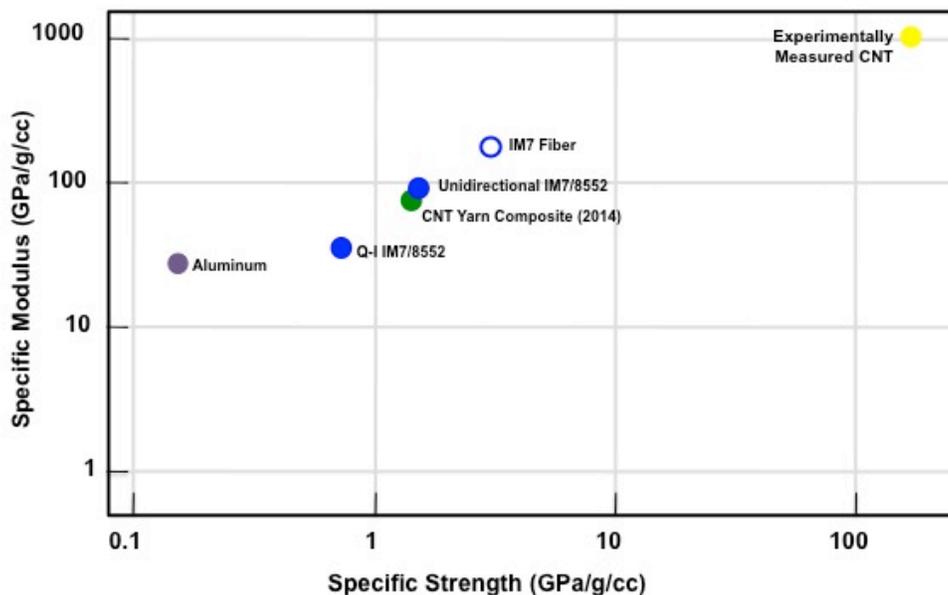
Figure 6: Summary of properties for structural aerospace materials [1,18].

Despite this caveat, it is important to note that CNT fibers or yarns are different from carbon fibers. The obvious difference in scale is visible in the Figures 7a and 7b for carbon fiber and CNT yarn respectively. Furthermore, while carbon fibers are continuous, the CNTs in the yarn studied here are on the order of 1 mm long, so the reinforcement is afforded by discontinuous CNTs, although the individual elements have very high aspect ratios (L/D ~100,000). This disparity in filament size is accompanied by other CNT properties that influence processing conditions. For instance, whether the high surface area that results from the three orders of magnitude difference in fiber diameter represents an advantage or disadvantage in load transfer is not well understood.

Figures 7c (unidirectional CFRP) and 7d (CNT yarn composite) are cross sectional x-ray CT images of carbon fiber and CNT composite wound around an aluminum ring. The data reveal

that the CFRP was highly consolidated while gaps/voids were visible in the CNT yarn composite. Further magnification of these samples in Figures 7e (CFRP) and 7f (CNT composite) confirmed that the unidirectional CFRP has been processed optimally, while there is much room for improvement in wetting and void reduction in the CNT composites. Yet, as shown in Figure 6, the non-optimized CNT yarn composite already exhibits tensile properties almost as good as those of unidirectional CFRP. Much remains to be understood with regards to process optimization to yield high quality, thick CNT composites, but the properties reported here hold some promise for the realization of the potential for CNTs to enable multifunctional components for structural aerospace applications.
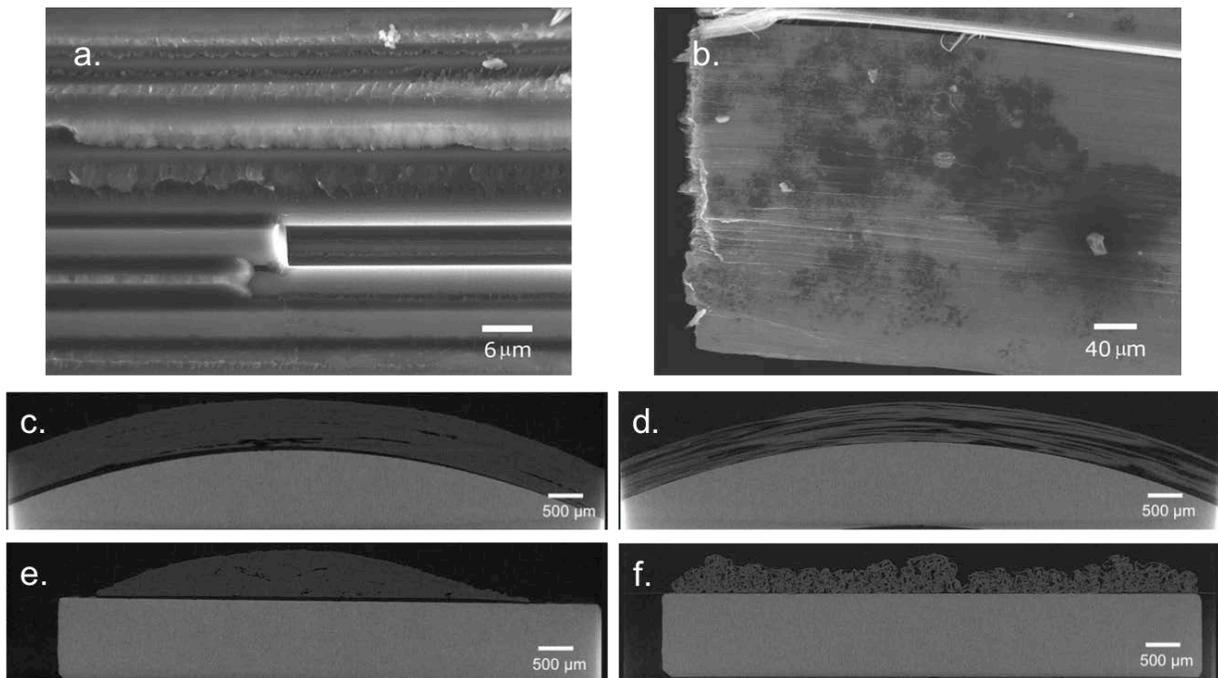
Figure 7: FE-SEM images of a. IM7/8552 composite and b. CNT yarn/BMI composite. CT image of c, e. cross section of IM7/API-60 overwrapped aluminum ring and d, f. cross section of CNT yarn/API-60 composite wound aluminum ring.

4. SUMMARY AND CONCLUSIONS

Advancements in the commercial scale manufacturing of CNT sheet and yarn formats have yielded increases in tensile properties of these nanoreinforcements over the three-year effort summarized here, along with attendant increases in the tensile properties of ~70% weight fraction composites produced from these CNT assemblies. Of note however is that maximum tensile properties obtained from CNT sheets with the best starting properties (~250 MPa/g/cc SS, ~5 GPa/g/cc SM) resulted in SM of ~70 GPa/g/cc for the CNT composite, almost double the SM of quasi-isotropic IM7/8552, although SS could not be increased beyond ~700 MPa/g/cc in spite of attempts to align CNTs as much as possible and maximize resin solution infiltration with the

assistance of resistive heating. Increased CNT bundle alignment and densification in yarns yielded much higher reinforcement properties and high volume CNT composite properties approaching those of unidirectional IM7/8552 composites, despite suboptimal CNT composite quality. These results suggest the potential for realizing even higher tensile properties for CNT composites if processing conditions to fabricate these composites can be understood and optimized to yield composites with higher quality in terms of void content and consolidation. Along with the improved tensile properties possible with CNT composites, other properties such as compressive and interlaminar properties need to be investigated. If the suite of mechanical properties typically used to support structural composite designs can be similarly improved, these parameters along with CNTs' excellent electrical and thermal properties can lead to multifunctional aerospace structures with meaningful structural mass savings to enable more affordable space exploration and enhanced fuel efficiency in aeronautics.

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