High Volume Fraction Carbon Nanotube Composites for Aerospace Applications

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ABSTRACT
Reported mechanical properties of carbon nanotubes (CNTs) at the nanoscale suggest their potential to enable significantly lighter structures of interest for space applications. However, their utility depends on the retention of these properties in bulk material formats that permit practical fabrication of large structures. This presentation summarizes recent progress made to produce carbon nanotube composites with specific tensile properties that begin to rival those of carbon fiber reinforced polymer composites. CNT content in these nanocomposites was greater than 70% by weight. Tested nanocomposite specimens were fabricated from kilometers or tens of square meters of CNT, depending on the starting material format. Processing methods to yield these results, and characterization and testing to evaluate the performance of these composites will be discussed. The final objective is the demonstration of a CNT composite overwrapped pressure vessel to be flight tested in the Fall of 2016.

Keywords: carbon nanotubes, carbon nanotube composites

1 INTRODUCTION

The mechanical properties for materials typically used for lightweight aerospace structures are shown in Figure 1 [1]. Data points for IM7 and M46J shown as open blue circles are representative of common carbon fiber tensile properties. While these fibers exhibit excellent tensile properties, the knockdown in these properties (shown in filled blue circles) when the fibers are used in carbon fiber reinforced polymer (CFRP) composites, prevents the full realization of carbon fiber’s potential to enable structural weight savings. Although CFRPs have been employed in a number of technically and economically important applications, progress in improving their properties has plateaued in recent years.

The advent of CNTs, along with an ever-growing need for lightweight materials and the exciting properties reported for individual CNTs led to significant investments to develop CNT based composites. As shown by the filled yellow circle in Figure 1, the theoretical nanoscale tensile properties of individual CNTs are much higher than those of carbon fibers. If a method for fabricating CNT-based structural composites with property knockdowns comparable to those typical of carbon fiber composites could be found, their specific mechanical properties would exceed those of any CFRP available today. If realized, these mechanical properties can lead to weight savings that enable more affordable space exploration.

Dispersing CNTs in polymer matrices at concentrations higher than a few percent is challenging because of their tendency to aggregate and the extremely large increases in viscosity that result from their high surface areas and aspect ratios. As a result, much of the work reported in the literature to date has focused on property enhancements produced by low loadings of CNTs in engineering polymer matrices, such as epoxies and polyimides. Several approaches to overcoming the processing difficulties have been documented [2-5]. Although investigations of lightly doped polymer matrices have yielded some understanding of processing approaches to improve the nanotube/matrix interface and enhance load transfer, it is evident that significantly more than 5-10% CNT doping will be necessary to attain the desired mechanical properties.

Figure 1. Tensile properties of aerospace materials [1].

The commercial availability of bulk CNT sheets and yarns [6] has permitted studies of high volume fraction CNT composites. 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 efforts to develop commercially-scalable, 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 specific strength (SS) of at least 1.6 GPa/(g/cm³) and specific modulus (SM) of 80 GPa/(g/cm³), approximately double the quasi-isotropic IM7/8552 properties reported in Reference 1 which were used as the basis for setting these goals. These values represent ~540% and ~1700% improvements in SS and SM, respectively, relative to starting bulk CNT sheet properties (open orange circle in Figure 1).

2 EXPERIMENTAL

2.1 Materials

CNT materials used in this study include acetone condensed, randomly aligned CNT sheets and highly densified CNT yarn obtained from Nanocomp Technologies, Inc. (Merrimack, NH, USA). Composites were fabricated by infiltrating these CNT reinforcements with bismaleimide (BMI) (RM-3010, Renegade Materials Corp., Miamisburg, OH, USA) or epoxy (API-60, Applied Poleramic, Inc., Benicia, CA, USA) resins. Resin solutions were prepared with 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 described in Reference 7. 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. 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 was designed to infiltrate CNT yarn as it passed through a resin bath and was wound under tension around the substrate of interest [7].

2.3 Characterization

2.3.1 Mechanical Testing  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. 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. 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 stress-strain curve in the region between 10-30% of the ultimate strength [8]. All mechanical data were normalized by the linear density of the specimen to eliminate ambiguity from determination of specimen thickness which can be irregular. Comparisons of mechanical properties were made using specific properties to account for density differences that result from the processing methods used.

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.

3 RESULTS AND DISCUSSION

Figure 2 summarizes the progress in materials development over the course of three years. The red star indicates the project target tensile properties which were twice those of specific properties of quasi-isotropic IM7/8552 carbon fiber/epoxy composite.

Figure 2. Advancement of CNT composite tensile properties.

In contrast to CFRPs, where composite tensile properties are typically lower than those of the carbon fiber used as reinforcement, the processed CNT composite properties tended to be greater than those of the CNT reinforcement. This trend is illustrated in Figure 2 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/cm³) and SM of ~6 GPa/(g/cm³). The best high volume CNT (~70% wt) composite properties obtained from these lots of sheets were ~400 MPa/(g/cm³) SS and ~20 GPa/(g/cm³) SM. This is ~167% and 233% greater than the SS and SM of the CNT sheets, respectively.

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 3 a-d. In particular, Figures 3b and 3d 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 [9-11]. Some resin infusion between and within the CNT bundles may also aid load transfer.

Figure 3. 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 also underway. By 2014, CNT yarns with mechanical properties yielding CNT composites with SS of 1.7 GPa/(g/cm³) and SM of 90 GPa/(g/cm³) 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 3c to 3f, where enhanced densification is evident especially at higher magnifications in Figures 3d and 3f.

As shown in Figure 4, 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/cm³) and SM = 104 GPa/(g/cm³) [12]. 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 4. Summary of properties for structural aerospace materials [1,12].

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 Figures 5a and 5b 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.

Figure 5. 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 overwrapped aluminum ring.

Figures 5c (unidirectional CFRP) and 5d (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 5e (CFRP) and 5f (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 4, the non-optimized CNT yarn composite already exhibits tensile properties comparable to 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 demonstrate the potential of CNTs to enable lightweight components for structural aerospace applications.

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/cm^3) SS, ~5 GPa/(g/cm^3) SM) resulted in SM of ~70 GPa/(g/cm^3) for the CNT composite, almost double the SM of quasi-isotropic IM7/8552, although SS could not be increased beyond ~700 MPa/(g/cm^3) in spite of attempts to align CNTs as much as possible and maximize resin solution infiltration. 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.

5 REFERENCES