COVER SHEET

Paper Number: **2718**

Title: **Thermal Properties of Hybrid Carbon Nanotube/Carbon Fiber Polymer Composites**

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ABSTRACT

Carbon fiber reinforced polymer (CFRP) composites possess many advantages for aircraft structures over conventional aluminum alloys: light weight, higher strength- and stiffness-to-weight ratio, and low life-cycle maintenance costs. However, the relatively low thermal and electrical conductivities of CFRP composites are deficient in providing structural safety under certain operational conditions such as lightning strikes. One possible solution to these issues is to interleave carbon nanotube (CNT) sheets between conventional carbon fiber (CF) composite layers. However, the thermal and electrical properties of the orthotropic hybrid CNT/CF composites have not been fully understood.

In this study, hybrid CNT/CF polymer composites were fabricated by interleaving layers of CNT sheets with Hexcel® IM7/8852 prepreg. The CNT sheets were infused with a 5% solution of a compatible epoxy resin prior to composite fabrication. Orthotropic thermal and electrical conductivities of the hybrid polymer composites were evaluated. The interleaved CNT sheets improved the in-plane thermal conductivity of the hybrid composite laminates by about 400% and the electrical conductivity by about 3 orders of magnitude.

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1. INTRODUCTION

State-of-the-art commercial aircraft such as the Boeing 787 and the Airbus XWB feature approximately 50% carbon fiber polymer (CFRP) composites, because their strength/stiffness to weight ratio enables increased fuel efficiency, and reduced pollutant emission. They also offer the advantage of lower life-cycle maintenance due to their superior fatigue and corrosion resistance [1-2]. However, CFRP airframes suffer from several problems in connection with lightning strike damage which statistically happens every 1,000 to 10,000 hours of flight, about one to two times a year, leading to cosmetic or structural damage [2-3]. Compared to traditional aluminum structures, CFRPs possess lower thermal and electrical conductivities, and are unable to dissipate the thermal energy and electrical current as effectively. The result can be embrittlement, delamination and/or structural failure [2]. For lightning strike protection (LSP), major aerospace companies utilize metallic woven mesh embedded beneath the exterior coating as a sacrificial layer that can dissipate the electrical and thermal energy by ablation during a lighting strike [3-6]. This provides excellent protection, but it can negate the cost and weight saving benefits from the use of CFRP composites [3].

An alternative method for LSP in CFRPs is incorporation of carbon nanotubes (CNTs) or CNT sheets to improve the thermal and electrical conductivity without degrading mechanical strength [1,3-9]. However, it is not widely known if the properties of CNT infused CFRP are good enough to replace the metallic LSP, and the 3-dimensional conductance of electrical current of the CNT infused CFRP has not been fully understood. Therefore, it is important to investigate the orthotropic properties of unidirectional hybrid CNT/CF composite for potential multifunctional applications. In this study, hybrid CNT/CF polymer composites were fabricated by interleaving layers of CNT sheets with Hexcel® IM7/8852 prepreg. Orthotropic thermal and electrical conductivities of the hybrid polymer composite (axial, perpendicular to axial/in-plane, and perpendicular to axial/out-of-plane) were evaluated. In addition, some mechanical properties of hybrid CNT/CF composites were characterized.

2. EXPERIMENTAL

2.1 Materials

Hexcel IM7/8552 prepreg was used for preparing hybrid CNT/CF polymer composites. CNT sheets were purchased from Nanocomp Technologies, Inc., Merrimack, NH (Lot# 71019, acetone condensed). The CNT sheets possessed an inherent directionality, this machine direction (MD) was designated as the 0° direction [1]. API-60 toughened epoxy resin (Applied Poleramic, Inc., Benicia, CA), was used to pre-impregnate the CNT sheets. Methyl ethyl ketone (MEK) and cyclohexanone (Sigma-Aldrich, St. Louis, MO) were used as-received.

2.2. Hybrid CNT/CF Composite Fabrication

Hybrid CNT/CF polymer composites were fabricated by following the National Aeronautics and Space Administration Langley Research Center (NASA LaRC) developed procedure [1,6-7] A toughened epoxy resin solution was prepared by dissolving API-60 epoxy resin to make a 5wt% solution in either MEK or a mixture of MEK and cyclohexanone (1:3 ratio). A predetermined amount of API-60 solution was painted on the CNT sheets to fabricate "pre-infused" CNT/epoxy prepreg sheets with the desired weight fractions of CNT after vacuum drying at room temperature overnight. The detailed processing method was described elsewhere [6]. The pre-infused CNT/epoxy prepreg sheets were used for further fabrication of hybrid CNT/CF composites. For short beam strength samples, panels (7.5 × 7.5cm) were fabricated by interleaving 16 plies of IM7/8552 prepreg with 16 plies of pre-infused CNT/epoxy prepreg sheets (7.6 × 7.6cm). For thermal and electrical conductivity test coupons, 80 plies of IM7/8552 prepreg (7.6 × 7.6cm) were interleaved with 80 plies of pre-infused CNT prepreg sheet. The 0° direction (machining direction, MD) of the CNT sheets was aligned with the 0° direction of the carbon fibers. The hybrid stack of plies was placed in a stainless steel mold and cured in a vacuum hot press according to a recommended Hexcel cure process [10]. After cure, the panels were cut along the three orthogonal directions by a wet-saw and polished.

2.3. Orthotropic Thermal and Electrical Conductivity Characterization

Composite plates – 80-ply control CF composites ($[0]_{80}$) and 160-ply hybrid CNT/CF polymer composites ($[0/CNT]_{80}$) (approximately 13 ~ 16 mm thick) were cut along the three orthogonal directions as shown in Figure 1. Hybrid CNT/unidirectional CF epoxy polymer composites have orthotropic thermal and electrical conductivity properties. The axial direction (1-), perpendicular/in-plane direction (2-), and perpendicular/out-of-plane (3-) direction to CF alignment formed the orthogonal principal directions for the unidirectional hybrid composites.

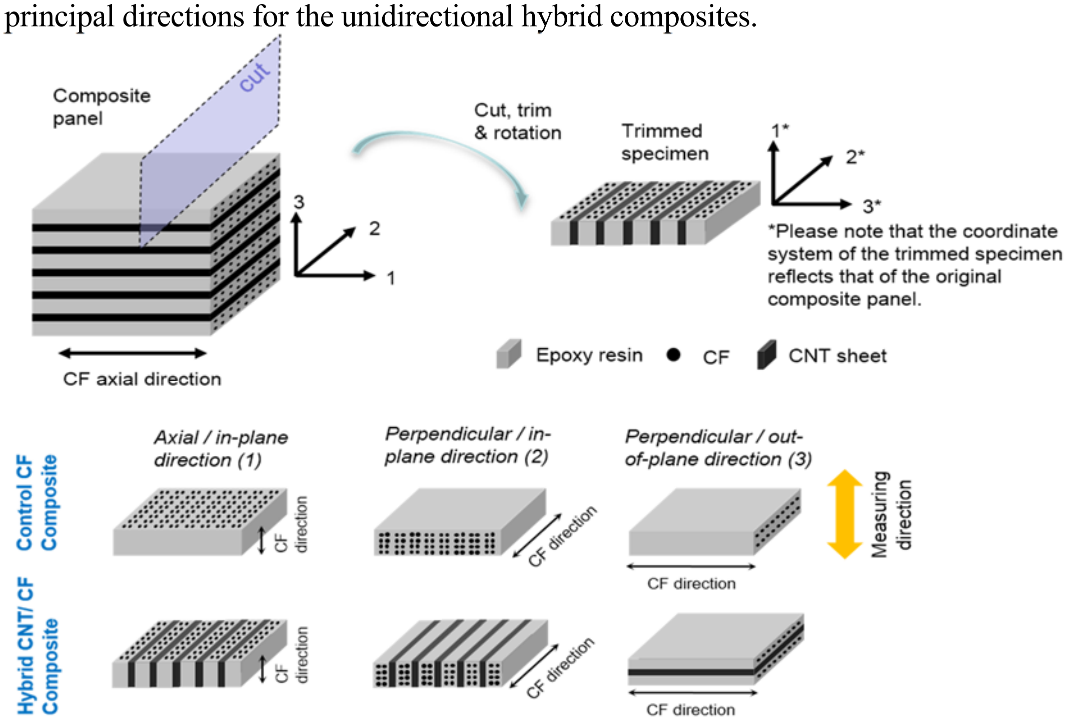

Figure 1. Preparation of orthotropic thermal and electrical conductivity test specimens.

Thermal conductivity was calculated from thermal diffusivity measured according to ASTM Standard E1461-13 [11]:

$$D = \frac{\lambda}{C_p \rho} \tag{1}$$

where D is the thermal diffusivity (mm^2/s), λ is the thermal conductivity (W/m·K), C_p is the specific heat (J/g·K), and ρ is the specimen density (g/cm^3). The thermal diffusivity, D, was measured by a laser flash method using a Netzsch LFA-457 MicroFlash®. Thin square specimens (10 mm ×10 mm, 2 mm thick) were subjected to a high intensity short duration laser radiant energy pulse at the pre-determined temperatures (0, 25, 50, 75, and 100°C) under a helium atmosphere. Thermal diffusivity, D, was calculated from the specimen thickness, L, and the time required for the rear surface temperature rise to reach half of its maximum value, $t_{1/2}$, according to Parker's suggestion for an ideal case [11]:

$$D = 0.13879 \frac{L^2}{t_{1/2}} \tag{2}$$

However, real processes violate the ideal boundary conditions, due to heat loss from the specimen surfaces and non-uniform heat flow. Correction factors suggested by Cowan, Clark and Taylor, and Heckman were employed to account for these issues. In this study, the correction factor suggested by Cowan, K_c, was used [11]:

$$D_{corrected} = \frac{K_C D}{0.13885} \tag{3}$$

The specific heat, C_p, was measured at the identical temperatures of the thermal diffusivity test by differential scanning calorimetry using a Netzsch DSC 204 F1 Phoenix®. Pyroceram 9606 and Inconel were used as the reference material for the thermal diffusivity /specific heat measurements.

The direct current (DC) electrical conductivity of orthotropic hybrid composites was measured by a 4 wire method using a Fluke 8846A digital multimeter (2x4 wire) at room temperature of approximately 23°C. Silver electrodes having a chromium adhesive promotion layer were coated onto the opposite faces (about 3 mm ×3 mm) of rectangular cuboid specimens (about 3 mm ×3 mm, 5 mm thick) by a thermal evaporation.

2.4. Mechanical Property Characterization

Short beam strength (SBS) test coupons were fabricated and tested at room temperature of approximately 23°C according to ASTM Standard D2344 [12]. Specimen size was about 3.05 mm thick, 6.35 mm wide and 19.05 mm long.

2.5. Morphology Analysis

The morphologies of the samples were studied using a Hitachi S-5200 field-emission scanning electron microscope (FE-SEM). The accelerating voltage and beam current were 25-30 KeV and 17-20 μA, respectively. The specimens were polished as needed and observed without a conductive coating.

3. RESULTS AND DISCUSSION

3.1. CNT Sheets

Figure 2 is a scanning electron image of an as-received CNT sheet. Highly crystalline and long CNTs exist as individual nanotubes or in the form of bundles with some impurities of catalyst and amorphous carbon. Average areal density of the CNT sheet was 9.8 g/m^2. Tensile strength and strain (for machining direction, MD) were reported as 430.2 ± 18.4 MPa and 45.8 ± 3.5 %, respectively, by the manufacturer. The CNT sheet was pre-impregnated with API-60 toughened epoxy resin which has similar properties to Hexcel 8552.

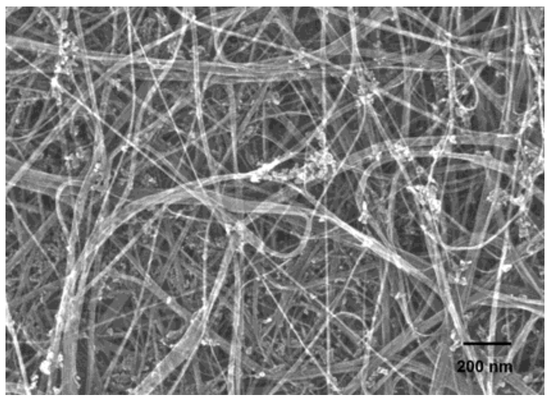

Figure 2. SEM image of as-received CNT sheet.

3.2. Short Beam Strength (SBS)

Short beam strength (SBS) of control CF composite and hybrid CNT/CF polymer composites are shown in Figure 3. The hybrid CNT/CF polymer composite exhibited a lower SBS value than the control CF composite. Poor interfacial strength between the CNT and polymer resin causes low fracture strength in the CNT sheets. For future work, interfacial enhancement between CNT and resin will be studied to improve the mechanical strength of hybrid CNT/CF polymer composites.

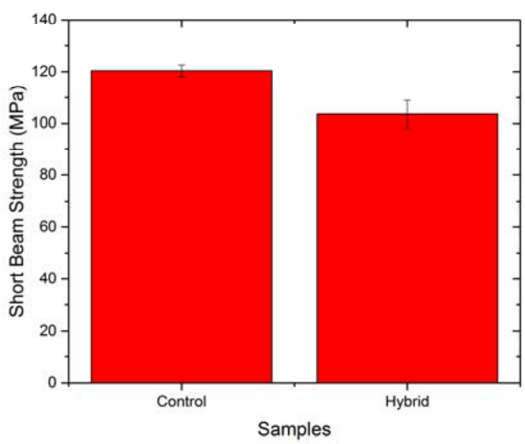

Figure 3. Short beam strength (SBS) of control CF composites and hybrid CNT/CF composites.

3.3. Orthotropic Thermal and Electrical Conductivities

Figure 4 shows the cross-sectional image of the directional hybrid CNT/CF polymer composite specimens illustrated in Figure 1. The volume fraction of the interleaved impregnated CNT sheet relative to the composite as a whole was about 22.5% v/v [7].

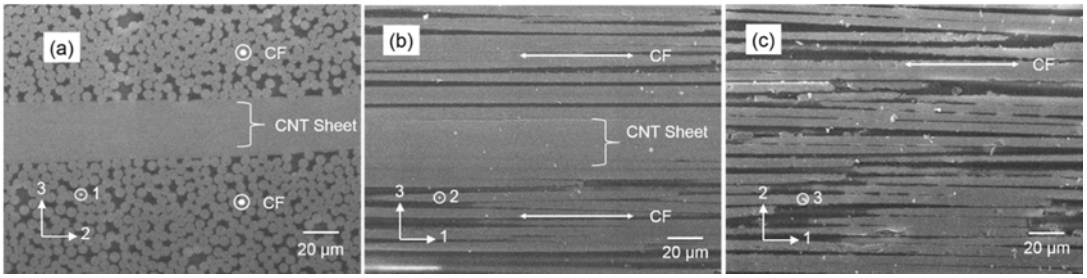

Figure 4. SEM images of surface of test specimens (hybrid CNT/CF composite) for measuring orthotropic thermal and electrical conductivity of (a) direction-1, (b) direction-2, and (c) direction-3.

Multi-directional thermal conductivities of the control CF composite, and the hybrid CNT/CF composite are shown in Figure 5. All the directional thermal conductivities of the control CF composites increased linearly with increasing temperature between 0°C to 100°C [7]. The thermal conductivity in the axial direction of the control CF composite, λ_1, was as high as 5.49 W/m·K at 25°C, similar to other literature values, due to direct thermal conduction through the axial CF [1,2]. However, the transverse thermal conductivities in-plane and out-of-plane, λ_2 and λ_3, were as low as approximately 0.7 W/m·K at 25°C. It is anticipated that the low values in the two in-plane directions will not afford effective thermal dissipation. The in-plane thermal conductivities of the hybrid CNT/CF polymer composites were as high as 8.38 W/m·K for λ_1 and 3.51 W/m·K for λ_2, approximately a 50 and 400% increase, respectively. This significant enhancement in thermal conductivity likely originated from the inherent high thermal conductivity of CNTs (200 W/m·K for bulk single-walled CNT (SWCNT) and 3000 W/m·K for individual multi-walled CNT (MWCNT)) [13-14]. However, the out-of-plane thermal conductivity, λ_3, did not exhibit any noticeable increase with the interleaved CNT sheets because of the high thermal resistance and phonon scattering between interfaces of the CNT, CF and resin.

The in-plane thermal conductivities of the pre-infused CNT sheet itself ($\lambda_{1,\,CNT}$ or $\lambda_{2,\,CNT}$) can be roughly estimated by a rule of mixtures. If it is assumed that the pre-infused CNT sheet and CF/epoxy ply are macroscopically homogenous [15]:

$$\lambda_{CNT} = \frac{\lambda - (1 - v_{CNT})\lambda_{CF}}{v_{CNT}} \tag{4}$$

where λ is the in-plane thermal conductivity of the CNT/CF hybrid composite, v_{CNT} is the volume fraction of the pre-infused CNT sheet, and λ_{CF} is the in-plane thermal conductivity of the CF/epoxy ply. The calculated axial/in-plane (1-direction) thermal conductivity, $\lambda_{1,CNT}$, and perpendicular/in-plane (2-direction) thermal conductivity, $\lambda_{2,CNT}$, of the pre-infused CNT sheet are 18.33 W/m·K and 13.15 W/m·K, respectively [7]. The higher thermal conductivity in the 1-direction, is likely due to inherent alignment of the CNTs in their as-manufactured state. The thermal conductivity of the pre-infused CNT sheet will be measured to confirm the estimated values.

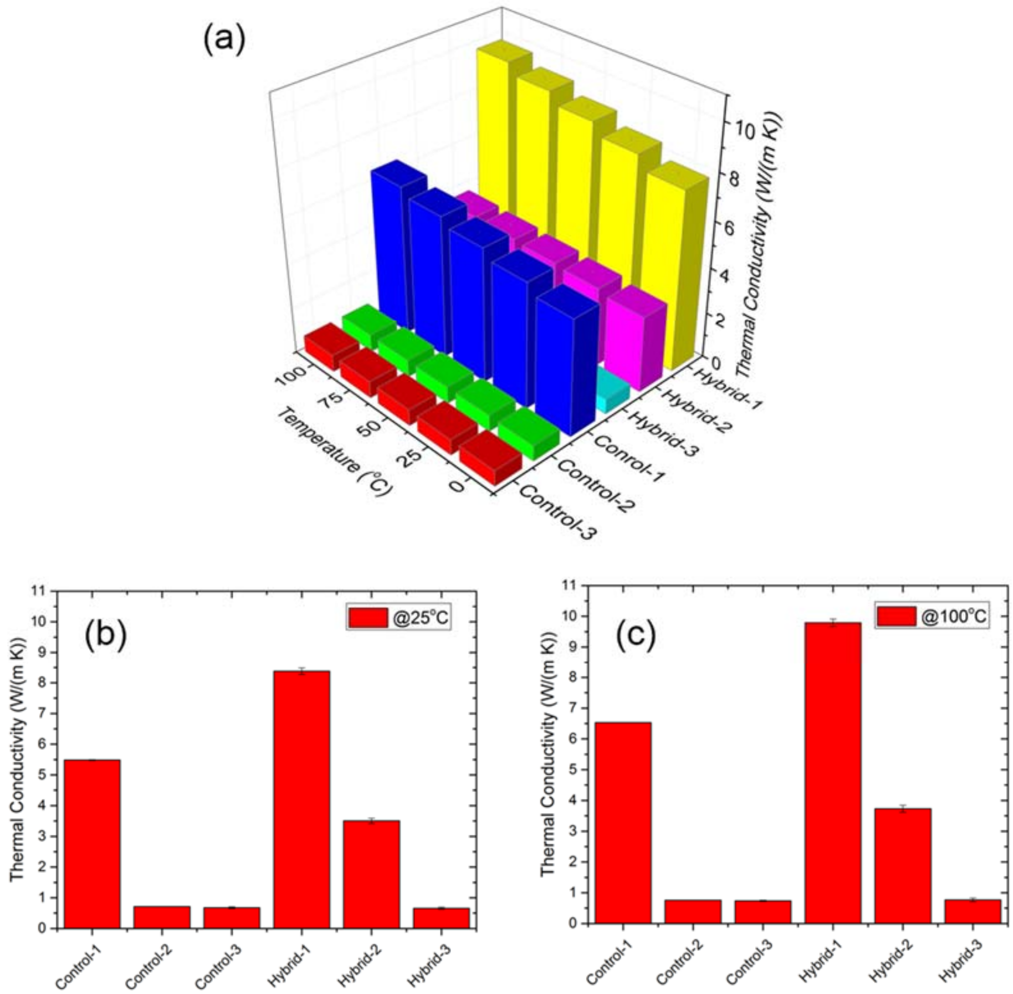

Figure 5. Orthotropic thermal conductivities (λ_1, λ_2 and λ_3) of control CF composite (Control-1, -2, and -3) and hybrid CNT/CF composite (Hybrid-1, -2, and -3).

DC electrical conductivities of the orthotropic control CF composite and hybrid CNT/CF composite are shown in Figure 6. The orthotropic electrical conductivities showed a trend similar to that of the thermal conductivities. The electrical conductivity in the axial direction of the control CF composite, σ_1, was about 12.1 S/cm, which is compatible to reported literature values [16]. However, the transverse electrical conductivities in-plane and out-of-plane, σ_2, and σ_3, were as low as about 0.01 and 0.002 S/cm, respectively, also consistent with literature values [16-17]. The low σ in the two in-plane directions will not afford effective electrical charge or current dissipation. As with the thermal conductivity, interleaving of CNT sheets between the CF plies enhanced the transverse electrical conductivity. The electrical conductivities of the hybrid CNT/CF composites are as high as about 21.4 S/cm for σ_1, 14.0 S/cm for σ_2, and 0.01 S/cm for σ_3, approximately 80% to 3 orders of magnitude increases compared to the conductivity of the control CF composite.

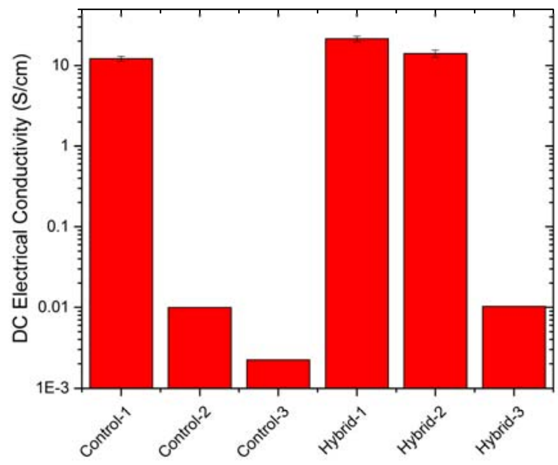

Figure 6. Orthotropic DC electrical conductivities (σ_1, σ_2 and σ_3) of control CF composite (Control-1, -2, and -3) and hybrid CNT/CF composite (Hybrid-1, -2, and -3).

4. CONCLUSION

Hybrid CNT/CF polymer composites were fabricated by interleaving layers of CNT sheets between Hexcel® IM7/8852 prepreg plies. Orthotropic thermal and electrical conductivities of the control CF composite and the hybrid CNT/CF polymer composite were characterized. Compared to the CF composite control, hybrid CNT/CF polymer composites exhibited approximately 50 and 400% increases in in-plane thermal conductivity in the axial- (1-direction) and perpendicular to axial (2-direction) directions. However, the out-of-plane (3-direction) thermal conductivity did not show any noticeable change when interleaved CNT sheets were added because of the large thermal resistance and phonon scattering in the interfaces of the CNT, CF and resin. The orthotropic electrical conductivities had a similar trend as the thermal conductivities. Interleaving of CNT sheets between the CF plies provided approximately 80% to 3 orders of magnitude increases in electrical conductivity. However, the electrical conductivity of the prepared hybrid CNT/CF polymer composite was not high enough to eliminate the usage of additional metal mesh LSP ($\sim 1\times10^5$ S/cm). The further studies of highly aligned CNT sheet, different layup configuration and highly densified carbon nanotube yarns are under research to improve the electrical conductivity. The hybrid CNT/CF polymer composite showed lower SBS than the control CF composite, because of poor interaction between the CNT and resin. These results will be utilized as a baseline for further interfacial enhancement studies.

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