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Title: **Structural CNT Composites Part II: Assessment of CNT Yarns as Reinforcement for Composite Overwrapped Pressure Vessels**

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ABSTRACT

Carbon nanotubes (CNTs) are one-dimensional nanomaterials with outstanding electrical and thermal conductivities and mechanical properties. This combination of properties offers routes to enable lightweight structural aerospace components. Recent advances in the manufacturing of CNTs have made bulk forms such as yarns, tapes and sheets available in commercial quantities to permit the evaluation of these materials for aerospace use, where the superior tensile properties of CNT composites can be exploited in tension dominated applications such as composite overwrapped pressure vessels (COPVs). To investigate their utility in this application, aluminum rings were overwrapped with thermoset/CNT yarn composite and their mechanical properties measured. CNT composite overwrap characteristics such as processing method, CNT/resin ratio, and applied tension during CNT yarn winding were varied to determine their effects on the mechanical performance of the CNT composite overwrapped Al rings (CCOARs). Mechanical properties of the CCOARs were measured under static and cyclic loads at room, elevated, and cryogenic temperatures to evaluate their mechanical performance relative to bare Al rings. At room temperature, the breaking load of CCOARs with a 10.8% additional weight due to the CNT yarn/thermoset overwrap increased by over 200% compared to the bare Al ring. The quality of the wound CNT composites was also investigated using x-ray computed tomography.

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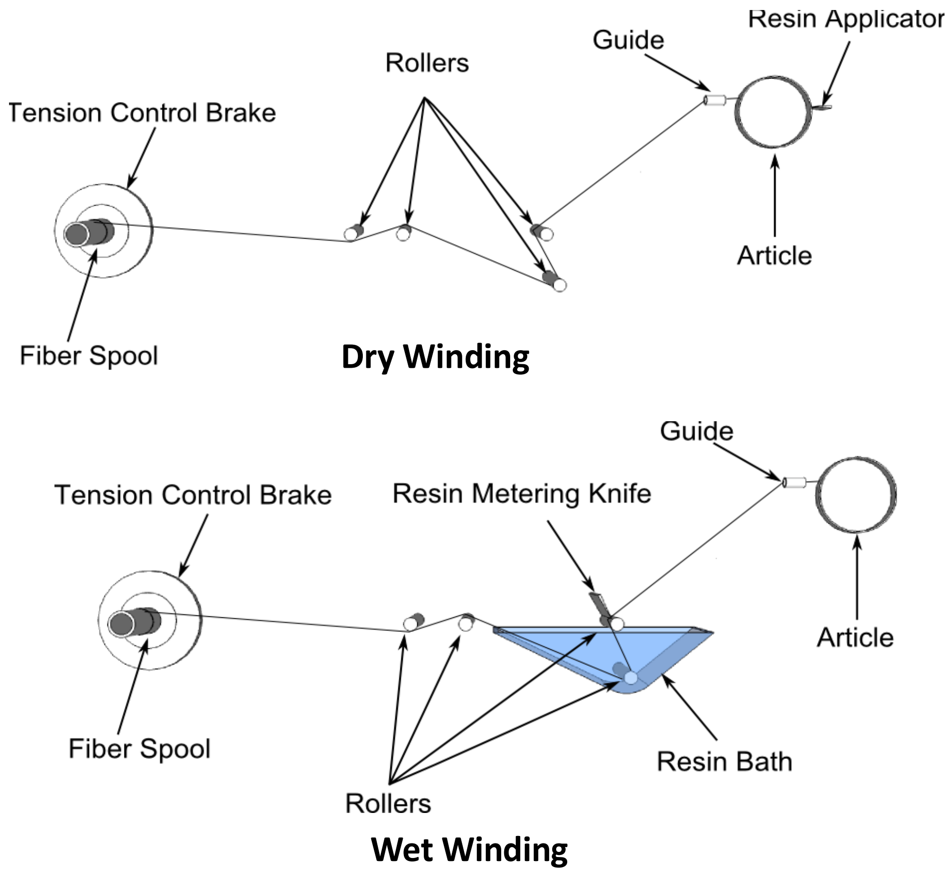
INTRODUCTION

Carbon nanotubes (CNTs) have been studied for various applications due to their superior electrical, thermal, and mechanical properties. However, the use of CNT based materials in structural applications remains a challenge due to high material cost, low volume availability, inconsistent and low quality, and processing difficulties. Recently, CNTs manufactured using a continuous floating iron catalyst chemical vapor deposition technique (Nanocomp Technologies, Inc.) have become commercially available in large quantities and material formats having quality high enough to be assessed for practical applications. In this process, the as-produced CNT web is condensed physically and chemically to create various carbon assemblages such as yarns, tapes, and sheets suitable for producing structural composites [1,2], especially in tension-dominated applications such as composite overwrapped pressure vessels (COPVs) [3-6] where strength-to-weight ratio exceeding state-of-the-art carbon fiber reinforced polymer (CFRP) composites can potentially yield significant weight savings.

The development of these nanomaterial based structural composites depends on the quality of the starting material as well as processing condition optimization. In this work, thermoset/CNT yarn composites were wrapped around aluminum rings to assess their performance as reinforcement of thermoset/CNT yarn nanocomposites in the COPV application. The CNT composite overwrapped aluminum (Al) rings (CCOARs) were fabricated under various winding conditions using a custom-built filament winder. The effects of these processing parameters on the mechanical performance of the CNT yarn layers were determined under various temperatures and loading conditions.

EXPERIMENTS

Thermoset/CNT yarn composite overwraps were prepared by direct winding of commercially available highly-densified CNT yarns (Nanocomp Technologies, Inc., 4 ply) onto a bare Al ring [McMaster-Carr Multipurpose Aluminum Tubing, 1.5 in (3.8 cm) and 1.43 in (3.6 cm) in outside and inside diameters respectively and 0.36 in (0.91 cm) nominal width] using a custom-built filament winder. The custom-built filament winder was constructed in-house by modifying a commercially available desktop filament winder (X-Winder®) as the starting platform. Modifications made to convert the as-received X-Winder 2.0 so it could be used to fabricate CCOARs included incorporation of a fine filament guide, a filament feeder system (breaker with a tension controller to handle the CNT spool), and winding substrate mounting hardware. These alterations provided greater control of the winding process and tailored the apparatus to handle CNT materials and are fully described in reference [7]. The filament winder was operated by X-Winder provided Designer and Executor software with some modifications to the G-code produced by the Designer to enable custom builds. The CNT yarns were wound in a 90 degree hoop direction, which is aligned with the tension direction during the mechanical tests, using various winding tensions. Thermoset Epon 828 with Epikure W cure agent (Hexion Inc.) was applied onto the CNT yarns by a "dry" or "wet" method as illustrated in Scheme I. In the dry winding process, CCOARs were prepared by applying resin directly onto each layer of the wound dry CNT yarn using a paintbrush with a 100 wt.% neat resin or 70 wt.% Epon



Scheme 1. Schematic diagrams of dry and wet winding.

828 solution in methyl ethyl ketone (MEK, Sigma-Aldrich). In the wet winding process, CNT yarn was passed through a resin bath containing a 70 wt.% Epon 828 solution diluted with MEK, and then directly wound onto an Al ring to produce Epon 828/CNT yarn composite overwrapped Al rings. Prior to winding the CNT yarn with resin, excess resin was removed by a metering blade located in the travel path of the CNT yarn. After depositing the desired length (based on number of turns) of CNT yarn, the as-prepared Epon 828/CNT overwrapped Al ring was removed from the winder and cured at 350 °F (177 °C) for 2 hrs with a 1 hr hold at 212 °F (100 °C) before ramping to 350 °F (177 °C). Curing was conducted under a vacuum bag environment. The cured CCOARs were kept at ambient conditions while awaiting further characterization.

The hoop tensile test method used was based on a modification of the ASTM standard D2290 (standard test method for apparent hoop tensile strength of plastic or reinforced plastic pipe by split disk method). In this method, tensile load is applied to the ring primarily in the region between split disks fitted into the cylinder. The physical dimensions and weight of the specimens were measured before and after the fabrication of thermoset/CNT yarn composite overwrap to determine weights of CNT yarn, polymer resin, and total reinforcement. A prepared CCOAR specimen was placed over a pair of steel split disks and the specimen/disk assembly was positioned into test fixture clevises and held in place using 0.28 in (0.71 cm) diameter steel pins. Ambient condition static tests were conducted in a servo-electric load frame equipped with a 20 kip (89 kN) load cell. For non-ambient static tests [-45 °F (-43 °C) and 120 °F (49 °C)], the mechanical properties were measured in a servo-hydraulic load frame equipped with a 20 kip (89 kN) load cell. The specimens were soaked for 15 min at the desired temperature before performing the static test. The static tests at various temperatures were conducted in displacement control mode at a crosshead speed of 0.02 in/min (0.05 cm/min). Specimens were loaded until observation of complete failure, which typically involved failure of the composite overwrap followed by failure of the Al ring on one side of the specimen. Force, stroke, temperature, and time data were recorded with a data acquisition frequency of 10 Hz over the complete duration of a static test. For the stiffness assessment test, specimens were subjected to three loading/unloading cycles followed by a final load to specimen failure. Peak forces of the three loading cycle were increased in the following order: 1375, 1650, and 1925 lbf (6116, 7340, and 8563 N); these loads were equivalent to 1.25, 1.5 and 1.75 times the load at yield of the bare Al ring [1100 lbf (4893 N) in this study], respectively. The specimen unloading rate was equal to the loading rate of 0.02 in/min (0.05 cm/min).

For the fatigue test, specimens were subjected to four sets of 15 loading/unloading cycles. Each cycle set included an initial load cycle up to a 1800 lbf (8007 N) [1.5 × 1200 lbf (5338 N, Al ring failure strength)] peak force and unloading to 5 lbf (22.2 N) followed by 14 cycles each up to a peak force of 1200 lbf (5338 N). The specimen loading and unloading rates were both 0.02 in/min (0.05 cm/min). This set of load cycles was repeated four times then the specimen was loaded to failure in order to calculate residual strength after the fatigue test cycles. Specimens tested at non-ambient conditions were soaked at the test condition for 15 min prior to testing.

Field emission-scanning electron microscopy (FE-SEM, Hitachi Model S-5200) was used to image as-received CNT yarns. A microfocus x-ray computed tomography (CT) system (Nikon Metrology) capable of high-resolution down to 5 microns and magnifications up to 160x was used for high-resolution nondestructive evaluation of as-prepared CCOARs. The detector used was a Perkin-Elmer 16 bit amorphous silicon digital detector with a 2000 × 2000 pixel array. The specimen was placed on the rotational stage, which was computer controlled and correlated to the position of the sample. As the sample was rotated 360 degrees (in 0.11 degree increments), the detector collected radiographs at each rotated angle as the x-ray path intersected the sample. Three-dimensional reconstruction of the collected radiographs produced a volume of data that can then be viewed along any plane in the volume.

RESULTS

The highly densified CNT yarns used in this study had linear densities that ranged between 22 and 30 g/km (tex) and were composed mostly of double walled CNTs with ~ 5 nm outer diameter. Figure 1 shows a representative photograph and CT images of an as-prepared Epon 828/CNT yarn overwrapped Al ring. The Al ring was overwrapped with a total 66 turns (8 m) of CNT yarn using the wet process (70 wt.% Epon 828 in MEK) at 0.55 lbf of winding tension. Two layers of Epon 828/CNT yarn composite fully covered the Al ring (Figures 1a and b) to yield a CCOAR without visible resin rich areas in the as-prepared CCOAR surface. However, the overwrapped composite contained a fairly high volume of micron-sized voids in both hoop direction (Figure 1c) and cross sectional (Figure 1d) views due to the physical characteristics of the yarn used and the relatively low winding tension.

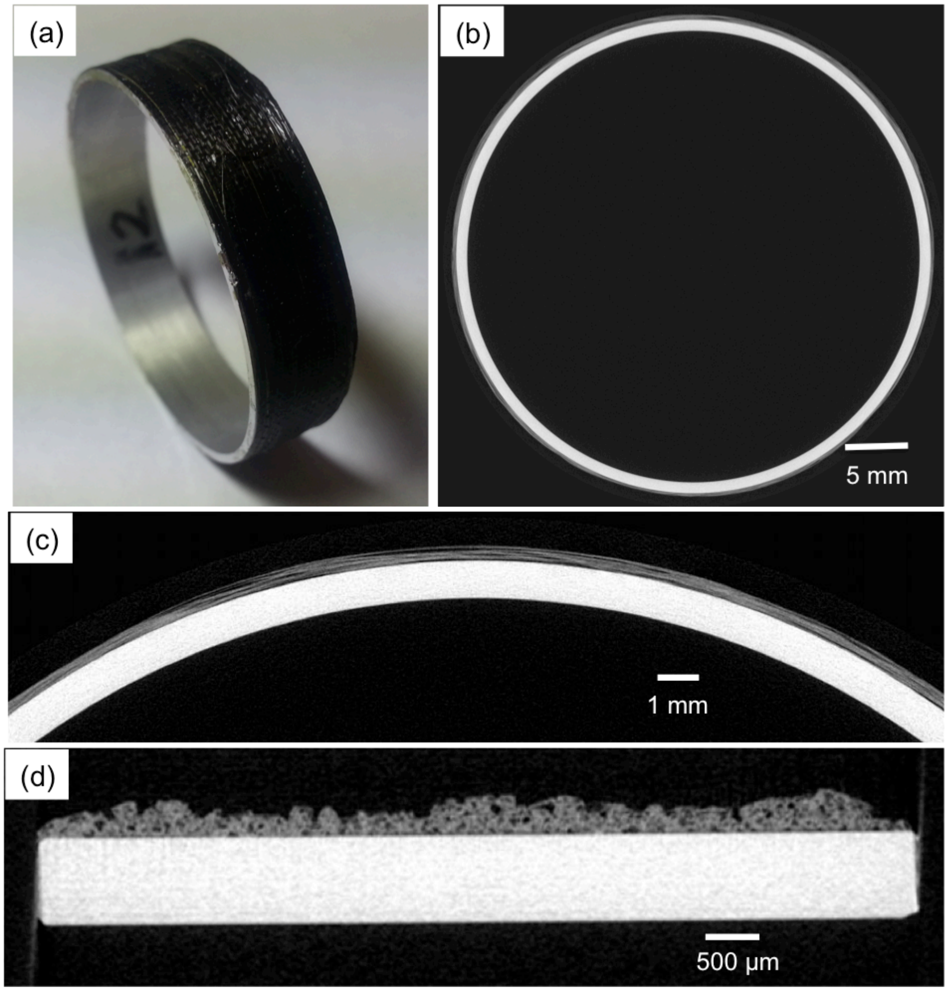


Figure 1. (a) Photograph of a prepared Epon 828/CNT yarn (66 turns) overwrapped Al ring. Related CT images of the prepared CCOAR were reconstructed parallel to (b and c) the CNT winding direction and (d) cross sectional cut of hoop direction. (c) is a magnified section of (b). The spatial resolutions are 20.7 μm in (b) and (c) and 5.3 μm in (d), respectively.

Figure 2 shows typical load-displacement curves of a bare Al ring, CCOARs prepared by various dry and wet processes with 66 turns of CNT yarns on an Al ring. The bare Al ring yielded at around 1100 lbf (4893 N) and continuously stretched until failure. The weight of bare Al ring and ultimate load at failure were 2585.8 ± 13.2 mg and 1187.5 ± 8.6 lbf (5282.3 ± 38.3 N), respectively. The CCOAR specimens were prepared by dry (70 and 100 wt.% Epon 828 resin) and wet (50, 70, and 100 wt.% Epon 828 resin) winding conditions at 0.55 lbf (2.45 N) of winding tension. The load-displacement characteristics of CCOARs were very similar, containing two linear regions before overwrapped composite failure. The first linear region was nearly identical to that of bare Al rings, followed by a second linear region whose slope depended on the overwrapped composite quality and amount of reinforcement (resin and CNT yarn). Overall, the breaking load of the CCOARs prepared by the wet process was slightly higher than those obtained from the dry process. The wet process most likely afforded the lubrication needed to improve CNT alignment and interfacial

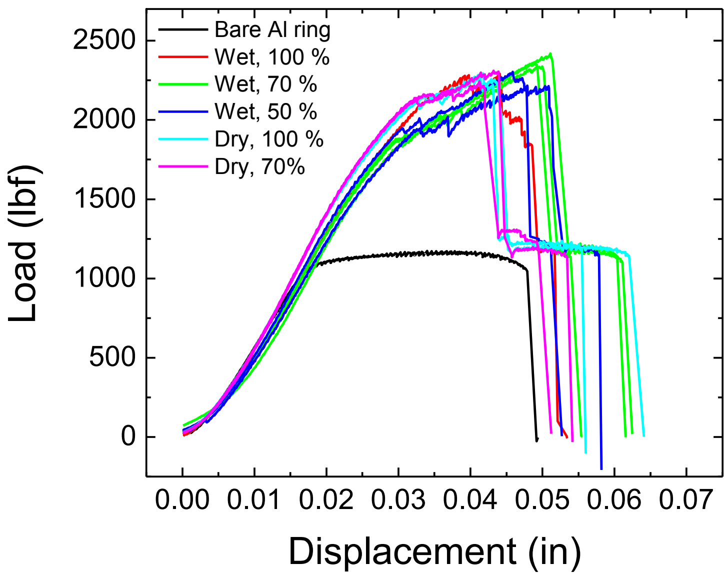


Figure 2. Load-displacement curves of CCOARs prepared by dry and wet processes at 0.55 lbf of winding tension. Percentages shown in the legend represent resin content (weight %) in MEK solvent. (1 lbf = 4.45 N)

adhesion between the wound CNT yarn and the applied resin.

The winding tension during the wet or dry process was an important variable controlling failure mode and the quality of composite overwraps, especially for void content. Figure 3a shows load-displacement curves of Epon 828/CNT yarn overwrapped Al rings, which were prepared at 0.55 and 1.00 lbf (2.45 and 4.45 N) of winding tension using the wet process with a 70 wt.% Epon 828 solution in MEK. All composite overwraps in the CCOARs catastrophically failed first before Al ring failure. The composite overwraps failed simultaneously at around 2500 lbf (11121 N). The slope of the linear region in the early part of the load-displacement curves increased when the winding tension increased as shown in Figure 3a. This behavior was most likely due to the strain-induced alignment of CNT networks under the tension applied during wet winding [8]. The ultimate load at failure did not significantly increase with higher winding tension. Stiffness assessment and fatigue tests data of CCOARs are presented in Figures 3b and c, respectively. The CCOAR continuously stiffened without failing when applied load was increased in the stiffness assessment test. Any significant changes or failures of overwrapped composites were not observed during load cycling during either the stiffness assessment or fatigue tests. The residual strength of the composite overwrap after the fatigue cycling [2225 lbf (9897 N)] decreased slightly in comparison to the room temperature static test [2378 lbf (10578 N)]. However, the composite overwrap continued to sustain load during fatigue cycling without significant mechanical degradation as shown in Figure 3c.

Based on the winding tension study, another set of CCOAR specimens with 2 layers (66 turns) of CNT composite overwrap was prepared using the wet process at 1.00 lbf (4.45 N) of winding tension to determine the effect of test temperature on the

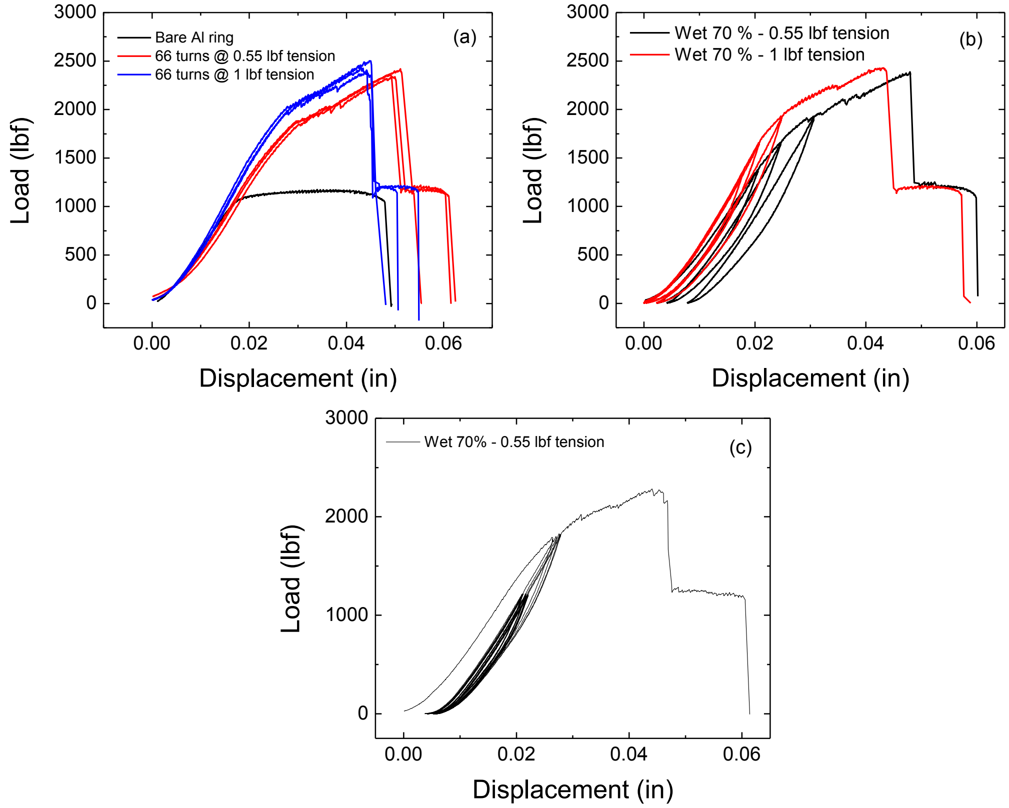


Figure 3. (a) Typical load-displacement (b) stiffness assessment, and (c) fatigue test curves of Epon 828/CNT yarn overwrapped Al rings prepared at 0.55 and 1.00 lbf of winding tensions. (1 lbf = 4.45 N)

mechanical performance of the overwrap. Figure 4 shows load-displacement curves of Epon 828/CNT yarn composite overwrapped Al rings tested at -45 °F (-43 °C), room temperature and 120 °F (49 °C). The shapes of the load-displacement curves at different temperatures were nearly identical. The ultimate load at failure increased slightly at the lower test temperature, while the stiffness of the composite overwraps decreased at both elevated and low temperatures compared to the room temperature test.

Figure 5 summarizes all room temperature static test data including CCOARs prepared by the dry and wet processes at various winding tensions. Note that the data from the wet process (70 wt.% Epon 828 solution) at 1.00 lbf (4.45 N) of winding tension included all tests data at various temperatures resulting in a large standard deviation in the plots. The delta load was calculated based on the type of failure observed. When the composite overwrap in CCOARs failed first followed by failure of the Al ring, the delta load was calculated by subtracting the maximum bare Al ring load for that particular test after composite failure from the ultimate failure load of the wrapping. When the composite overwrap and Al ring in CCOARs failed at the same time, the delta load was calculated by subtracting the average ultimate load of the Al ring [1187.5 lbf (5282.3 N)] from the ultimate load of the composite wrapping. In the CCOARs prepared by the wet process at 0.55 lbf (2.45 N) tension, the delta load was highest at 21 wt.% of resin content. The delta load/number of turns for dry 100 wt.%,

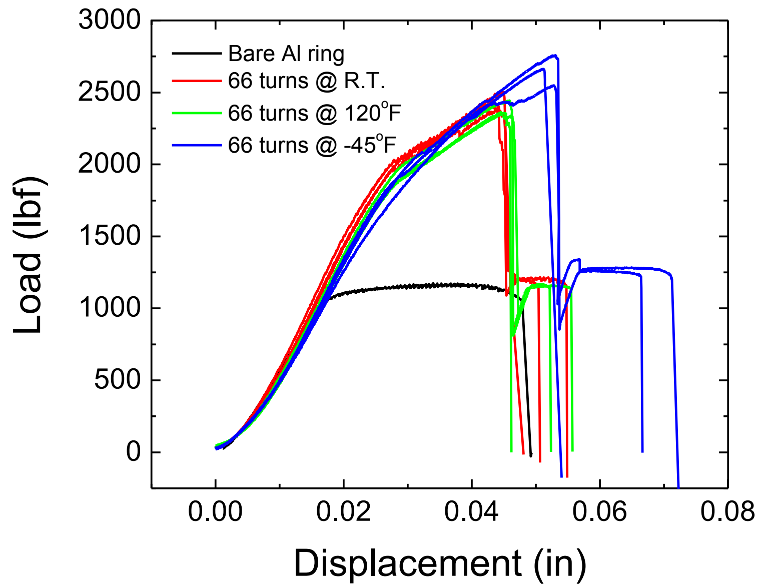


Figure 4. Load-displacement curves of CCOARs at various test temperatures. (1 lbf = 4.45 N)

dry 70 wt.%, wet 50 wt.%, wet 70wt.%, wet 100wt.%, and wet 70 wt% at 1.00 lbf (4.45 N) winding tension were 16.5, 16.4, 16.6, 17.7, 16.0, and 19.5 lbf/turn (73.4, 73.0, 73.8, 78.7, 71.2, and 86.7 N/turn), respectively. Based on the starting yarn specific strength and tex values, the ultimate load of the yarn used for the sample prepared by wet 70 wt.% winding at 1.00 lbf (4.45 N) was 8.65 lbf (38.48 N). If two sides of CNT yarn experienced tensile load in the hoop direction with one turn of CNT yarn wrapped around Al ring, the ultimate load of the processed CNT yarns [wet 70 wt.% at 1.00 lbf (4.45 N)] was 9.75 lbf (43.37 N). Therefore, the wet process, especially when used to wind at 1.00 lbf (4.45 N), significantly improved mechanical properties compared to the dry wound CCOARs. The improvement is most likely due to greater CNT alignment and interfacial adhesion between the CNT yarn and the applied resin.

CONCLUSION

Various Epon 828/CNT yarn composite overwrapped Al rings were assessed for potential use of CNT yarns in composite overwrapped pressure vessel applications. The systems studied were processed by both dry and wet winding conditions. Winding conditions including winding tension, resin application method, and number of CNT yarn composite layers were investigated to find the optimum conditions for enhancing the mechanical properties of CCOARs for structural applications. The wet winding process at 1.00 lbf (4.45 N) tension showed significantly improved load transfer [19.5 lbf/turn (86.7 N/turn) at 66 turns] through better interfacial adhesion between the CNT yarn and the applied resin. The optimum resin content in CCOARs ranged between 20 and 25 wt.%. Wrapping 10.2 wt.% of CNT/Epon 828 over Al rings resulted in a 208 % increase in hoop tensile properties compared to that of the bare Al ring.

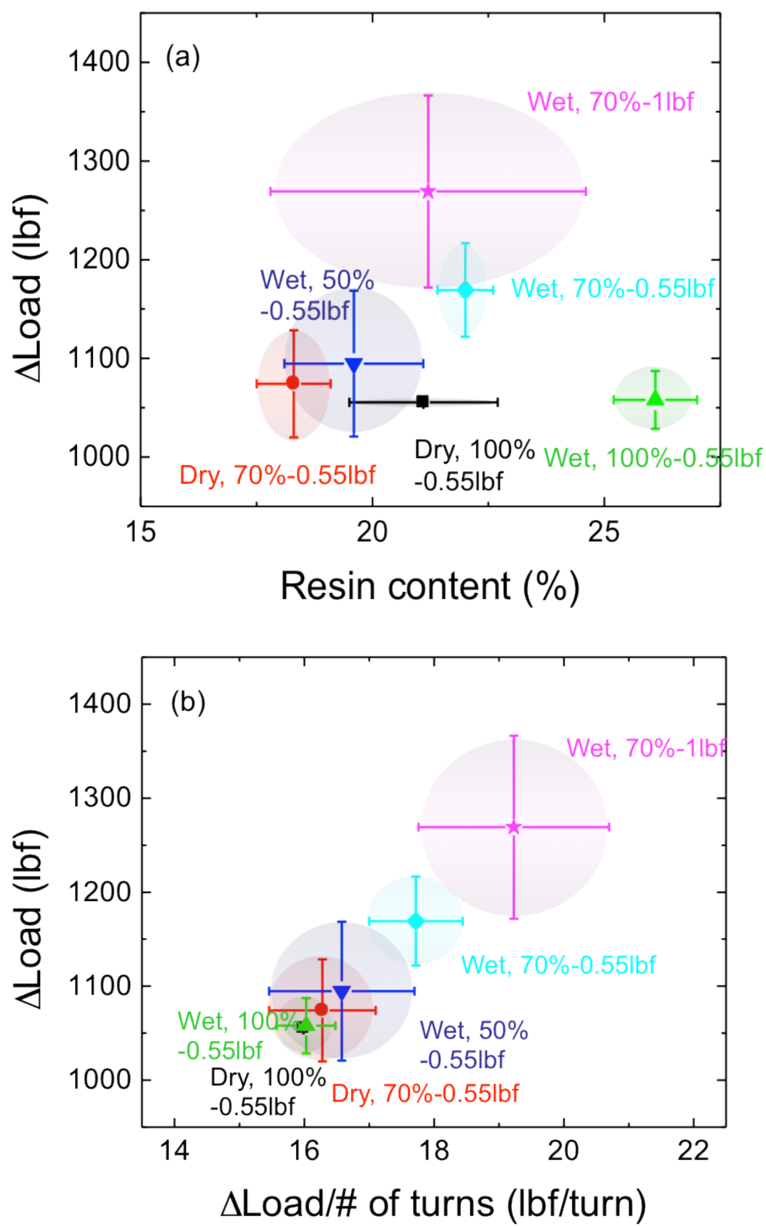


Figure 5. (a) Delta load vs. resin content and (b) delta load vs. delta load/number of turns plots of CCOARs prepared by various processes. (1 lbf = 4.45 N)

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