COVER SHEET

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Title: **Structural CNT Composites Part I: Developing a Carbon Nanotube Filament Winder**

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ABSTRACT

Carbon nanotube (CNT) based materials promise advances in the production of high strength and multifunctional components for aerospace and other applications. Specifically, in tension dominated applications, the latest CNT based filaments are yielding composite properties comparable to or exceeding composites from more established fibers such as Kevlar and carbon fiber. However, for the properties of these materials to be fully realized at the component level, suitable manufacturing processes have to be developed. These materials handle differently from conventional fibers, with different wetting characteristics and behavior under load. The limited availability of bulk forms also requires that the equipment be scaled down accordingly to tailor the process development approach to material availability. Here, the development of hardware and software for filament winding of carbon nanotube based tapes and yarns is described. This hardware features precision guidance of the CNT material and control of the winding tension over a wide range in an open architecture that allows for effective process control and troubleshooting during winding. Use of the filament winder to develop CNT based Composite Overwrapped Pressure Vessels (COPVs) shall also be discussed.

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INTRODUCTION

Nanomaterials, especially carbon nanotubes (CNTs) have been touted as the next generation of materials for use in aerospace structures due to their impressive properties at the nanoscale [1]. The combination of high strength, high electrical and thermal conductivities together with their low density suggested their potential utility as multifunctional reinforcements for composites [2, 3]. However, in order for these properties to be realized in practical applications, the nanomaterials need to be available in forms suitable for processing into structures, and tools have to be developed to enable these structures to be fabricated. This requires modification of existing tooling to accommodate the new material form or the creation of new capability. The carbon nanomaterials used in the current work came in the form of 1.2 m x 2.4 m (4 ft x 8 ft) sheets, 19 mm x 2.4 m (0.75 in x 8 ft) tapes and yarns 250-350 μm (0.0098-0.0137 in) in diameter and up to 300 m (328 yd.) long per spool (Nanocomp Technologies Inc.). In order to process these different material forms, a number of methods were developed. The processing of tapes and yarns will be discussed here while the processing of CNT sheets has been previously described in Ref. 4.

The aim of the present work is to use carbon nanotube based reinforcement in Composite Overwrapped Pressure Vessels (COPVs), a tension-dominated application. COPVs have a range of industrial applications. They can be found in a number of areas in aerospace vehicles including gas storage for pressurizing rocket fuel and oxidizer tanks, cold gas thrusters, and life support systems among others [5, 6]. Increasing the strength to weight ratio of the COPVs reduces structural weight and allows tanks to be filled to higher pressures. Both improvements yield enhanced system performance and an increase in payload that can be flown.

EXPERIMENTS

Continuous Carbon Nanotube Tape Stretcher and Winder

Carbon nanotube tapes obtained by slicing large sheets were considered for making large area composites and pressure vessel liner overwraps. The CNT sheets consist of carbon nanotubes that are somewhat loosely bound and only partially aligned during their manufacture. The tapes offered the advantage of the sheet being windable to cover large areas. Previous work showed that aligning the CNTs in the reinforcement greatly increased the mechanical properties of the resulting nanocomposites in the drawing direction [4, 7, 8], therefore, stretching of the CNT tapes was a necessary step to enhance their performance. While the batch processing method developed previously [4] was suited to fabricating composite panels, it was not readily scalable to handling large volumes of material. To overcome these deficiencies, a continuous stretcher and winder apparatus for CNT tapes was developed.

Figure 1 shows schematics of the continuous CNT tape stretcher and winder. Figure 1a is an isometric view of the setup while Figure 1b shows a top view. The setup consists of three stepper motors, X and Y for controlling the material supply and

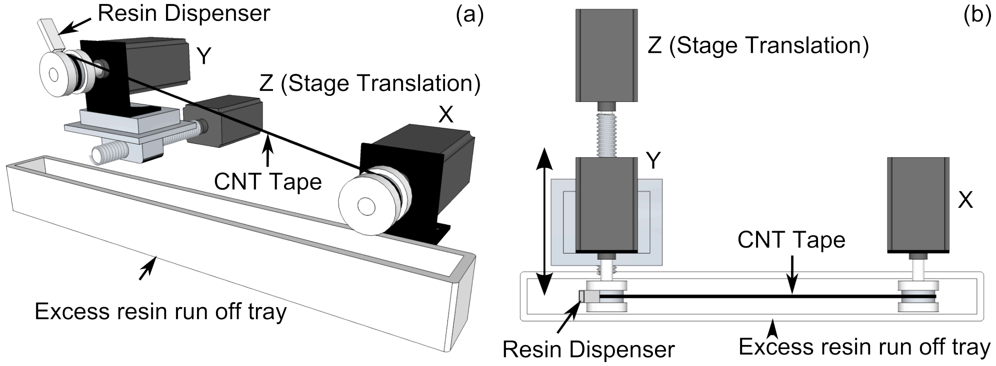


Figure 1. Schematics showing (a) an isometric and (b) top view of the continuous tape stretcher and winder.

the stretching level and Z for the stage translation. Note that the motor Y is mounted onto a stage controlled by the motor Z. Initially, the CNT material is wound around the spindle attached to motor X, and the substrate onto which the material is to be finally wound, an aluminum (Al) ring to simulate COPV liners in this case, is mounted onto the spindle Y. During stretching and winding, material is transferred between X and Y. By controlling the ratio of the tangential speed of the motors X and Y, stretching of the material is achieved. The stretching level per pass is obtained from

$$S_2 = (1 + x)\, S_1, \tag{1}$$

where x is the fractional stretching and S_2 and S_1 are the speeds of the leading and following motors, respectively. When material is being transferred from X to Y, Y is the leading motor and rotates at $(1+x)$ times the speed of motor X. On the reverse passes, when material is being transferred from Y to X, motor X rotates faster than motor Y. To gradually achieve a high degree of stretching and therefore alignment of the CNTs, the material can be passed between X and Y several times with the speed difference in the motors leading to incremental stretching on each pass.

On the final pass, the stretched CNT material is wound onto the Al ring substrate and resin applied. The stage translation motor Z ensures that the stretched CNT material, which would have significantly narrowed at this stage, evenly covers the full area of the substrate. A heat gun is used to initially dry out solvent from the resin and heat shrink tape or a breather bag is applied for oven curing of the articles.

Figure 2 shows a photograph of the experimental setup for continuous stretching and winding of CNT tapes. Three NEMA 23 Motors (DMX-A2-DRV-23, ARCUS Technology) were used. A 4-axis motion controller equipped with USB input (PMX-4EX-SA-TB9, ARCUS Technology) was used to drive the motors X, Y and Z. A custom LabVIEW based software code for the Continuous Stretcher and Winder (CSAW) was developed in-house and deployed onto a PC to control the motors. Figure 3 shows the user interface to this code. Three modes of operation were programmed: a. "Manual" mode in which the motors are under the direct control of the user and which is used for setting up (Figure 3a), b. "Auto-XY" in which both the X and Y motors are in motion (Figure 3b) and which is used for stretching and c. "Auto-XYZ" which, with the additional translation of the stage is used in the final pass to wrap the substrate (Figure 3c). Various controls on the CSAW interface are enabled or disabled depending on the selected mode.

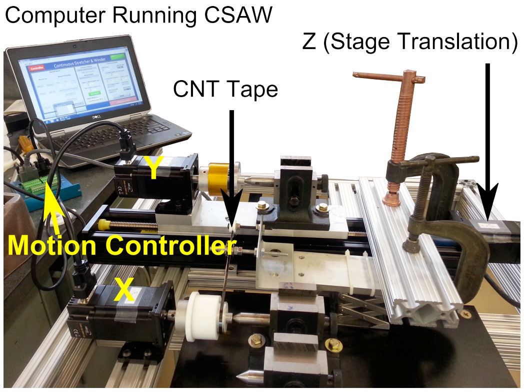


Figure 2. A photograph showing the apparatus that was assembled for continuous CNT tape stretching and winding.

(a)
X Pos: 0; Y Pos: 0; Z Pos: 0
Current Position: 0:0:0:0
10000 steps/revolution
Motor Status: 0:0:0:0:0:0:36:0:
Base X-Y Motor Speed (rps): 10000
Base Z Motor Speed (rps): 0.2
Switch Mode To ...: Manual
Strain (ΔL/L): 1
Initial Direction: ○ -1 ◉ +1
Set/Initial Number of Turns (Leader): 1
Z- Advance Rate (Steps/in): 100000
Z-Travel (+-Inch): 0
Turns Target (Leader): 1
Cycle Number: 0
Next Turns Target: NaN
Next Direction: ● -1 ● +1

(b)
X Pos: 0; Y Pos: 0; Z Pos: 0
Current Position: 0:0:0:0
10000 steps/revolution
Motor Status: 0:0:0:0:0:0:36:0:
Base X-Y Motor Speed (rps): 10000
Base Z Motor Speed (rps): 0.2
Switch Mode To ...: Auto-XY
Strain (ΔL/L): 1
Initial Direction: ○ -1 ◉ +1
Set/Initial Number of Turns (Leader): 1
Z- Advance Rate (Steps/in): 100000
Z-Travel (+-Inch): 0
Turns Target (Leader): 1
Cycle Number: 0
Next Turns Target: NaN
Next Direction: ● -1 ● +1

(c)
X Pos: 0; Y Pos: 0; Z Pos: 0
Current Position: 0:0:0:0
10000 steps/revolution
Motor Status: 0:0:0:0:0:0:36:0:
Base X-Y Motor Speed (rps): 10000
Base Z Motor Speed (rps): 0.2
Switch Mode To ...: Auto-XYZ
Strain (ΔL/L): 1
Initial Direction: ○ -1 ◉ +1
Set/Initial Number of Turns (Leader): 1
Z- Advance Rate (Steps/in): 100000
Z-Travel (+-Inch): 0
Turns Target (Leader): 1
Cycle Number: 0
Next Turns Target: NaN
Next Direction: ● -1 ● +1

Figure 3. Screenshots from the user interface of CSAW, a LabVIEW based tool developed for controlling a continuous tape stretcher and winder showing options available under (a) the "Manual" (initial setup), (b) "Auto-XY" (stretching) and (c) "Auto-XYZ" (winding) modes.

Carbon Nanotube Yarn Winding

For the COPV application which requires CNT composite wound around the pressure vessel with minimum splices, CNT yarn was deemed to be the more appropriate format.

An initial carbon nanotube filament winder was developed based on a tabletop computerized numerical control (CNC) lathe. This was used to make small tensile test specimens of the CNT composite. Figure 4 shows this setup. In order to wind CNT yarns, a number of modifications were made to the lathe. A carbon nanotube spool holder was mounted onto the lathe's translation table via an extension arm. To facilitate ready entry of the winding parameters, a LabVIEW based interface was developed that interpreted user parameters to create G-code to run the lathe. Figure 5a shows the user interface to the code. A fixture for making tensile test "sheet" specimens from the CNT yarn was designed and built for the CNC lathe based winder. The fixture features winding surfaces, as well as spindles that can be mounted onto the lathe. Figures 5b and 5c show the schematic of this fixture and the fixture with carbon nanotube yarn wound to produce a test specimen, respectively.

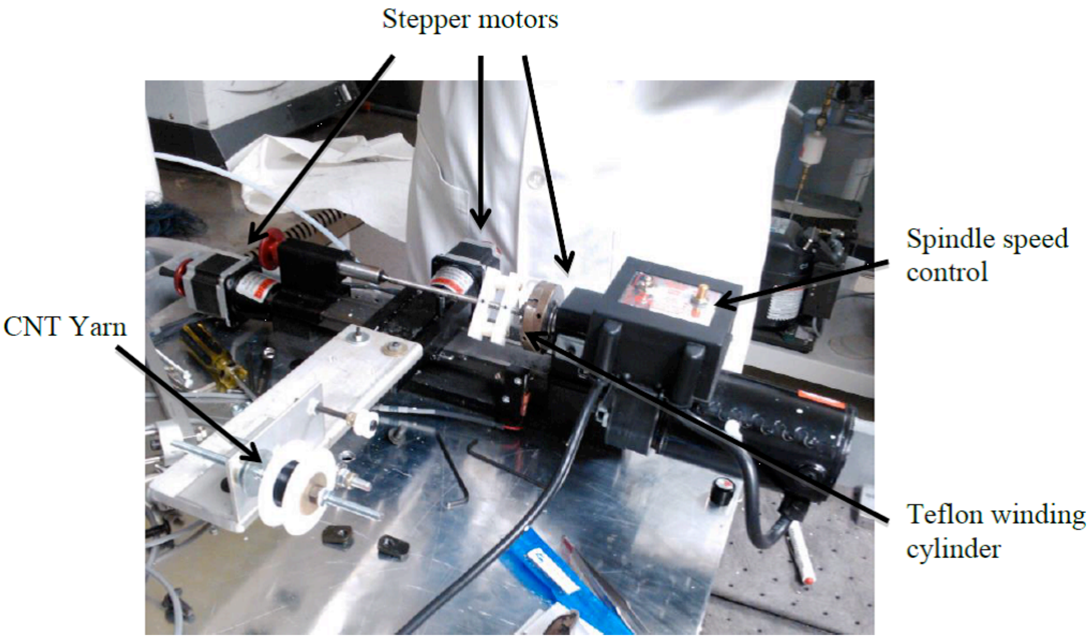
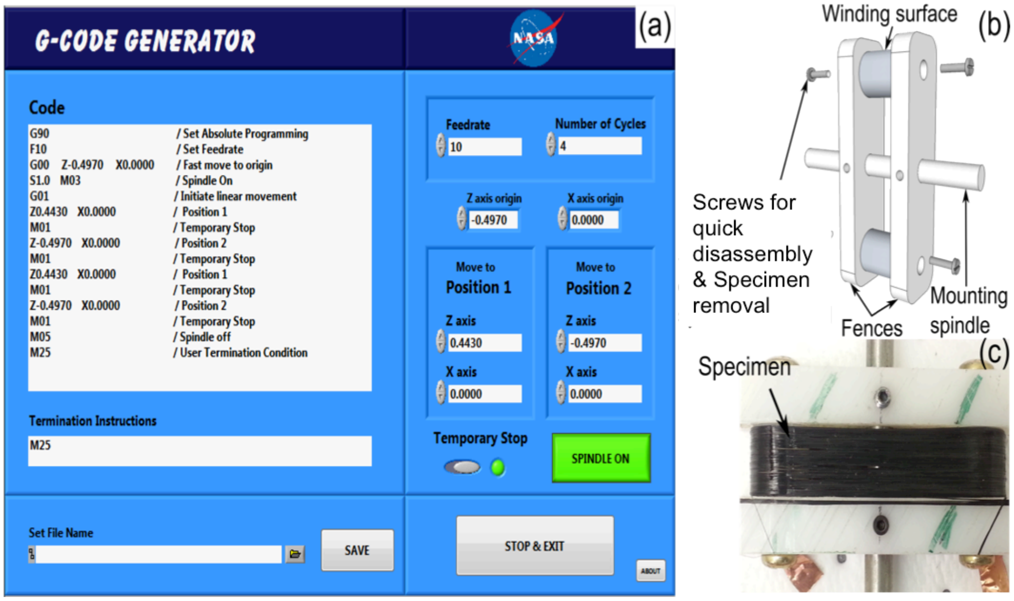


Figure 4. A tabletop CNC lathe based filament winder. Modifications to the lathe to enable filament winding included the mount for the CNT yarn spool.



Code

```
G90                        / Set Absolute Programming
F10                        / Set Feedrate
G00   Z-0.4970   X0.0000   / Fast move to origin
S1.0   M03                 / Spindle On
G01                        / Initiate linear movement
Z0.4430   X0.0000          /  Position 1
M01                        / Temporary Stop
Z-0.4970   X0.0000         / Position 2
M01                        / Temporary Stop
Z0.4430   X0.0000          /  Position 1
M01                        / Temporary Stop
Z-0.4970   X0.0000         / Position 2
M01                        / Temporary Stop
M05                        / Spindle off
M25                        / User Termination Condition
```

Termination Instructions: M25

Set File Name:

Feedrate: 10

Number of Cycles: 4

Z axis origin: -0.4970

X axis origin: 0.0000

Move to Position 1
Z axis: 0.4430
X axis: 0.0000

Move to Position 2
Z axis: -0.4970
X axis: 0.0000

Figure 5. (a) A screenshot of the user interface to the LabVIEW based code developed to generate winder control G-Code from user winding parameters. (b) A schematic of fixture designed for making tensile test specimens from wound CNT yarn and, (c) a sample of an as-prepared specimen.

Winding of CNT yarns onto larger substrates and achieving finer control required more work room and flexibility than was offered by the CNC lathe platform. Therefore, a recently developed commercial desktop filament winder (X-Winder®, www.xwinder.com) was obtained in kit form, assembled and used as the basis for a CNT yarn winder. X-Winder supplied Designer and Executor software was used to control this winder. For some builds, G-code created by the X-Winder Designer was modified for input into the Executor for winding. In order to better control the winding substrates and filament placement, a number of modifications were made to the as-received X-Winder 2.0. Figure 6 shows some of these modifications to the winder. To enable handling of a range of article geometries, the original work piece mounting hardware was replaced with the scroll chucks shown in Figure 6a (Bison-Bial Type 3286, 49 mm (1.9 in) 3-Jaw (Solid) Scroll chucks). To hold the Al rings which were used to simulate winding onto a pressure vessel liner, custom designed holders were 3D printed (Figure 6a and 6b). Two types of payout eyes with diameters around 300 µm (0.0118 in) were used for improved guidance of the CNT filament, which is much thinner than commercial carbon, glass and Kevlar fibers for which the X-Winder was initially designed. Figures 6a and 6c show the payout eyes used for wet and dry winding, respectively. For wet fiber winding, a custom built 5 ml syringe was used with the tip of a plastic pipette as a glued insert. A fly tying bobbin was used for dry winding. For both the wet and dry payout eyes, a fly tying bobbin threader was used to feed the filament through the payout eye. In addition to controlling the placement of the filament, tension control was essential for high quality winding. Therefore, a table mounted tension brake (Magnetic Technologies LTD) was added to the system (Figure 6d). This brake steps from 0 to 100 % non-linearly. The tension at different settings of the brake was verified using hand held tension meters. Load cells and an indicator for online (as the operator winds) tension measurements were also added to the winder. Figure 6e shows one of these load cells. A two Zone Digital Indicator and 10 lb (45 N) load cells (Montalvo Corp) were used for the online measurements. Resin metering was achieved by addition of a foam squeegee (slit McMaster Weather

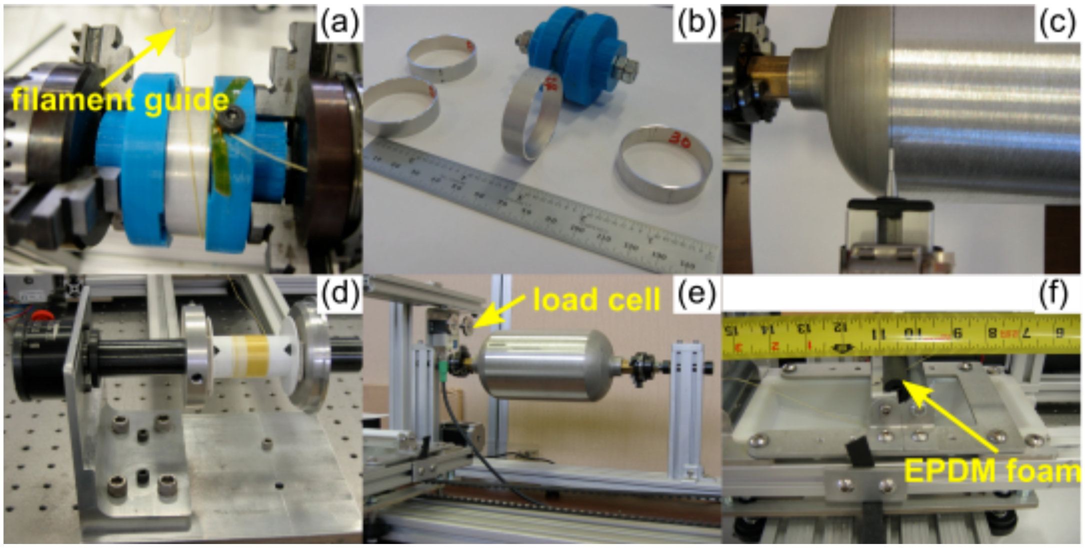


Figure 6. The key modifications made to a commercial desktop filament winder to enable winding of CNT yarns include (a) chucks to hold various work pieces and a custom wet winding filament guide, (b) a 3D printed Al ring holding fixture, (c) a dry winding filament guide, (d) a tension control brake and yarn feeder, (e) tension measuring load cells and (f) a resin metering foam element.

Resistance EPDM Foam Tube) to the as-provided doctor blade pressed against a cylindrical roller (Figure 6f). In dry winding, the resin reservoir was kept empty and resin only applied, with a soft artists paintbrush, when the material reached the substrate. Pulling the dry fiber through the system potentially allowed for higher winding tensions to be achieved without the lubricating effect of the resin. In the wet winding process, the filament went through a resin filled bath, passed the resin metering blade which removed any excess resin and then met the substrate. The wet process was expected to more thoroughly soak the filament with resin, ensure even coating of the filament, as well as be more amenable to full automation of a continuous yarn infusion and winding process.

In addition to the above machine modifications, a number of protocols were adopted to optimize the machines for CNT winding while minimizing the waste of material, thus reducing the cost of the process development effort. Magnetic tape was used to optimize the parameters of the continuous stretcher and winder. As part of the initial investigation of the CNT yarn winder performance, and to determine the effect of various winding parameters on a larger substrate, the payout eye was replaced with a spring loaded pencil and the surface of the substrate was covered with plain paper for winding pattern tracing. Regular cotton thread of a diameter close to that of the carbon nanotube yarn was used to study winding speed, material placement and to determine material length requirements. Winding tension was verified using Kevlar fiber.

RESULTS

While stretching the CNT tapes enhances their properties significantly, the improvement was insufficient to match the tensile properties of CNT yarns which are significantly drawn and therefore highly aligned during the initial manufacturing and densification process. Furthermore, stretching the CNT tapes led to significant shrinkage in width. While this post-processing step yielded their highest properties, these properties were still far lower than those obtained for CNT yarns, even as the width of the stretched tape approached that of the CNT yarns. Additionally, as the tapes were cut from sheets with maximum length of 2.4 m (8 ft), segments had to be spliced together to obtain continuous reinforcement. This splicing will likely lead to weak joints in large scale composite fabrication where continuous reinforcements are desirable.

Figure 7 shows the final yarn winder. After exploring a range of platforms and settings, it was possible to obtain a winder that can efficiently handle carbon nanotube filament winding with high throughput, control and repeatability to enable routine fabrication of test articles. Figure 8 shows some of the CNT yarn composite wrapped test articles that were built using this winder. These included numerous test rings (Figure 8a) and a 270 mm long x 120 mm diameter (10.8 in x 4.75 in) pressure vessel completely wound with CNT yarn composite in the hoop direction (Figure 8b).

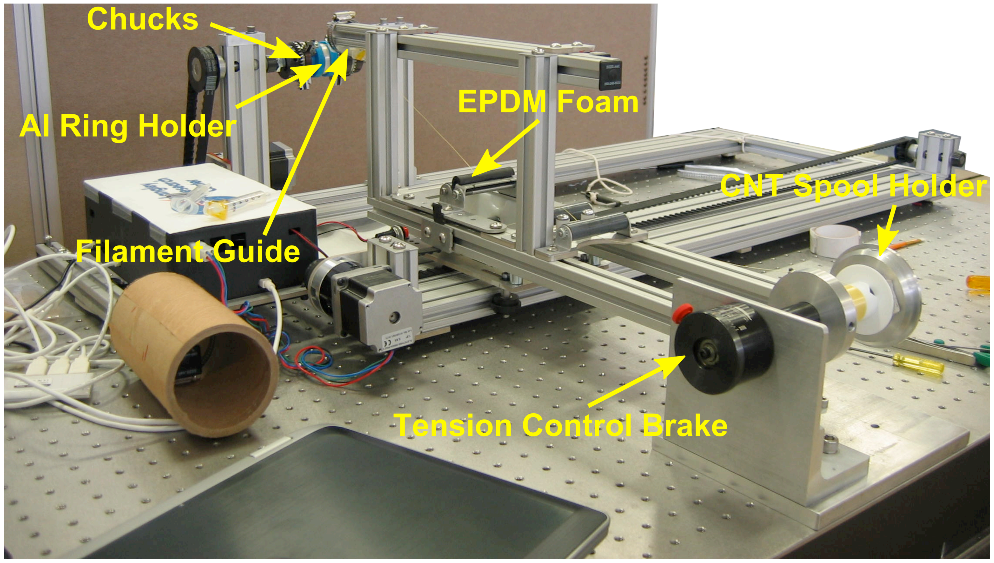


Figure 7. A photograph of the final winder showing some key modifications.

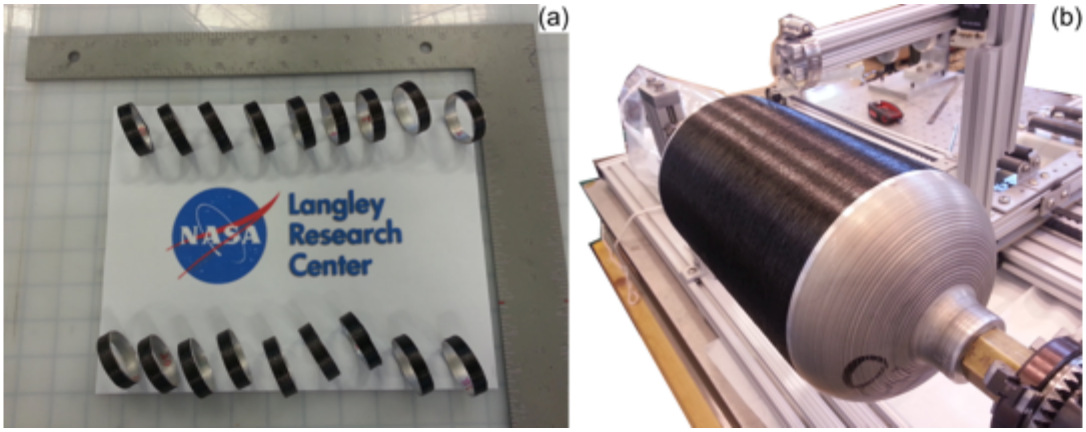


Figure 8. Test articles made using the winder include (a) CNT overwrapped aluminum rings and (b) a carbon nanotube yarn overwrapped pressure vessel.

CONCLUSION

Nanomaterials processing remains a significant challenge to be overcome in order for the potential of these materials to be fully realized. A series of apparatuses developed to accommodate the fast evolving development of CNT materials formats was described here. Designing and testing these processing methods yielded lessons on the handling of these materials in an efficient and cost effective way, while optimizing a lab scale process amenable to eventual adoption on commercial winders that will be used to produce articles that pass the rigorous requirements for flight test articles.

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