TECHNICAL REPORT
NATICK/TR-19/007

AD ________________

CARBON NANOTUBE COMPOSITES FOR ENERGY ABSORPTION

by

Melissa J. Roth

February 2019

Final Report
October 2015 – December 2017

Approved for public release; distribution is unlimited

U.S. Army Natick Soldier Research, Development and Engineering Center
Natick, Massachusetts 01760-5000

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YYYY)* 07-02-2019	**2. REPORT TYPE** Final	**3. DATES COVERED** *(From - To)* October 2015 – December 2017

4. TITLE AND SUBTITLE CARBON NANOTUBE COMPOSITES FOR ENERGY ABSORPTION	**5a. CONTRACT NUMBER**
	5b. GRANT NUMBER
	5c. PROGRAM ELEMENT NUMBER
6. AUTHOR(S) Melissa J. Roth	**5d. PROJECT NUMBER** IMTP 16-153
	5e. TASK NUMBER
	5f. WORK UNIT NUMBER
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) U.S. Army Natick Soldier Research, Development and Engineering Center ATTN: RDNS-SES-WI 10 General Greene Avenue, Natick, MA 01760-5000	**8. PERFORMING ORGANIZATION REPORT NUMBER** NATICK/TR-19/007
9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)	**10. SPONSOR/MONITOR'S ACRONYM(S)**
	11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

This report contains the results of work performed during the period October 2015 to December 2017 in support of the Product Manager – Soldier Protective Equipment (PM – SPE) goal of improving blunt impact protection of helmets. The work reported herein was performed by the U.S. Army Natick Soldier Research, Development, and Engineering Center (NSRDEC) in conjunction with North Carolina State University (NCSU) and CF Technologies, Inc. The goal of this effort was to enhance the resiliency of carbon nanotube (CNT) structures produced by NCSU by infusing the structures with a polymer matrix. The end result was a compressible foam-like structure with good recoverability after impact and good temperature stability.

15. SUBJECT TERMS

FOAM
IMPACT
LAYERS
HELMETS
PRESSURE
INFUSIONS
POLYMERS
CNT FOAMS
DISPERSION
RESILIENCY
COMPOSITES
TEAM WENDY
FABRICATION
HELMET PADS
IMPACT TESTS
BLUNT IMPACT
HIGH STRENGTH
PADS(CUSHIONS)
CNT COMPOSITES
RECOVERABILITY
MICROSTRUCTURE
NANOSTRUCTURES
STRAIN(MECHANICS)
CARBON NANOTUBES
ENERGY ABSORPTION
FOAMED MATERIALS
TEST AND EVALUATION
STRESS STRAIN CURVES
PROTECTIVE EQUIPMENT
TEMPERATURE STABILITY
CNT(CARBON NANOTUBES)
PERFORMANCE(ENGINEERING)

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	**b. ABSTRACT**	**c. THIS PAGE**			Melissa J. Roth
U	U	U	SAR	80	**19b. TELEPHONE NUMBER** *(include area code)* 508-233-6055

Table of Contents

Table of Contents iii

List of Figures iv

List of Tables v

CARBON NANOTUBE COMPOSITES FOR ENERGY ABSORPTION 1

1 Introduction 1

2 Materials 4

3 Methods 5

3.1 Randomly Dispersed CNTs 5
3.1.1 MWCNTs in polyurethane 5
3.1.2 Chemically induced phase separation 5

3.2 Composite fabrication with vertically aligned CNT arrays 6
3.2.1 Vacuum infusion 6
3.2.2 Capillary infusion 6
3.2.3 End encapsulation 7
3.2.4 Freeze drying 7

3.3 Composite fabrication with spun CNT sheet foams 7
3.3.1 Capillary infusion 8
3.3.2 Freeze drying 8
3.3.3 Supercritical CO_2 8

3.4 Mechanical testing 9
3.4.1 Microscopy 9
3.4.2 Compression testing 9
3.4.3 Dynamic mechanical analysis 9
3.4.4 High impact testing 9

4 Results and Discussion 10

4.1 Randomly Dispersed CNTs 10

4.2 Vertically aligned CNT arrays 12

4.3 Spun CNT sheet foams 19

5 Conclusions 24

6. References 25

Appendix A 26

Appendix B 65

List of Figures

Figure 1 - (A) A VACNT array 5 mm in height and (B) a spun CNT sheet foam prepared by spinning a VACNT array (courtesy of NCSU) 2
Figure 2 - Schematic showing end-encapsulation of CNT arrays with a polymer film (courtesy of NCSU).......... 2
Figure 3 - Materials used to produce an epoxy foam via CIPS 6
Figure 4 - Fabrication of spun CNT sheet foams from VACNT arrays (courtesy of NCSU) 8
Figure 5 - Microscope images of 0.5% CNTs in polyurethane without the use of toluene as a CNT solvent and with toluene. Poor dispersion of the nanotubes is somewhat mitigated by the use of toluene; however, the toluene prevented foaming and caused the polyurethane to be more rubber-like. 10
Figure 6 - Stress-strain curves for Team Wendy pads and polyurethane foams 11
Figure 7 - Storage modulus of polyurethane foams as a function of temperature 12
Figure 8 - SEM image of a 60 min post treated VACNT array vacuum infiltrated with PVA shows that the PVA will not wet the CNTs without a surfactant. 13
Figure 9 - A 60 min post treated VACNT array vacuum infiltrated with PVA using Triton™ X-100 showing surface damage caused to the array by capillary action during drying. 14
Figure 10 - 30 min post treated VACNT arrays infiltrated with solvents and passively dried cracked during drying of the solvents. 14
Figure 11 - SEM images of a top-down view of a 30 min post treated VACNT array freeze dried with PVA/Triton™ X-100 and an image of the array after drying. Note the cracking and surface damage. 15
Figure 12 - a 2" x 2" x 3/4" sample consisting of five stacked 20% PDMS VACNT arrays (courtesy of NCSU).......... 15
Figure 13 - Storage modulus as a function of temperature for CNT arrays as compared to Team Wendy pads 16
Figure 14 – Stress-strain curves for Team Wendy pads and polymer-free VACNT arrays.......... 18
Figure 15 - Stress-strain curves of infused CNT arrays compared to a polymer-free VACNT array 19
Figure 16 - SEM images of CNT sheet foams infiltrated with polymer.......... 20
Figure 17 - DMA results for sheet foams show minimal temperature dependence of the storage modulus for infiltrated CNT foams (CSA1 and SA5). 21
Figure 18 - Spun CNT sheet foams with PVA after compression testing in the horizontal and vertical alignment directions. Buckling can be seen after compression (courtesy of NCSU).......... 22
Figure 19 - Stress-strain curves of select infused spun CNT sheet foams compared to a polymer-free sheet foam.......... 23

List of Tables

TABLE 1 - MODULUS AND RECOVERABILITY OF TEAM WENDY PADS AND POLYURETHANE FOAMS WITH RANDOMLY DISPERSED CNTS 11
TABLE 2 - HIGH IMPACT TEST RESULTS OF TEAM WENDY AND VACNT ARRAYS INFILTRATED WITH PDMS 16
TABLE 3 - STORAGE MODULUS AND RECOVERABILITY OF TEAM WENDY AND VACNT ARRAY SAMPLES AT 60% COMPRESSION FOR 10 CYCLES 17
TABLE 4 - STORAGE MODULUS AND RECOVERABILITY OF SPUN CNT SHEET FOAM SAMPLES AT 60% COMPRESSION FOR 10 CYCLES 22
TABLE 5- HIGH IMPACT TEST RESULTS OF TEAM WENDY AND SPUN CNT ARRAYS INFILTRATED WITH PVB 23

Preface

The work reported herein was performed by the U.S. Army Natick Soldier Research, Development, and Engineering Center (NSRDEC) in conjunction with North Carolina State University (NCSU) and CF Technologies, Inc. in support of the Product Manager – Soldier Protective Equipment (PM – SPE) goal of improving blunt impact protection of helmets. Work was performed during the period October 2015 to December 2017 using Core Science and Technology (S&T) funds under Carbon Nanotube Foam Composite for Energy Absorption [IMTP 16-153]. The goal of this effort was to enhance the resiliency of carbon nanotube (CNT) structures produced by NCSU by infusing the structures with a polymer matrix. The end result was a compressible foam-like structure with good recoverability after impact and good temperature stability.

Acknowledgements

The authors would like to thank John Fitek, Thomas Tiano, Pearl Yip, Robert DiLalla, and David Colanto for their technical support on this project.

CARBON NANOTUBE COMPOSITES FOR ENERGY ABSORPTION

1 Introduction

The work reported herein was performed by the U.S. Army Natick Soldier Research, Development and Engineering Center (NSRDEC) in conjunction with North Carolina State University (NCSU) and CF Technologies, Inc. in support of the Product Manager – Soldier Protective Equipment (PM-SPE) goal of improving blunt impact protection of helmets.

Current Army Combat Helmets (ACH) are lined with polyurethane-based Zorbium® Action Pads (ZAP™) from Team Wendy for comfort and energy absorption during impacts. These pads are lightweight, comfortable, inexpensive, and meet the current ACH purchase description blunt impact protection requirement of maintaining a peak acceleration of less than 150 Gs for impacts at 10 ft/s [1]. Unfortunately, the performance of these polyurethane-based foam pads is temperature-dependent and does not meet the blunt impact protection requirements at higher impact velocities often experienced during blast events and airborne operations. The end goal of this project is a foam with maximized recoverability, improved impact energy absorption over Team Wendy ZAP™, and better temperature stability at a density comparable to the Team Wendy ZAP™ pads.

In this effort, the potential of utilizing vertically aligned CNT (VACNT) arrays developed by Dr. Phillip Bradford at NCSU was investigated as the foundation for a higher performance helmet pad. NCSU has developed a method of growing VACNT arrays up to 5 mm tall and post-treating them by chemical vapor deposition (CVD) to stabilize the arrays [2]. This post-treatment grows carbon material radially from each nanotube in the array. They have shown that the mechanical properties of these arrays can be tuned by varying the post-growth CVD treatment times and that the post-growth treatment improved the recoverability of the arrays after compression [2]. However, studies have also shown that CNT arrays are not typically recoverable after compression due to localized buckling of the arrays [3] [4] [5]. When compressed, the CNTs buckle and can come into contact with neighboring CNTs. Due to significant van der Waals interactions between CNTs, the deformation caused by buckling may be permanent depending on the density and surface area of the arrays. The project team attempted to mitigate this issue by infusing the arrays with a polymer.

NCSU has also developed a novel method of spinning these VACNT arrays into an aligned low-density carbon “foam”. These VACNT arrays and foams can be seen in Figure 1. The work described herein is an effort to infiltrate these two types of CNT structures with polymer materials to attempt to mitigate buckling of the CNT vertical arrays during compression. Multiple approaches were used to determine the best method of polymer infiltration that would allow for good stabilization without interfering with the alignment of the arrays. Loose CNTs randomly dispersed in polyurethane were also fabricated as a baseline to determine if the unaligned CNTs would improve the strength and temperature stability of the foam.

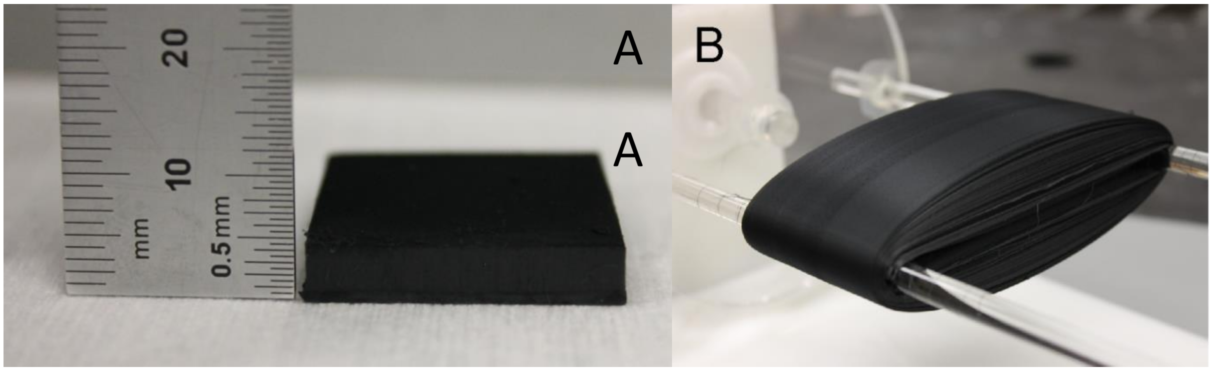


Figure 1 - (A) A VACNT array 5 mm in height and (B) a spun CNT sheet foam prepared by spinning a VACNT array (courtesy of NCSU)

Vacuum assisted polymer infusion was performed at NSRDEC using polydimethylsiloxane (PDMS), which can be easily dissolved in organic solvents to adjust the viscosity as needed. The vacuum removed the air within the CNT structure, which provided a driving force for polymer resin wetting. NCSU also infiltrated arrays with PDMS solution through the use of capillary action.

NCSU also used PDMS to encapsulate the ends of the CNT arrays in order to stabilize the arrays. This was done by casting a thin polymer film (50-200 µm) onto two flat plate mold surfaces and then sandwiching the CNT array between the filmcoated plates during curing, as shown in Figure 2. The PDMS viscosity and film thickness determined how deeply the polymer film infiltrated the CNT array. The low-density spun arrays were also infiltrated with varying concentrations of PDMS.

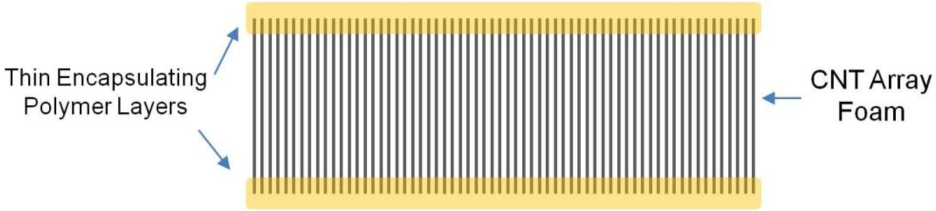


Figure 2 - Schematic showing end-encapsulation of CNT arrays with a polymer film (courtesy of NCSU)

In addition, NSRDEC and NCSU tried creating a foam structure within the CNT arrays by freeze drying and supercritical drying. Freeze drying has previously been used to create polymer microstructures [6], and was thus used to create a lightweight foam within the CNTs. Polyvinyl alcohol (PVA) was used because of its solubility in water. Triton™ X-100 was used as a surfactant to aid in wetting the CNTs. The CNT arrays were first infiltrated with a PVA/water/Triton™ X-100 solution and frozen. The water was then removed in a freeze-drier, leaving behind the CNT array infused with a PVA powder.

Supercritical carbon dioxide (scCO_2) drying and in-situ polymerization was also used as a method of infiltrating the CNTs with a polymer stabilizer through a contract with CF Technologies, Inc. (Hyde Park, MA). Their methods are outlined in Appendix A. Polyvinyl butyral (PVB) was selected for infiltration for its low cost, flexibility, good solubility, and high adhesion [7].

Another set of experiments performed at CF Technologies focused on in-situ polymerization of aerogels inside the polymer arrays. Aerogels are low density materials characterized by three-dimensional nanostructures [8] which can offer lightweight reinforcement to the CNT arrays.

All materials were evaluated by compression testing, dynamic mechanical analysis (DMA), and scanning electron microscopy (SEM). Cyclical compression testing was performed to determine the storage modulus and recoverability of the foams after 10 compression cycles. DMA was performed to show the temperature dependence of the modulus of the foam. SEM images were taken in order to obtain for visual confirmation of polymer infiltration. Several materials selected for their promising traits were scaled up in size to 2” x 2” squares for high impact testing.

The materials, test methods, and results described in the following chapters detail the efforts by NSRDEC, NCSU, and CF Technologies to find a recoverable, temperature stable reinforced CNT foam material.

2 Materials

Loose multiwalled carbon nanotubes (MWCNTs) were purchased from NanoTechLabs (Yadkinville, NC). All VACNT arrays and spun arrays were provided by NCSU as a deliverable under contract W911NF-11-D-0001. A two-part polyurethane foaming mix (PolyFoam F-3, 3 lb/ft^3) was purchased from Polytek Development Corp (Easton, PA). Poly(propylene glycol) bis(2-aminopropyl ether), 1-octadecanol, 1-methylimidazole, bisphenol A diglycidyl ether, N,N-dimethylformamide (DMF), tetrahydrofuran (THF), and Triton™ X-100 were purchased from Sigma Aldrich (St. Louis, MO). Exceval™ AQ4104 polyvinaly alcohol was obtained from Kuraray America. Toluene was purchased from VWR (Radnor, PA).

Vacuum experiments were conducted in a Binder vacuum oven model VDL-23.The SEM used for imaging was an FEI Company model XL-30. A Keyence digital imaging microscope was used for the porous polyurethane foam imaging. An Instron 5969 universal test machine with flat platens was used for compression testing. A Cadex drop tower with a modular elastomer pad (MEP) and 5 kg spherical impactor was used for high impact testing. A TA Instruments DMA model Q800 was used for DMA testing.

3 Methods

3.1 Randomly Dispersed CNTs

3.1.1 MWCNTs in polyurethane

MWCNTs from NanoTechLabs were dispersed in a 3 lb/ft^3 dense polyurethane foam at 0.1%, 0.25%, 0.5%, and 1% loadings by weight. A CNT dispersion in toluene was mixed using a magnetic stir bar with the methylenediphenyl diisocyanate-containing Part A of the PolyFoam kit and sonicated for 30 min to disperse the CNTs. Part A was then mixed with Part B (dibutyltin dilaurate) in a 1:2 ratio of Part A:Part B to obtain a polyurethane foam with randomly dispersed CNTs.

To improve dispersion of the CNTs, a toluene dispersion was prepared by sonication for 30 min to obtain uniformity. The toluene dispersion was then combined with PolyFoam Part A and the mixture was placed in a fume hood to allow the toluene to passively evaporate out of the solution. The Part A and CNT mixture was then combined with Part B in a 1:2 ratio of Part A:Part B.

3.1.2 Chemically induced phase separation

CNTs were also randomly dispersed in an epoxy foam prepared via chemically induced phase separation (CIPS). CIPS allows for the control of pore size, which could prove useful in tailoring foam properties [7]. Poly(propylene glycol) bis(2-aminopropyl ether) was selected as an amine source, with bisphenol A diglycidyl ether as the epoxide. 1-methylimidazole was used as a catalyst and 1-octadecanol was used as the sacrificial phase. These structures are shown in Figure 3. Samples were prepared with 0% CNTs and 0.1% wt/wt CNTs. For the sample containing CNTs, the CNTs were first mixed into the amine along with 10 µL of Triton™ X-100 and sonicated for 30 min. The epoxide and amine were mixed with a mechanical mixer in a 2:1 mol ratio of epoxide:amine for 5 min and heated to 90 °C. Meanwhile, 1-octadecanol was melted in an oven at 90 °C before being added to the epoxide/amine to make a 40% wt/wt 1-octadecanol in epoxy solution. This was mixed over heat with a mechanical mixer for 2 min, with 96 µL added at the beginning of the 2 min period. After mixing, the solution was placed in an oven at 90 °C overnight. The following day, samples were placed in a -20 °C freezer for 4 h. They were then transferred to a vacuum oven at 125 °C, 20 mbar overnight to cure. Epoxy was not used to infuse the CNT arrays due to its short cure time and high viscosity.

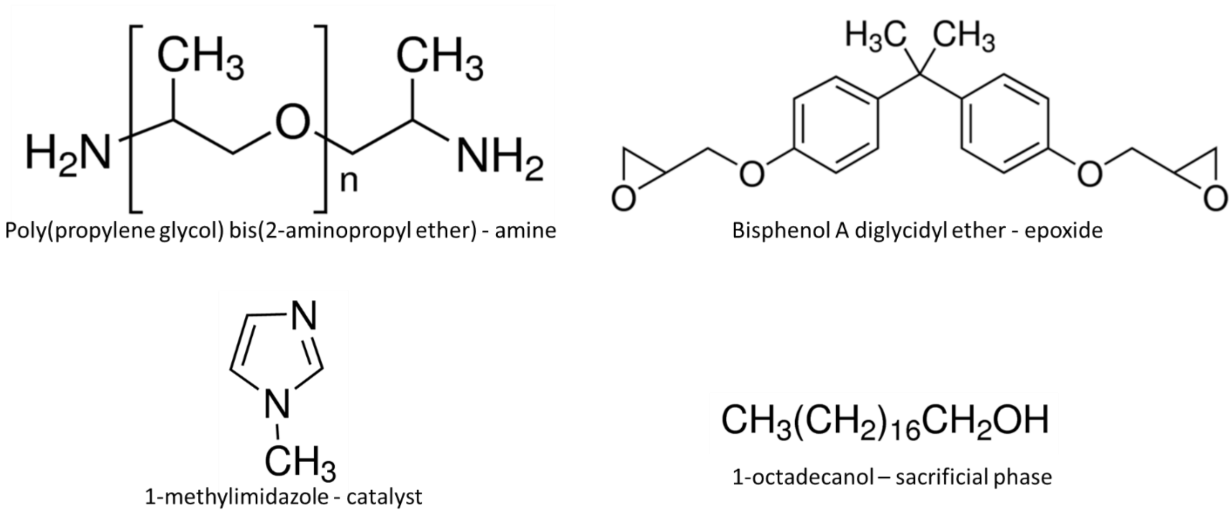


Figure 3 - Materials used to produce an epoxy foam via CIPS

3.2 Composite fabrication with vertically aligned CNT arrays

VACNT arrays are prepared by NCSU on a quartz substrate. A chamber containing the substrates and the catalyst iron chloride ($FeCl_2$) is sealed and pumped down to under 10 mTorr, then heated to 810 °C. Acetylene is then pumped into the chamber as a carbon precursor. Arrays are grown for 60 min under acetylene flow. After 60 min, the flow is stopped. For post-treated arrays, growth is initiated again for a specified amount of time. During the post treatment phase, carbon grows radially from the CNTs to prepare a stable base. The amount of post treatment time affects the density of the arrays, and therefore it is possible to tune. Adjusting the temperature, pressure, and catalyst amount affects the height of the arrays.

3.2.1 Vacuum infusion

VACNTs were infused with polymers by vacuum infusion in a Binder VDL-23 vacuum oven. A solution of 1.5% PVA (brand name Exceval™ AQ4104) and 0.1% Triton™ X-100 in water was prepared. CNT arrays provided by NCSU were placed in individual petri dishes. The VACNT arrays had CVD post-treatment times of 0 min, 30 min, and 60 min. Enough PVA solution was poured over the arrays to cover them, and the dishes were placed under vacuum at 100 mbar overnight to remove the water.

3.2.2 Capillary infusion

CNT arrays infiltration was also performed using capillary action to infuse the arrays with polymer solutions. Some of the arrays showed cracking and shrinking after polymer infusion due to strong capillary forces during evaporation and the strong van der Waals forces between the CNTs [8]. A variety of solvents were used to determine which solvents were best suited for infiltration with minimal surface damage to the arrays during solvent removal. Four petri dishes were filled with the following solutions: a) water and 0.1% Triton™ X-100, b) water, 1.5% PVA, and 0.1% Triton™ X-100, c) toluene, and d) DMF. A 30 min post-treated array was placed into each petri dish such that the arrays were totally covered by the fluids. The dishes were placed in a fume hood to allow for solvent evaporation overnight.

At NCSU, arrays were infiltrated with PDMS using 5, 10, 25, and 50% weight fractions of PDMS in hexane. First, a 200 µm PDMS film mixed with curing agent was cast onto the top of the array and cured. This allowed for the easy removal of the quartz substrate without damaging the arrays. The PDMS in hexane solutions were applied to the arrays using a pipette, and the samples were then heated in an oven at 150 °C for 60 min to remove the hexane and cure the PDMS.

3.2.3 End encapsulation

At NCSU, VACNT arrays were encapsulated with PDMS in order to stabilize the structure while maintaining the physical properties of the arrays. PDMS was cast onto a glass substrate with a doctor blade at thicknesses of 0.5 mm and 1 mm. VACNT arrays were placed onto this glass substrate to soak in the solutions for 2 h on one side and 2 h on the opposite side to coat both ends of the CNTs.

3.2.4 Freeze drying

Freeze drying was utilized as a method to coat the nanotubes in the array with PVA to impart stability. 1.5% wt/wt PVA and 0.1% Triton™ C-100 were dissolved in water and poured over a 30 min post-treated array and a 60 min post-treated array. The samples were placed in a -80 °C freezer until frozen and then placed in a freeze drier under vacuum overnight.

3.3 Composite fabrication with spun CNT sheet foams

Spun CNT sheet foams provided by NCSU were fabricated by drawing out the VACNTs into a sheet and winding the sheet around two spindles to create an aligned foam-like structure as shown in Figure 4. The sheet foams were then post-treated with carbon for 120 min to increase the stability of the array and prevent damage to the structure while handling.

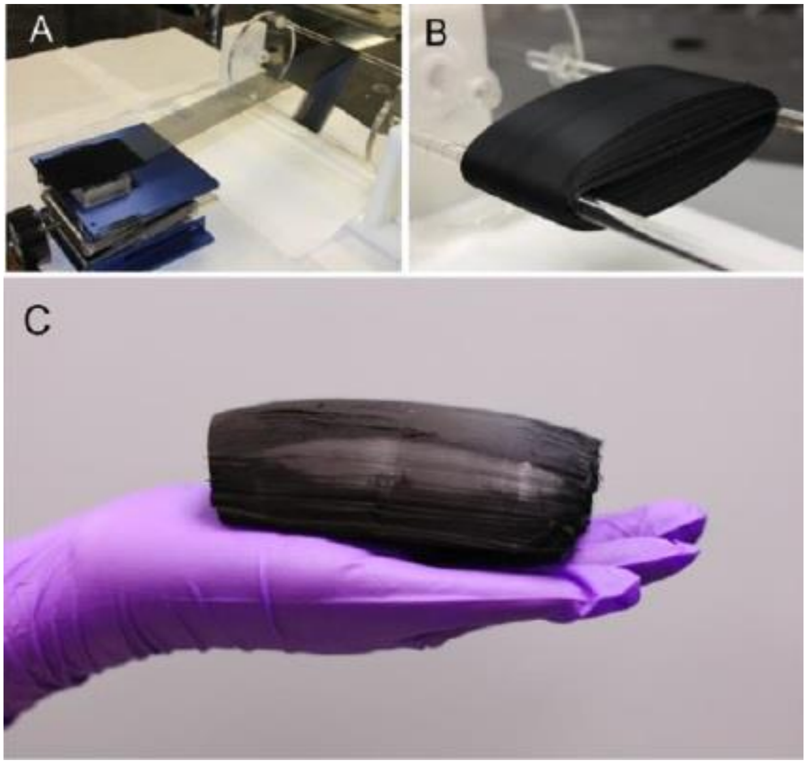


Figure 4 - Fabrication of spun CNT sheet foams from VACNT arrays (courtesy of NCSU)

3.3.1 Capillary infusion

Spun CNT sheet foams were infiltrated with 5%, 10%, 20%, 30%, 40%, and 50% PDMS by capillary action. Various concentrations of PDMS in hexane were allowed to saturate the sheet foams and then heated in an oven at 150 °C for 2 h to remove the hexane and cure the PDMS.

3.3.2 Freeze drying

At NCSU, CNT sheet foams were corona treated to improve wettability of the CNTs and then soaked in a solution of water with 5% PVA by weight. The soaked CNT foams were then frozen in a bath of isopropanol and dry ice before being placed in a freeze dryer to remove the water.

3.3.3 Supercritical CO_2

Supercritical CO_2 was used both for 1) polymer infusion and drying, and 2) in-situ polymerization for both the VACNTs and CNT sheet foam materials. Details of this process, performed by CF Technologies, Inc., can be found in Appendix A. The polymer PVB was dissolved in ethanol and placed in a $scCO_2$ vessel for infiltration and drying at 1%, 2%, 3%, 4%, and 5% polymer uptake for 30 min post-treated VACNT arrays and sheet foams.

The CNT sheet foams had traits more in line with the currently fielded pads than the VACNT arrays. After initial experiments and mechanical testing to characterize the infused sheet foams, CF Tech attempted to improve performance by first compressing the foams in the horizontally aligned direction by 50% of their original height before infusing with polymer. This created a composite with a density of 1.2 lb/ft^3 to 1.4 lb/ft^3.

CF Technologies, Inc. also tried in-situ polymerization using an aerogel process. VACNT arrays were infiltrated with a monomer and oligomer. They were then crosslinked while within the VACNT array to form a sol-gel and dried using $scCO_2$. One polymer was a polyurea and the other was a polyimide.

3.4 Mechanical testing

3.4.1 Microscopy

A SEM (FEI Company model XL-30) was used to obtain images of the VACNT and sheet foams. The open-celled polyurethane foams were analyzed with a Keyence digital microscope, which was better suited for three dimensional geometries.

3.4.2 Compression testing

Compression testing was performed using an Instron electromechanical universal testing machine model 5969. The foam samples were compressed between two flat platens to 60% strain at a rate of 5%/s for 10 cycles. The percent recovery was calculated for 1 and 10 cycles based on the height of the platen at which the load force returned to 0 N.

3.4.3 Dynamic mechanical analysis

A TA Instrument DMA Q800 was used for dynamic mechanical analysis of foam samples. Samples were equilibrated at -20 °C for 5 min. The temperature was ramped from -20 °C to 70 °C at 3 °C/min. The preload force was 0.1 N with an amplitude of 20 µm and frequency of 1 Hz. The DMA recorded storage modulus and loss modulus as a function of temperature in order to observe the temperature stability of the foams.

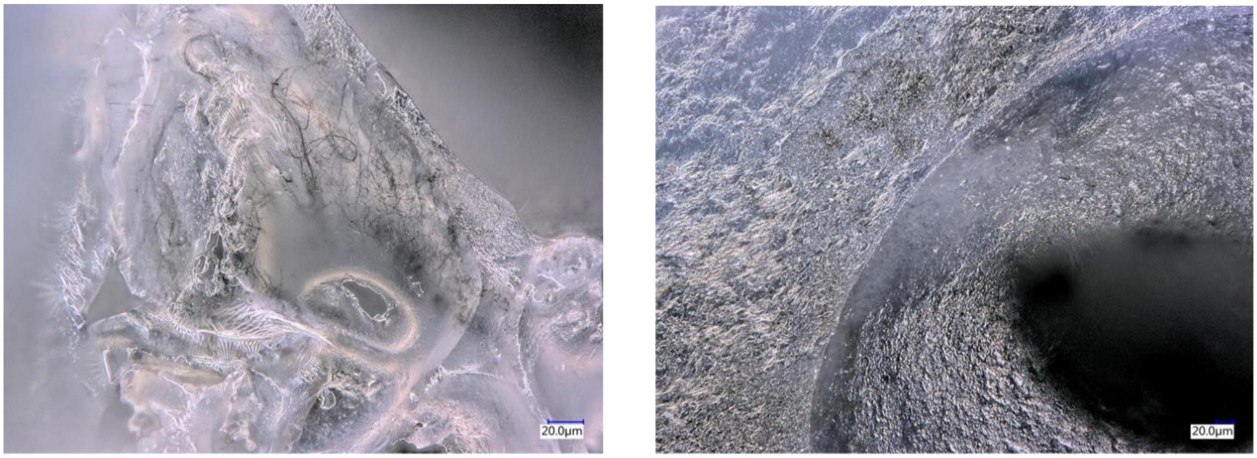
3.4.4 High impact testing

A Cadex Inc. drop tower with a spherical impactor (5 kg, model 050715-01) was used for high impact testing. Foams 2” wide x 2” deep x 0.75” thick were placed on a MEP. The spherical impactor was raised to a height of 148 cm and dropped such that the impact velocity was 17.5 ft/s. The Cadex software measured the peak acceleration and samples were visually inspected for physical damage after impact. Samples that were not clearly damaged were impacted a second time within 90 s of the first impact.

4 Results and Discussion

4.1 Randomly Dispersed CNTs

Images of CNTs randomly dispersed in polyurethane showed that the CNTs inhibited foaming of the two part polyurethane mix. The CNTs were also poorly dispersed. Toluene was successfully used to improve the dispersion of the CNTs throughout the material, but prevented foaming and resulted in a rubber-like porous material due to the toluene only partially evaporating from the PolyFoam Part A solution. Micrographs comparing materials are shown in Figure 5.



0.5% CNTs in polyurethane, 500x

0.5% CNTs with toluene in polyurethane, 500x

Figure 5 - Microscope images of 0.5% CNTs in polyurethane without the use of toluene as a CNT solvent and with toluene. Poor dispersion of the nanotubes is somewhat mitigated by the use of toluene; however, the toluene prevented foaming and caused the polyurethane to be more rubber-like.

Compression testing to 60% strain was performed on the CNT in polyurethane samples and on the Team Wendy materials. The Team Wendy ZAP™ is comprised of a hard protective outer layer and a soft inner comfort layer, denoted as “hard” and “soft” in the following sample IDs. The full pad (soft and hard layers with adhesive glue between them, air bag, and fabric cover) was also tested. The stress strain curves can be seen in Figure 6 and the modulus and recoverability are shown in Table 1. Results suggest that the CNTs offer some structural support to the foams in terms of the improved recoverability, though this may be due to the smaller pores from inhibited foaming.

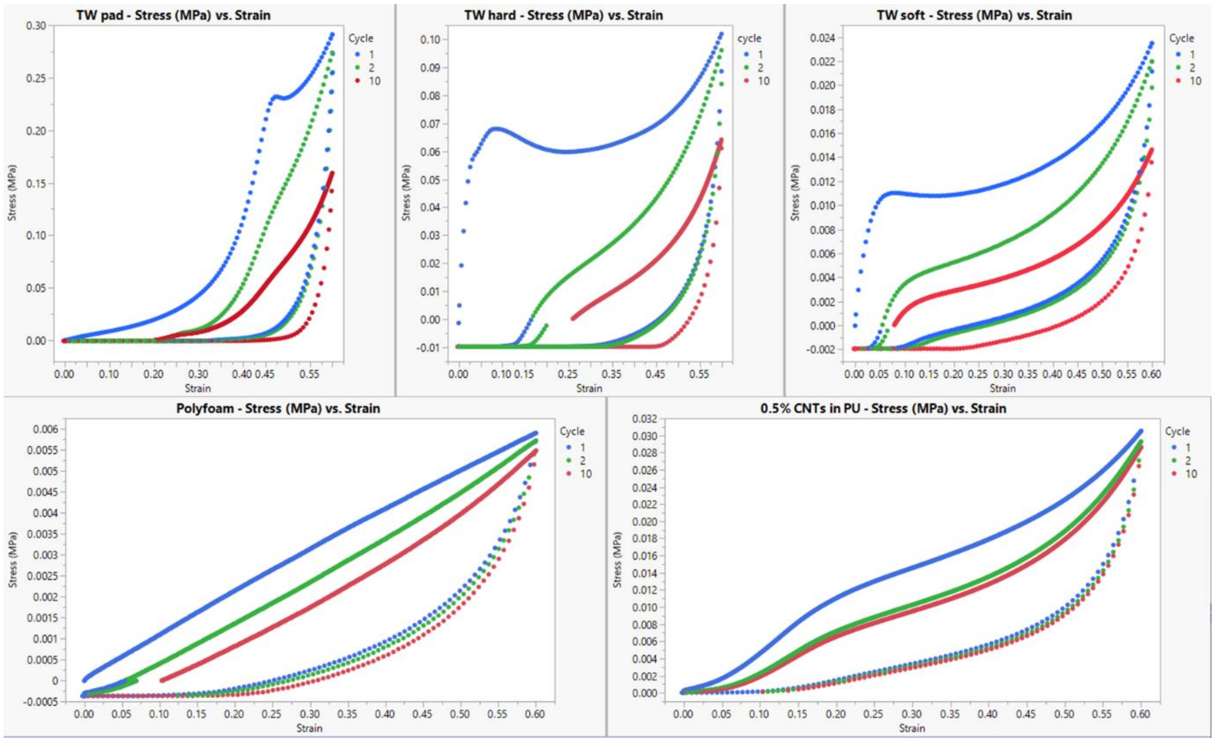


Figure 6 - Stress-strain curves for Team Wendy pads and polyurethane foams

Table 1 - Modulus and recoverability of Team Wendy pads and polyurethane foams with randomly dispersed CNTs

Sample ID	Storage Modulus (Mpa)	Recoverability after 1 cycle	Recoverability after 10 cycles
Team Wendy pad	1.0	67%	57%
Team Wendy soft	0.4	57%	50%
Team Wendy hard	2.5	75%	56%
polyurethane	0.01	75%	69%
0.1% CNT in polyurethane	0.07	85%	80%
0.25% CNT in polyurethane	0.10	86%	82%
0.5% CNT in polyurethane	0.09	76%	70%

DMA testing was performed over the temperature range of -20 °C and 70 °C. The storage modulus of polyurethane foams plotted as a function of temperature is shown in Figure 7. The results agree with compression testing in that the randomly dispersed CNTs increased the modulus of the polyurethane foams with increasing CNT concentration. However, the randomly dispersed CNTs did not prevent the foam from becoming stiff at low temperatures and soft at high temperatures.

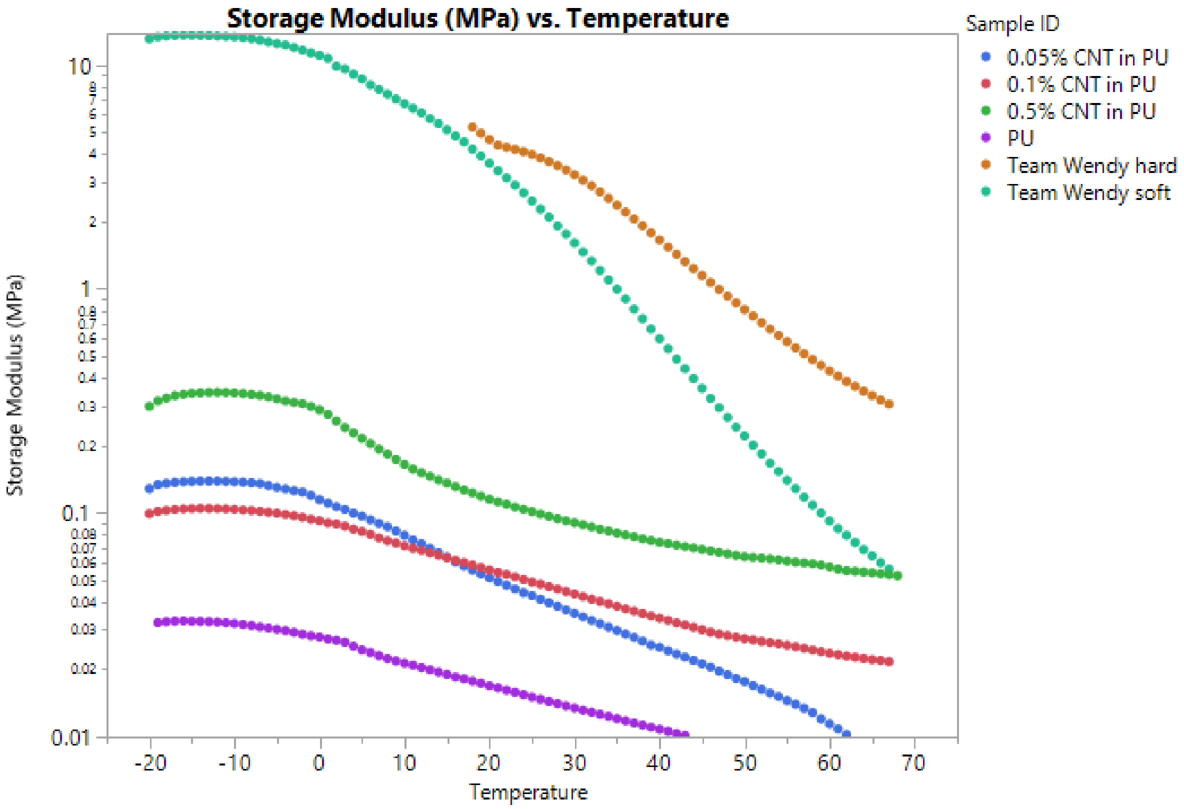


Figure 7 - Storage modulus of polyurethane foams as a function of temperature

The CIPS method of creating a porous epoxy resulted in a glass-like substance. This method was utilized successfully to prepare a porous material with some degree of control over the pore size, but the resulting material was inappropriate for the purpose of helmet foams. The cure time was too short to allow for array infiltration, which eliminated this epoxy polymer as a candidate for CNT array stabilization.

4.2 Vertically aligned CNT arrays

Vacuum infusion of the arrays required Triton™ X-100 as a surfactant to sufficiently wet the CNTs. Without it, the PVA remained on the surface of the CNTs as shown in Figure 8. The SEM image shows a layer of PVA on the surface of the array with some infusion into the top portion of the array. Infiltration depth decreased as the post treatment time of the arrays increased due to increasing density of the arrays.

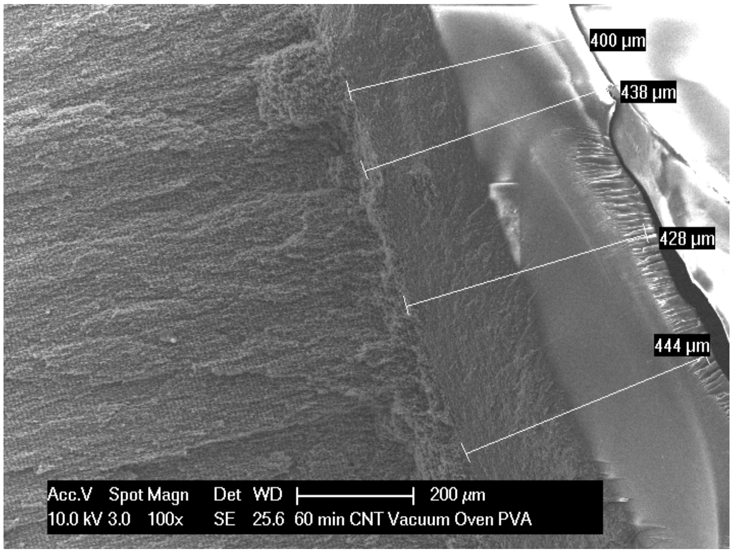
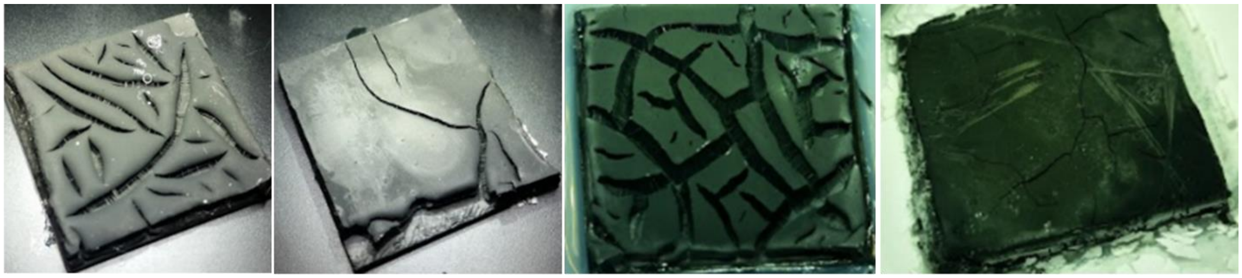


Figure 8 - SEM image of a 60 min post treated VACNT array vacuum infiltrated with PVA shows that the PVA will not wet the CNTs without a surfactant.

Using Triton™ X-100 as a surfactant improved infiltration but caused surface damage to the arrays due to capillary forces, as shown in Figure 9. Previous work has explored using capillary forces to create these structures demonstrated in Figure 9 for the purpose of creating shock-absorbent structures [7]. The configurations of these two-dimensional foams can be controlled using different solvents and evaporation rates [7]. Water, PVA, and Triton™ X-100 were again infused into a 30 min post treated VACNT array and dried passively without a vacuum. In addition to the polymer solution, 30 min post treated VACNT arrays were infused with a water and Triton™ X-100 solution, toluene, and DMF. The results are shown in Figure 10. The sample containing water/Triton™ X-100 showed significant cracking across the entire surface while the solution containing PVA exhibited significantly less cracking. The samples containing toluene also displayed extensive cracking with features 500 µm in size, while the sample soaked in DMF had significantly smaller (80-90 µm) cracks.

Figure 9 - A 60 min post treated VACNT array vacuum infiltrated with PVA using Triton™ X-100 showing surface damage caused to the array by capillary action during drying.



water, triton X
~493 µm gaps

water, PVA, triton X

Toluene
~500 µm gaps

DMF
~80-90 µm gaps

Figure 10 - 30 min post treated VACNT arrays infiltrated with solvents and passively dried cracked during drying of the solvents.

Freeze drying of PVA/Triton™ X-100/water in a 30 min post treated VACNT array showed that the PVA infiltrated the polymer to create a foam-like polymer matrix within the CNT structure. SEM images of the results are shown in Figure 11. However, the SEM images show cracking around the outside of the array and some surface damage. This can most likely be attributed to surface tension and the brittle nature of PVA.

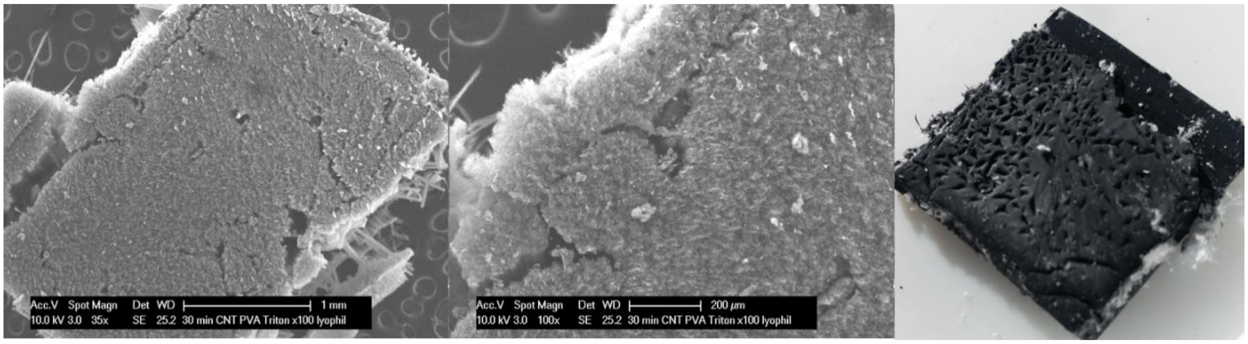


Figure 11 - SEM images of a top-down view of a 30 min post treated VACNT array freeze dried with PVA/Triton™ X-100 and an image of the array after drying. Note the cracking and surface damage.

NCSU used capillary action to coat the ends of VACNT arrays using pure PDMS solutions. In addition to fabricating 1” x 1” single arrays, they were also able to prepare thicker composites by stacking the arrays together as demonstrated in Figure 12. The first sample consisted of five stacked layers of arrays infiltrated with 20% PDMS. The overall density of the sample was 0.483 g/cm^3 (30.15 lb/ft^3). The density was much too high for foam purposes, but performed well in high impact testing. The second sample consisted of four stacked arrays but with the same overall thickness of ¾” and less PDMS. The average density was 0.145 g/cm^3 (9.05 lb/ft^3).

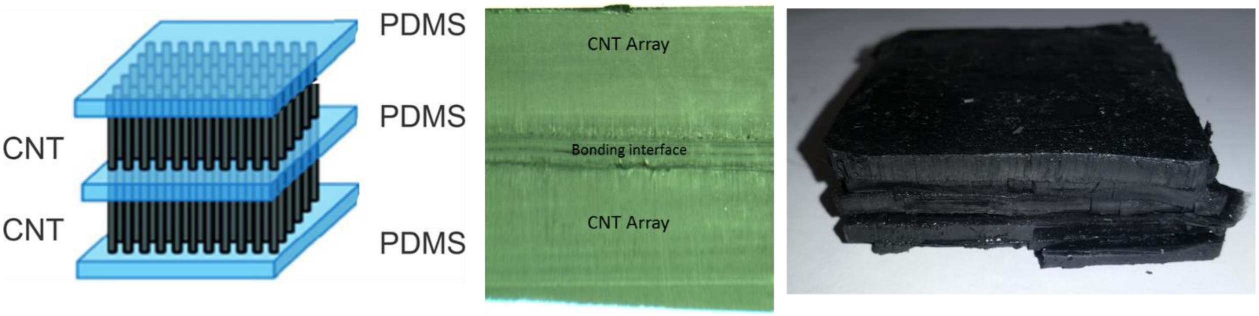


Figure 12 - a 2" x 2" x 3/4" sample consisting of five stacked 20% PDMS VACNT arrays (courtesy of NCSU)

High impact testing results using the Cadex drop tower are shown in Table 2. The Team Wendy pad was able to maintain good impact absorption performance between drops with only a 5% increase in maximum acceleration during Drop 2. The poor performance between impacts for the PDMS infused VACNT arrays can be attributed to permanent damage after the first impact. The four-layer sample displayed extensive cracking after testing. While the arrays were more effective than Team Wendy pads at absorbing impact energy, the high densities eliminate them as potential Team Wendy replacements.

Table 2 - High impact test results of Team Wendy and VACNT arrays infiltrated with PDMS

Sample	Drop	Impact Velocity (ft/s)	Maximum Acceleration (Gs)	% change between drops	% difference from TW	Density (lb/ft3)
TW crown pad	1	17.3	272.3	5%		3.4
	2	17.4	286.7			
5 layer CNT array, 30.15 lb/ft3	1	17.5	195.5	17%	-28%	30.15
	2	17.3	229.0		-20%	
4 layer CNT array, 9.05 lb/ft3	1	17.4	252.8	16%	-7%	9.05
	2	17.4	294.2		3%	

The DMA results for the arrays are shown in Figure 13. The untreated CNT arrays show temperature stability over a range of temperatures. The VACNT arrays infiltrated with PDMS showed a 57% decrease in storage modulus as temperature increased from 0 °C to 100 °C. This can be attributed to the 0.1 μm coating of PDMS on the surface of the array, which was on the same order of magnitude as the amplitude of the DMA compressions. Therefore, the DMA is measuring the response of the PDMS to temperature as opposed to the VACNT array.

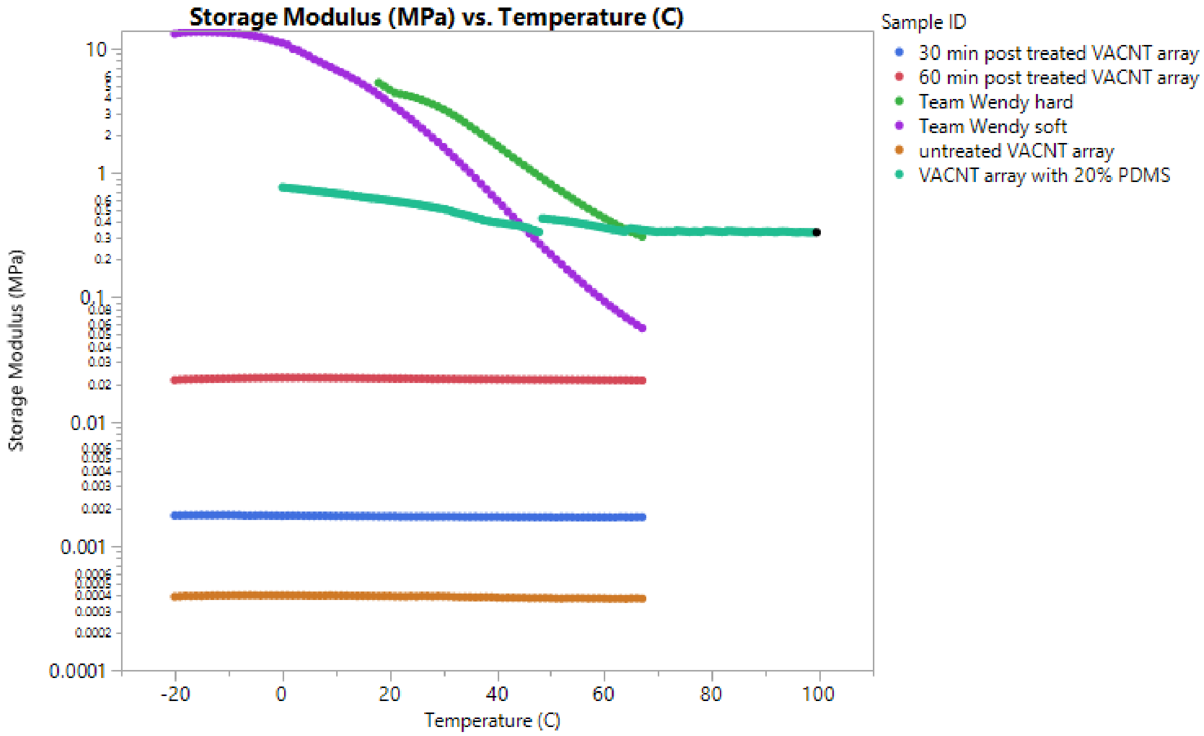
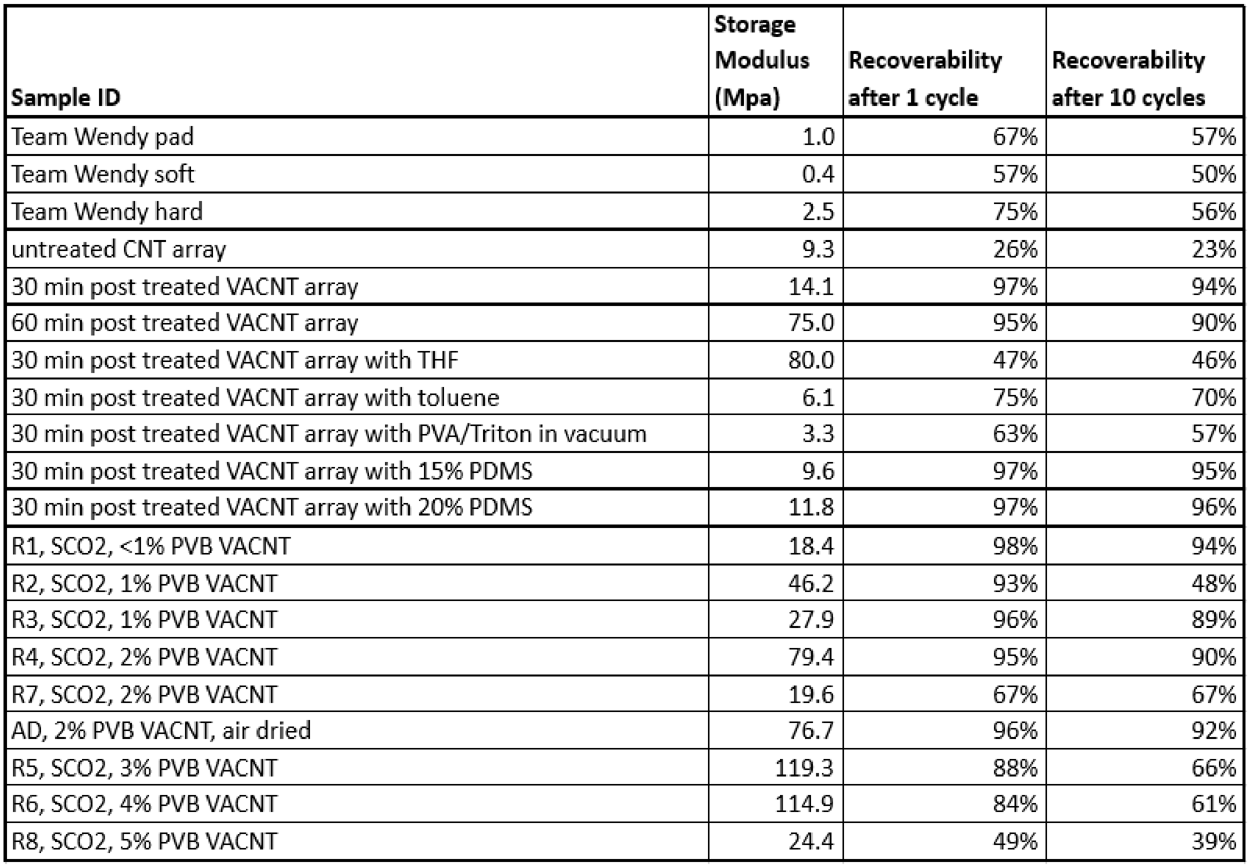


Figure 13 - Storage modulus as a function of temperature for CNT arrays as compared to Team Wendy pads

The cyclical compression testing results are shown in Table 3, with several of the stress-strain curves shown in Figures 13 and 14. All stress-strain curves can be found in Appendix B. The moduli of the VACNT array samples were too high for the purposes of an objectively comfortable helmet foam, but showed good recoverability when infiltrated with PDMS. The Team Wendy pad modulus was used as a baseline for both comfort and performance. The collapsed arrays (30 min post treated VACNT array with THF and toluene) had very high moduli but poor recoverability, indicating that they are too stiff for blunt impact protection.

The stress-strain curves in Figures 14 and 15 show degradation in performance for all materials after just one compression cycle. The initial nonlinear portion of the curve can be attributed to the deformation of the outermost foam cells in the case of Team Wendy foams, while the modulus is measured from the slope of the linear portion of the graph. Given all of these results, the project focus shifted to the spun CNT sheet foams, which offered mechanical properties better suited to a comfortable helmet lining.

Table 3 - Storage modulus and recoverability of Team Wendy and VACNT array samples at 60% compression for 10 cycles



Sample ID	Storage Modulus (Mpa)	Recoverability after 1 cycle	Recoverability after 10 cycles
Team Wendy pad	1.0	67%	57%
Team Wendy soft	0.4	57%	50%
Team Wendy hard	2.5	75%	56%
untreated CNT array	9.3	26%	23%
30 min post treated VACNT array	14.1	97%	94%
60 min post treated VACNT array	75.0	95%	90%
30 min post treated VACNT array with THF	80.0	47%	46%
30 min post treated VACNT array with toluene	6.1	75%	70%
30 min post treated VACNT array with PVA/Triton in vacuum	3.3	63%	57%
30 min post treated VACNT array with 15% PDMS	9.6	97%	95%
30 min post treated VACNT array with 20% PDMS	11.8	97%	96%
R1, SCO2, <1% PVB VACNT	18.4	98%	94%
R2, SCO2, 1% PVB VACNT	46.2	93%	48%
R3, SCO2, 1% PVB VACNT	27.9	96%	89%
R4, SCO2, 2% PVB VACNT	79.4	95%	90%
R7, SCO2, 2% PVB VACNT	19.6	67%	67%
AD, 2% PVB VACNT, air dried	76.7	96%	92%
R5, SCO2, 3% PVB VACNT	119.3	88%	66%
R6, SCO2, 4% PVB VACNT	114.9	84%	61%
R8, SCO2, 5% PVB VACNT	24.4	49%	39%

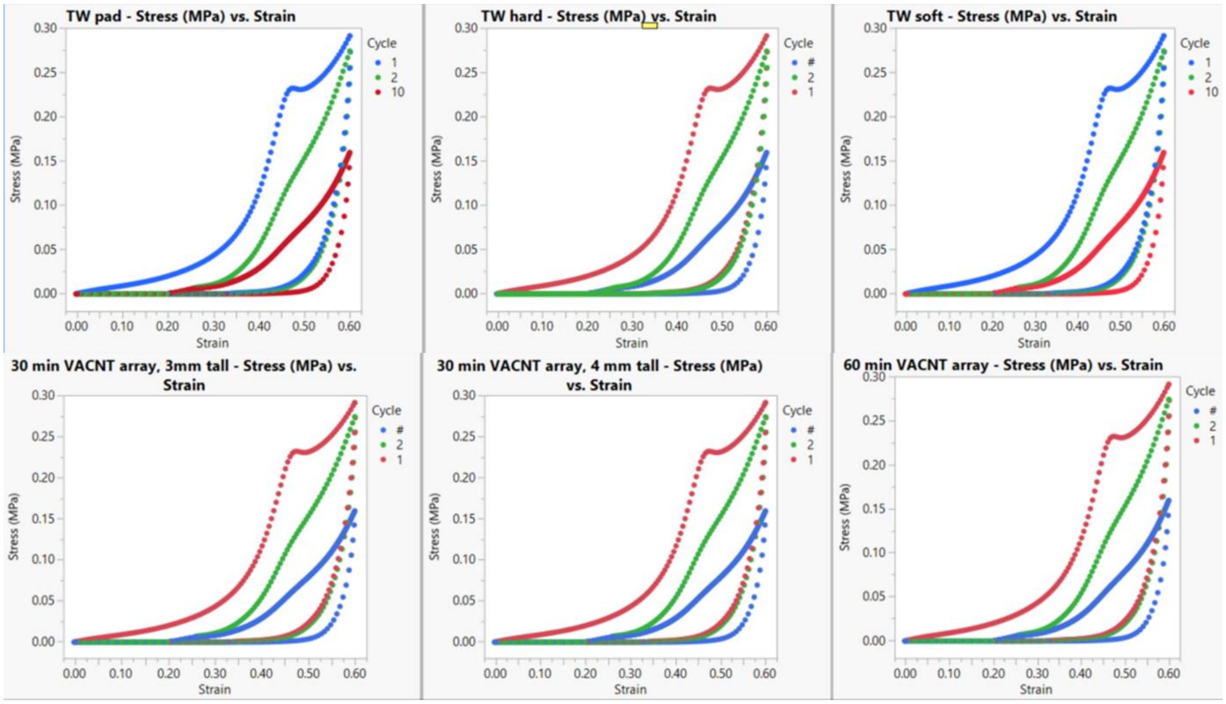


Figure 14 – Stress-strain curves for Team Wendy pads and polymer-free VACNT arrays

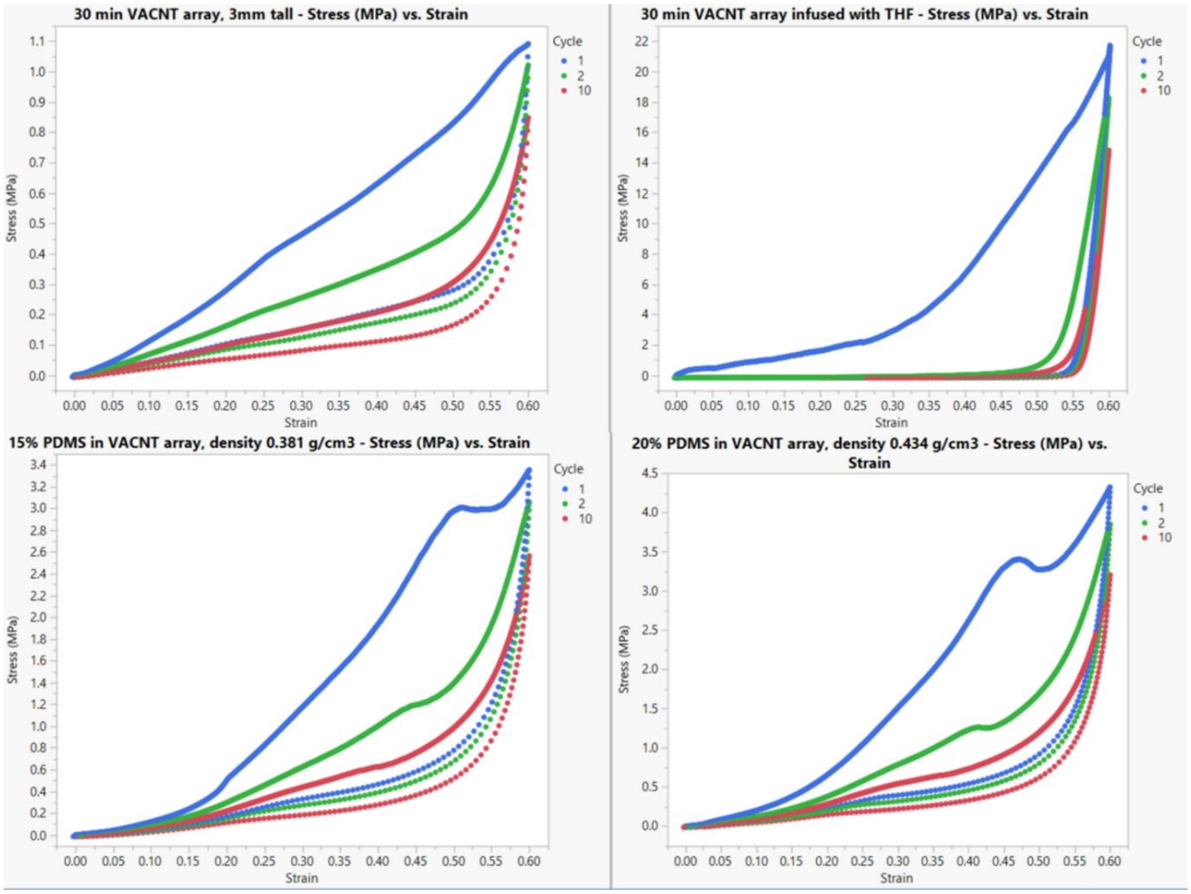
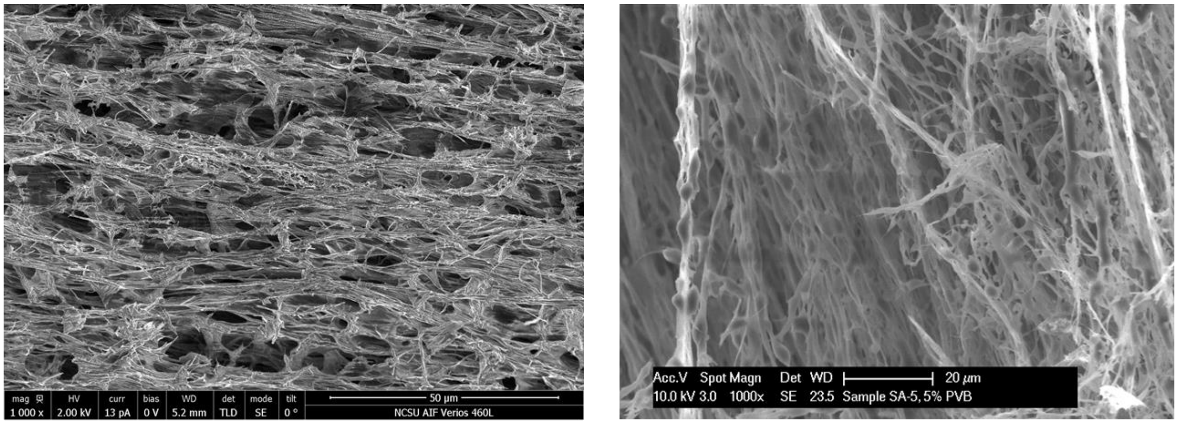


Figure 15 - Stress-strain curves of infused CNT arrays compared to a polymer-free VACNT array

4.3 Spun CNT sheet foams

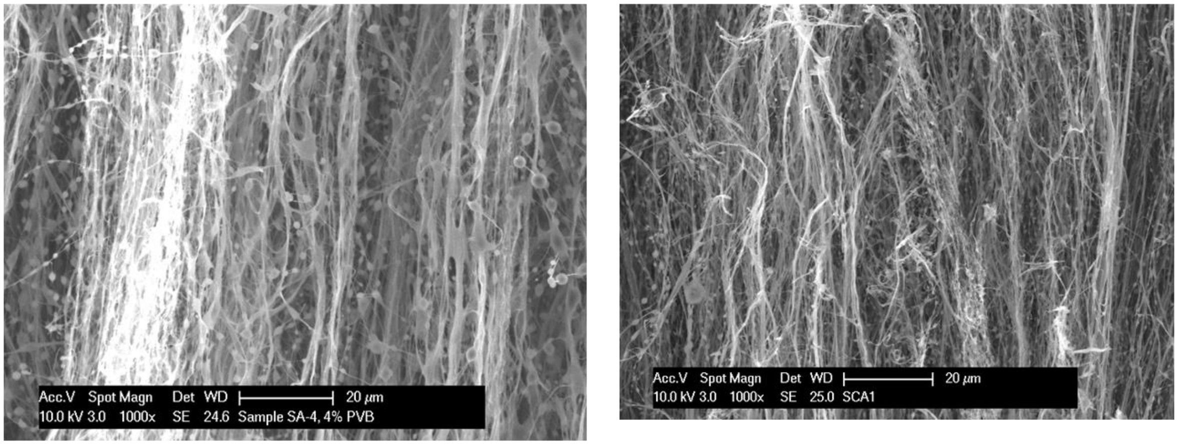
In addition to uninfiltrated sheet foams for $scCO_2$ infusion, NCSU also provided samples infiltrated with PDMS and PVA for testing. CF Technologies infiltrated sheet foam samples with PVB, a polyamide, and a polyurea.

SEM images shown in Figure 16 indicate good infiltration of the polymer within the CNTs for the freeze-dried PVA and $scCO_2$-dried PVB. The polymers have evenly coated the CNTs and created networks between them.



Spun array with 5% PVA, freeze-dried, image courtesy of NCSU

Spun array with 5% PVB, $scCO_2$



Spun array with 4% PVB, $scCO_2$

Compressed spun array with 2% PVB, $scCO_2$

Figure 16 - SEM images of CNT sheet foams infiltrated with polymer

As shown by the DMA results in Figure 17, the added polymer has little to no effect on the stability of the materials over a temperature range of -20 °C to 70 °C.

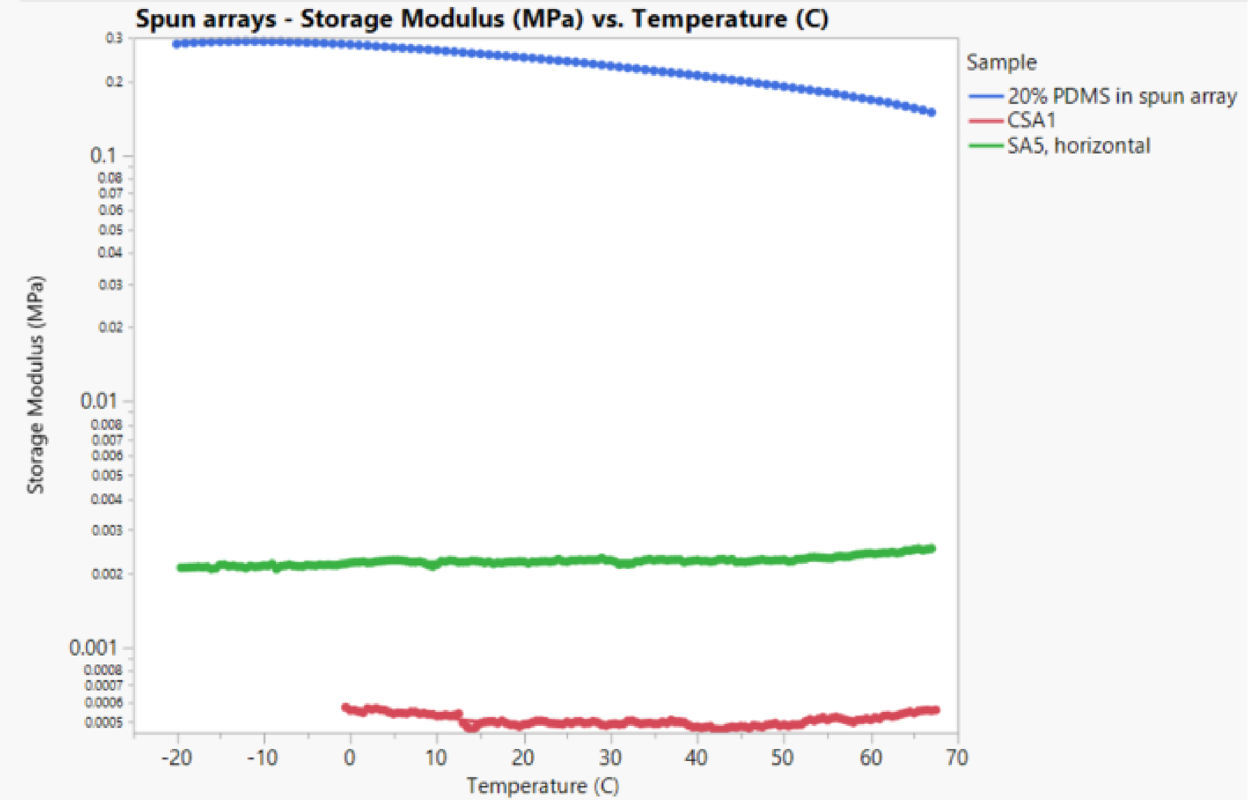


Figure 17 - DMA results for sheet foams show minimal temperature dependence of the storage modulus for infiltrated CNT foams (CSA1 and SA5).

Compression was performed on the CNT sheet foams in both the vertical and horizontal CNT alignment. The results in Table 4 show that when tested with the CNTs aligned vertically, the modulus is closer to the target range of 0.3-0.6 MPa, but the recoverability was poor due to buckling. With the CNTs aligned horizontally, the sheet foams have a much lower modulus but higher recoverability. The permanent damage from compression to the vertically aligned arrays can be seen in Figure 18. By compressing the sheet foams horizontally before infiltrating them with polymer, the modulus of the material increased while maintaining the good recoverability. These compressed sheet foams (CSA1-CSA6) had densities in the range of 1-3.1 lb/ft^3, which is below the target of 4 lb/ft^3. The large range in densities can be attributed to the anisotropic nature of the spun sheet foams.

Horizontally aligned spun array after compression tests.

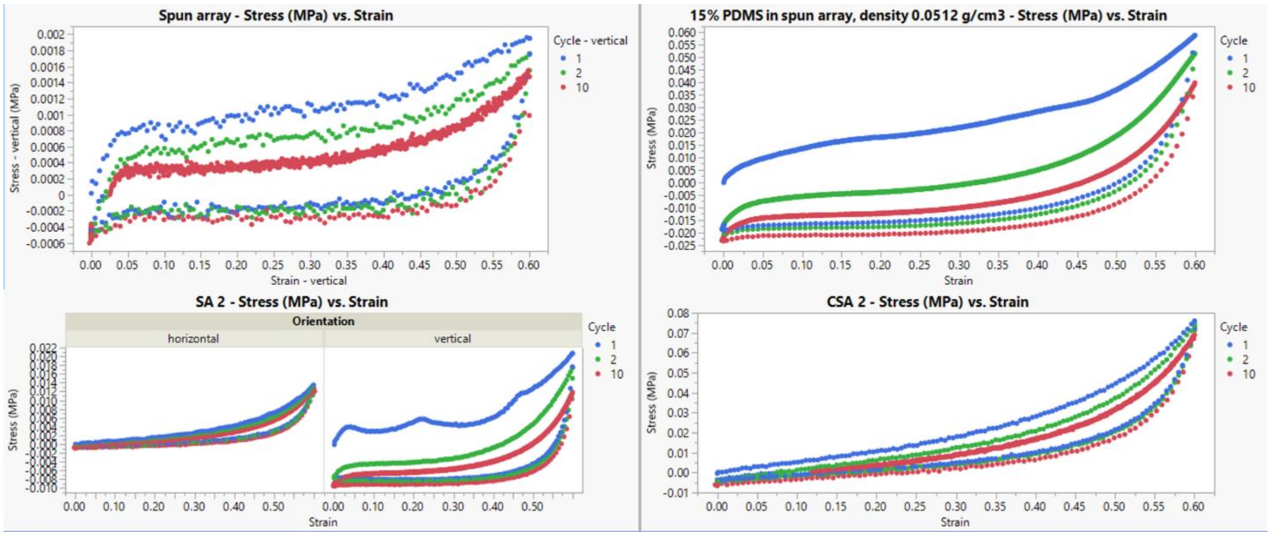
Vertically aligned spun array after compression tests.

Figure 18 - Spun CNT sheet foams with PVA after compression testing in the horizontal and vertical alignment directions. Buckling can be seen after compression (courtesy of NCSU).

Table 4 - Storage modulus and recoverability of spun CNT sheet foam samples at 60% compression for 10 cycles

Sample ID	**Storage Modulus (Mpa)**	**Recoverability after 1 cycle**	**Recoverability after 10 cycles**
Team Wendy pad	1.0	67%	57%
Team Wendy soft	0.4	57%	50%
Team Wendy hard	2.5	75%	56%
30 min CNT array	14.1	97%	94%
untreated sheet foam, horizontal	0.0025	44%	43%
untreated sheet foam, vertical	0.0058	55%	48%
SA1, SCO2, 1% PVB sheet foam, horizontal	0.027	88%	84%
SA6, SCO2, 2% PVB sheet foam, horizontal	0.052	91%	
SA6, SCO2, 2% PVB sheet foam, vertical	0.233	45%	43%
SA3, SCO2, 3% PVB sheet foam, horizontal	0.09	69%	61%
SA3, SCO2, 3% PVB sheet foam, vertical	0.33	42%	40%
SA4, SCO2, 4% PVB sheet foam, horizontal	0.23	78%	70%
SA4, SCO2, 4% PVB sheet foam, vertical	0.05	49%	45%
SA5, SCO2, 5% PVB sheet foam, horizontal	0.24	75%	68%
CSA1, SCO2, 2% PVB in compressed sheet foam	0.12	91%	81%
CSA2, SCO2, 2% PVB in compressed sheet foam	0.32	87%	76%
CSA3, SCO2, 2% PVB in compressed sheet foam	0.52	93%	89%
CSA4, SCO2, 2% PVB in compressed sheetn foam	0.22	89%	83%
CSA5, SCO2, 2% PVB in compressed sheet foam	0.28	95%	91%
CSA6, SCO2, 5% PVB in compressed sheet foam	0.57	86%	78%
10% PDMS in sheet foam	0.32	62%	84%
15% PDMS in sheet foam	0.22	50%	92%
20% PDMS in sheet foam	0.94	77%	85%

The stress-strain curves for select infused sheet foams are compared to a polymer-free spun foam in Figure 19. The curves for samples SA2 show the difference in performance between the horizontal and vertical orientations. The vertically aligned sheet foams buckle under compression and suffer permanent deformation, which is supported by the image in Figure 18. Stress-strain curves for all samples can be found in Appendix B.


Spun array - Stress (MPa) vs. Strain

15% PDMS in spun array, density 0.0512 g/cm3 - Stress (MPa) vs. Strain

SA 2 - Stress (MPa) vs. Strain

CSA 2 - Stress (MPa) vs. Strain

Figure 19 - Stress-strain curves of select infused spun CNT sheet foams compared to a polymer-free sheet foam

Large samples for high impact testing were prepared by CF Technologies. The samples were prepared by compressing a sheet foam to 50% of its height and infusing with 3% (CSA7) and 5% (CSA8) PVB in ethanol, then dried with $scCO_2$. Drop testing results are shown in Table 5 with results from the Team Wendy pads for comparison. The arrays suffered extensive cracking after the initial impact and could not be impacted twice.

Table 5- High impact test results of Team Wendy and spun CNT arrays infiltrated with PVB

Sample	Drop	Impact Velocity (ft/s)	Maximum Acceleration (Gs)	% change between drops	% difference from TW	Density (lb/ft3)
TW crown pad	1	17.3	272.3	5%		3.4
	2	17.4	286.7			
CSA7	1	17.3	280.2		3%	2.64
CSA8	1	17.5	295.1		8%	2.65

Despite these larger 2”x2”x0.75” samples being replicates of the smaller CSA samples previously prepared by CF Technologies for compression and DMA testing, the physical properties were much different. The large arrays were stiffer than the smaller specimens which could be due to the longer drying time needed for the larger samples. The extended drying time most likely removed not only the ethanol solvent, but some of the plasticizer in the PVB, which would contribute to the stiff feeling and brittle nature of the samples.

5 Conclusions

Infiltration of the VACNT arrays using polymer resulted in improved mechanical performance of the VACNTs but proved too dense for helmet foam applications. The sheet foams manufactured from the VACNT arrays have a much lower starting density, making them more ideal candidates for helmet foams. Infusing the sheet foams with PVB and drying using $scCO_2$ produced the most promising results.

Samples CSA7 and CSA8 (large spun arrays infused with 3% and 5% PVB respectively and dried by scCO2) had densities of 2.6 lb/ft^3, which leaves room for optimizing polymer loading level and pre-strain while still remaining under the Team Wendy density. Despite performing poorly, the compression and DMA results on the smaller samples suggest that optimizing the drying time to account for the samples size could lead to better high impact results.

Another recommendation for future work would be to find a method of making the spun arrays a uniform density. The current method of spinning the arrays results in an anisotropic material which makes duplicating results difficult. Using SWCNTs may also provide good results because they are thinner than the MWCNTs grown by NCSU and can be more easily infused with polymer.

This document reports research undertaken at the
U.S. Army Natick Soldier Research, Development and
Engineering Center, Natick, MA, and has been
assigned No. NATICK/TR- 19/007 in a
series of reports approved for publication.

6. References

[1] Army - PM SPE, *AR.PD 10-02, Purchase Description Helmet, Advanced Combat (ACH),* 2010.

[2] P. D. Bradford, X. Wang, H. Zhao and Y. Zhu, "Tuning the compressive mechanical properties of carbon nanotube foam," *Carbon,* vol. 49, pp. 2834-2841, 2011.

[3] A. Cao, P. L. Dickrell, W. G. Sawyer, M. N. Ghasemi-Nejhad and P. M. Ajayan, "Super-compressible foamlike carbon nanotube films," *Science,* vol. 310, pp. 1307-1310, 2005.

[4] M. R. Maschmann, Q. Zhang, F. Du, L. Dai and J. Bauer, "Length dependent foam-like mechanical repsonse of axially indented vertically oriented carbon nanotube arrays," *Carbon,* vol. 49, pp. 386-397, 2011.

[5] R. Theuamaran, E. R. Meshot and C. Daraio, "Shock formation and rate effects in impacted carbon nanotube foams," *Carbon,* vol. 84, pp. 390-398, 2015.

[6] A. J. Svagan, P. Jensen, S. V. Dvinskikh, I. Furo and L. A. Berglund, "Towards tailored heirarchical structures in cellulose nanocomposite biofoams prepared by freezing/freeze-drying," *Journal of Materials Chemistry,* vol. 20, pp. 6646-6654, 2010.

[7] B. Weng, F. Xu, G. Garza, M. Alcoutlabi, A. Salinas and K. Lozano, "The production of carbon nanotube reinforced poly(vinyl) butyral nanofibers by the Forcespinning method," *Polymer Engineering and Science,* vol. 55, no. 1, pp. 81-87, 2015.

[8] S. A. Steiner, "Layered aerogel composites, related aerogel materials, and methods of manufacture". US Patent 20140287641 A1, 25 Sep 2014.

[9] J. Bahr, M. C. Celina, B. J. Chisholm, S. M. Dirk, N. Gubbins, A. Kallam, R. J. Klein, E. Lee, J. L. Lenhart, P. Majumdar and P. S. Sawyer, "Control of Pore Size in Epoxy Systems," Sandia National Laboratories, Albuquerque, NM, 2009.

[10] N. Chakrapani, B. Wei, A. Carrillo, P. M. Ajayan and R. S. Kane, "Capillarity-driven assembly of two-dimensional carbon nanotube foams," *Proceedings of the National Academy of Sciences,* vol. 101, no. 12, pp. 4009-4012, 2004.

[11] N. Chakrapani, B. Wei, A. Carrillo, P. M. Ajayan and R. S. Kane, "Capillarity-driven assembly of two-dimensional cellular carbon nanotube foams," *Proceedings of the National Academy of Sciences,* vol. 101, no. 12, pp. 4009-4012, 2004.

Appendix A

Supercritical Carbon Dioxide ($scCO_2$) for in-situ Polymerization and Foaming within Carbon Nanotube (CNT) Arrays

By

John M. Moses
CF Technologies, Inc.
1 Westinghouse Plaza
Hyde Park, MA 02136
(617) 364-2500
johnmoses@cftechnologies.com

for

US Army Natick Soldier Research, Development, and Engineering Center
General Greene Avenue
Natick, MA 01760

Battelle
1204 Technology Drive
Aberdeen, MD 21001
Todd Weidner
(410) 306-8649
weidnert@battelle.org

November 30, 2017

Table of Figures

Figure 1. Compressive Strength of current material “Team Wendy pad”, VACNT as received, and VACNTs infiltrated with PVB, with one air dried “AD”, and others infiltrated with solutions of varying PVB concentrations and $scCO_2$ dried. The AD sample tested well, but had significant structural defects after air drying. 29
Figure 2. Process Flow Diagram Dissolution and Infiltration System 31
Figure 3. Process Flow Diagram for system configuration used for $scCO_2$ drying after PVB-EtOH infiltration of VACNTs 32
Figure 4. Recovery of VACNTs with varying PVB solutions 35
Figure 5. Comparison of strength with various polymers 36
Figure 6. Comparison of recovery with various polymers 37
Figure 7. Strength Comparison of Spun Arrays with Team Wendy Pads (TWP) 37
Figure 8. Compressive Strength of Compressed Spun CNTs compared with Team Wendy pad. 38
Figure 9. Recovery of Compressed Spun CNT arrays. 38
Figure 10. NSSC DMA testing results of Team Wendy Hard Pad 39
Figure 11. NSSC DMA testing results of CF Tech CSA1 from Set #5. The noise in the data is presumed due to the uneven surface of the array, as seen in Photo 7 40

Acknowledgement

CF Technologies, Inc. would like to thank Ms. Melissa Roth, Chemical Engineer, and Mr. Thomas Tiano at NSSC; colleagues Peter Farmer, Justin Griffin and Ryan Nelson; and Dr. Philip Bradford, Mostakima Mafuha Lubna and Ozkan Yildiz of NCSU; and the US Army for funding this project.

Introduction

U.S. Army Natick Soldier Systems Center (NSSC) performs soldier safety testing. An important piece of soldier protection is the helmet. NSSC is exploring methods to reduce weight, improve function over the full temperature range experienced in practice, and at the same time matching the compressive strength of the foam currently used while improving recovery after compression.

The padding currently used in Army helmets is a two-layer polyurethane foam, “Team Wendy Zorbium® Action Pads”, hereafter referred to as “Team Wendy”. These pads consist of a stiffer outer layer and a softer inner layer which are held together with adhesive, and encapsulated in a polymer film. These pads perform well at room temperature in their first compression; however, at the high and low ends of their potential service temperature their performance deteriorates, and they do not recover well for re-use, so they are generally considered “single use”.

The objective of this effort is to provide to the Army (NSSC) a better helmet foam, which includes testing methods of infiltrating vertically arrayed carbon nanotubes with a polymer matrix to reinforce the area with minimal disruption of carbon nanotube alignment while creating voids within the polymer matrix. With a plan to produce a set of samples every 2 weeks, with prompt mechanical testing, microscopic analysis, and reporting by the Army (NSSC) to hone in on a process that meets or approaches the objective properties by the 6th set of samples, then in the final set to produce one or more larger pads on the order of 2” x 2” square or 2” in diameter round for performance testing in addition to the mechanical testing and microscopic analysis.

The desired final product will have minimal loss of strength after compression and good thermal stability as compared to currently fielded Team Wendy Pads. The properties needed at a minimum should meet or exceed Team Wendy pads, with a target compressive strength modulus of 0.3 to 0.6 MPa, the desired recovery after 10 compressions is at least 85%, a bulk density of less than 3 pounds per cubic foot, and performance of the temperature range of -10–70 °C. Supercritical fluids, supercritical carbon dioxide ($scCO_2$) in particular, can be used to accomplish both good polymer infiltration and void formation, and $scCO_2$ drying creates the lightweight product without the distortion, cracking, and shrinkage of other drying methods.

CF Technologies, Inc. proposed a variety of methods that could be tested to achieve the objective of lightweight, polymer reinforced vertically arrayed carbon nanotubes (VACNT) using supercritical carbon dioxide. With the following experimental method: produce a material, test it, then based on the test results, design the next experimental material. CF Tech performed seven sets of experimental tests as proposed, starting with VACNT and then switching to spun carbon nanotubes; infiltrating and drying with various methods, materials, and concentrations, for mechanical testing and microscopic analysis by the Army.

Technical Discussion

Summary:

A variety of polymers, methods of delivery of polymers, and drying were selected for the initial rounds of testing polymer supported VACNTs. The first few rounds of testing showed significant (order of magnitude) improvement in storage modulus and compressive stress. The polymers tested were polyvinyl butyral (PVB), polyurea (PU), and polyimide (PI); and the methods tested included infiltration of polymer with a liquefied gas-supercritical solvent system; infiltration with a solution of polymer in a conventional solvent system; infiltration with monomers and dimers, in conventional solvent and polymerization in situ; with supercritical, liquefied gas, and air drying tested. While all of these methods improved the strength of the VACNTs, the best results were obtained with infiltration with PVB in ethanol (EtOH) with $scCO_2$ drying. However, the strength of all samples was much greater than the target. Due to these results, an untreated VACNT was tested with no polymer reinforcement, and was found to be significantly stiffer than both the target compressive strength and the Team Wendy Pads (TWP). Figure A-1 shows the results with a general trend of higher strength as the concentration of polymer was increased, as much as 100 times stronger than TWP, and 10 times the strength of the VACNT which was not polymer reinforced.

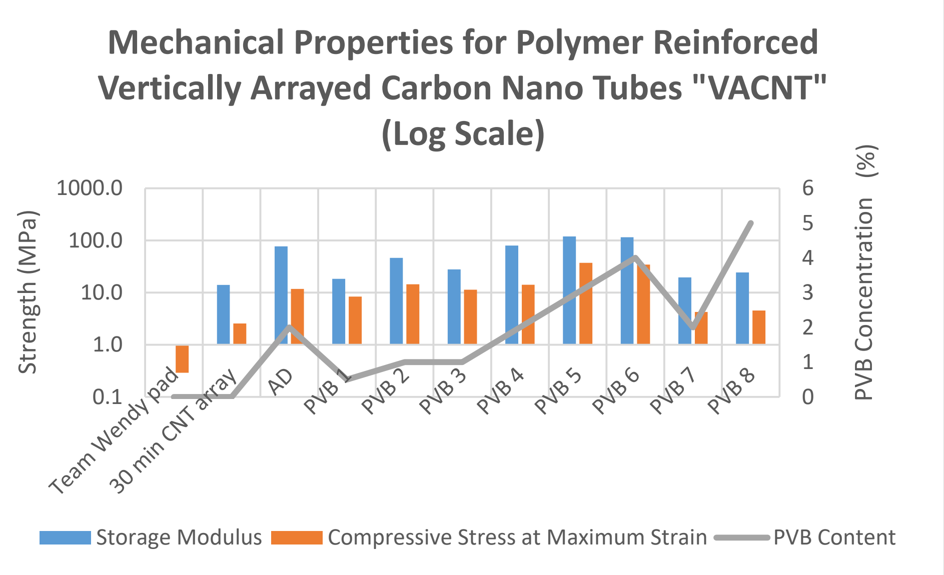


Figure A-1. Compressive Strength of current material TWP, VACNT as received, and VACNTs infiltrated with PVB, with one air dried (AD), and others infiltrated with solutions of varying PVB concentrations and $scCO_2$ dried.

The AD sample tested well, but had significant structural defects after air drying. Maximum strain was 60% in these tests.

Therefore, the starting carbon nanotube (CNT) material was changed from VACNT to spun CNT “foam” array supplied by NSSC and North Carolina State University (NCSU). These foams are low density, and the most favorable method, i.e. the “best” method found with the VACNTs, infiltration with PVB in ethanol followed by $scCO_2$ drying, was used with them. In the initial spun CNT tests, the compressive stress was improved by the polymer; however, they were still much softer (1 – 2 orders of magnitude) than the target. Samples of the spun CNT foam were then compressed and infiltrated with different concentrations of PVB in ethanol. One of the resultant samples had a strength within the desired 0.3 to 0.6 MPa, good thermal stability and compressive recovery. Therefore, the final test to produce a large sample for high impact drop testing sought to duplicate the compression, infiltration and drying of that sample.

NCSU delivered to CF Tech a large spun CNT foam for the final experiments. Unfortunately, the impact performance of the two large pieces did not align well with the promising mechanical properties from the sixth set of experimental materials. While there is speculation regarding the cause of the variance, discovering it is a task for a future program.

Technical Activities

The project was contractually separated into four sub-tasks. Tasks 1 - 3 are discussed as project work assignments and Task 4 is the evaluation of the mechanical testing and microscopic analysis of the test materials produced.

In July 2017, prior to planning any experiments, the team, consisting of two senior engineers, a laboratory technician and a project manager met internally and with the NSSC soldier safety testing team lead. Discussions included past work with polymers, $scCO_2$ drying and aerogel formations, helmet safety importance and testing procedures, CNT manufacturing processes and developments within the CNT industry.

Preliminary efforts included literature reviews on polymer solubility, CNTs and current state of the art. Relevant articles are found in the References. The solvent and polymer solubility (DeFelice & Lipson, 2014) (Rindfleisch, DiNoia, & McHugh, 1996), polymer information, infiltration method, and CNT (Charitidis, Koumoulos, Giorcelli, Musso, Jagadale, & Tagliaferro, 2013) (Antunes & Velasco, 2014) data were input into spreadsheets to facilitate sorting of the data. After reviewing the data, a short list of preliminary polymers, solvents, and methods were selected for project testing.

Test and measurement procedures and methods were selected and preliminary tests with polymers and arrays were conducted in order to gain a better understanding of the material properties and to start testing processes.

After the preliminary research and testing was complete, the first set of experiments and experimental procedures including chemicals, solvents and polymers were selected.

Sub - Task 1. Name: Experimental strategies and experimental matrix.

Sub-task 1 was an ongoing effort, as experimental materials were produced and tested, the matrix evolved as best practices were explored and successes were guided method development towards the best infiltration of VACNT arrays.

A broad literature review was conducted, experimental strategies and experimental matrix set to include polymers and solvents to study and infiltration methods. An infiltration pressure vessel system was set up and is documented in the Process Flow Diagram in Figure A-2.

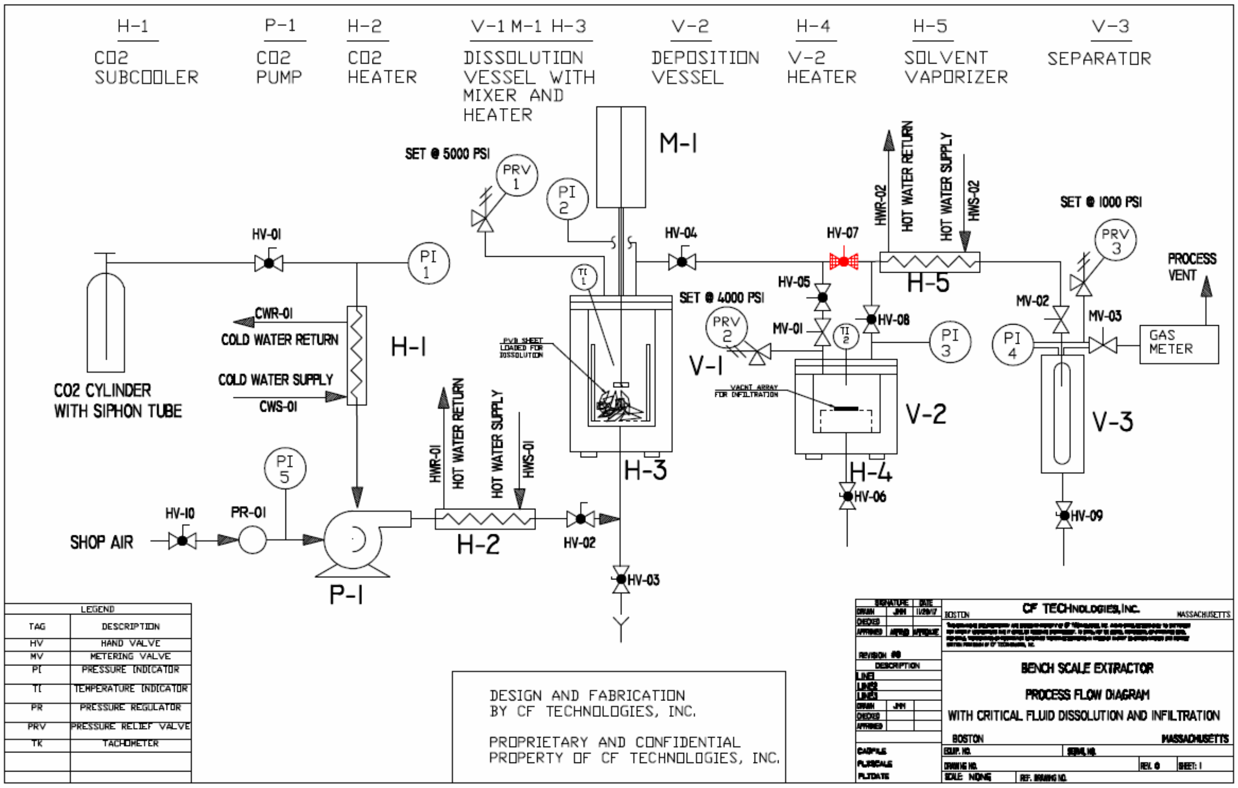


Figure A-2. Process Flow Diagram Dissolution and Infiltration System

The internal kick-off meeting included John Moses (PI), John Markiewicz (Sr Eng.), Jessica Sweeney (PM), and Jared Wills (Tech), presenting the literature reviews and the formulation of the data matrix on CNTs, SWCNT (single wall CNTs), MWCNT (multi-wall CNTs); a polymer list including published and in-house data on solubility in carbon dioxide (CO_2), and existing and past uses and methods of CNT infiltration, polymer solubility in conventional solvents, and discussion of schedule, existing knowledge base and predictions of experimental matrix directions. CF Tech also conducted an external kick off meeting with NSSC staff which included the hand-off of Government Furnished Property (GFP) of CNT arrays necessary for Tasks 2, 3 and 4; kick-off also included discussions of current array turn-around. CF Tech then began system set up and process vessel selection and preparation.

CF Tech selected polyvinyl butyral (PVB) to use as the initial infiltration polymer, as it has similar qualities to polyvinyl alcohol (PVA), which has been successfully used to reinforce CNTs, but unlike PVA, PVB is not water soluble. PVB's primary use is in safety glass interlayer. It has strong adhesion to glass, flexibility, mechanical strength and impact resistance; can withstand low temperatures; and its glass transition temperature can be lowered with the addition of plasticizers if needed. Other uses are based on its good bonding qualities to a variety of materials. PVB is a bacteria, microorganism, alkali and diluent acid rejecter (Li, Tang, Liu, Xia, & Jiang, 2008), potentially adding to the benefits of soldier protection; therefore, it was selected for initial testing. Literature review and past CF Tech experience provided data showing that PVB was soluble in dimethyl acetamide (DMAC) and dimethyl ether (DME) (Weng, Xu, Garza, Alcoutlabi, Salinas, & Lozano, 2015).

Testing began with a preliminary set (one 1" x 1" VACNT cut into smaller pieces) for internal use, to test handling and measurement methods, solubility, structure assessment and durability. These preliminary tests are not included in the results portion of this report.

These preliminary experiments included evaluation of potential PVB solvents. PVB was dissolved into ethanol, acetone and hexane, and was most soluble in EtOH. Before working with arrays, methods of measuring the arrays before and after experiments were developed. This included the use of a tools maker microscope to measure the dimensions of the arrays with a precision of 0.000 1”, and weighing with an analytical balance with precision of 0.000 1 g. The microscope was also used to observe the surface of the arrays before and after infiltration.

EtOH infiltration of VACNTs were tested with and without applying vacuum. Since no difference was observed, atmospheric infiltration with EtOH solutions was selected for simplicity. The next preliminary experiments included exposing VACNT to EtOH and $scCO_2$ without adverse effect.

Two PVB infiltration methods were initially tested: conventional solvent (EtOH) and critical fluid solvent (DME). The drying system was set up with a stirred pressure vessel for critical fluid solvent polymer dissolution and a second pressure vessel for infiltration and drying of VACNTs (see Figure A-2). For VACNTs infiltrated with EtOH solution, solvent exchange and drying with CO_2 occurred in the stirred vessel, and the second vessel was isolated off-line (see Figure A-3). Other components of the system are a liquefied gas feed pump; heat exchangers; separator; temperature, pressure, and flow measurement; and valves for manual process control.

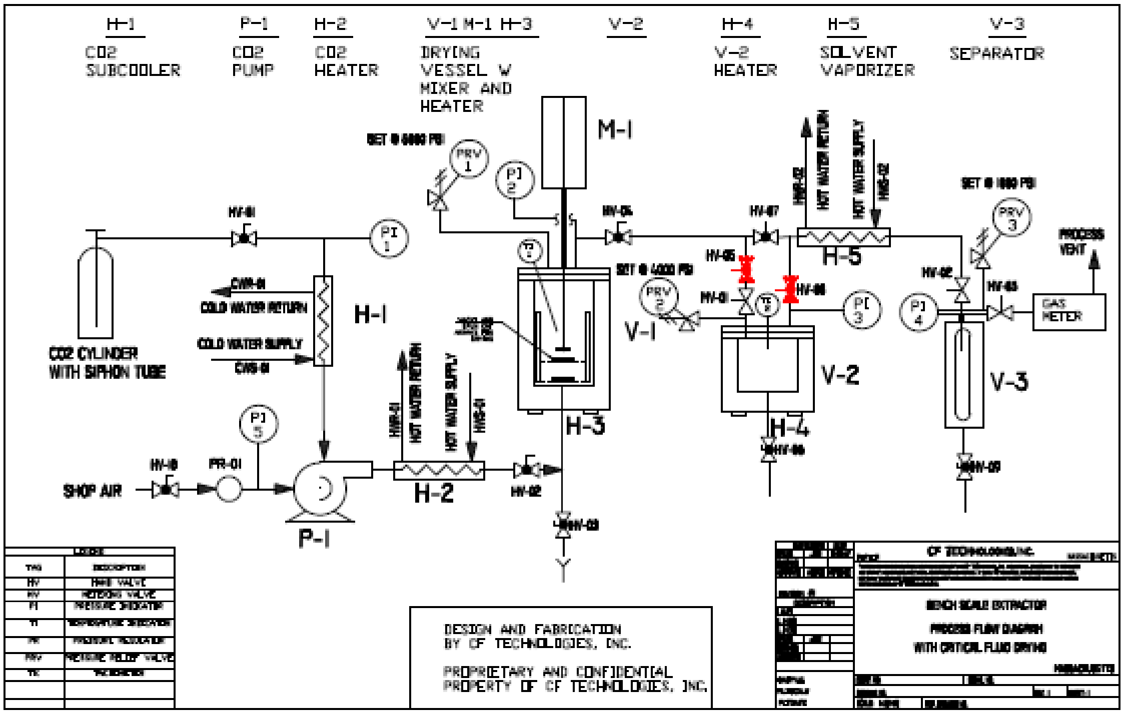


Figure A-3. Process Flow Diagram for system configuration used for $scCO_2$ drying after PVB-EtOH infiltration of VACNTs

CF Tech received 1" x 1" and 2" x 2" square VACNT arrays that had different post treatment times. The NSSC team lead presented data showing the most favorable properties were obtained 30 min post treatment, and therefore, they were used for the bulk of the VACNT arrays supplied by the Army, and used for experimental Set #1, 2, and 4.

CF Tech also received the foam spun arrays. In Set #3, 5, 6 and 7, CF Tech used the CNT spun arrays for infiltration, with less anticipated compressive strength than VACNTs, presumably comparable with the TWP. Photos of the starting materials are shown in Photos 1-5.

Photo 1. Team Wendy Hard and Soft Pads

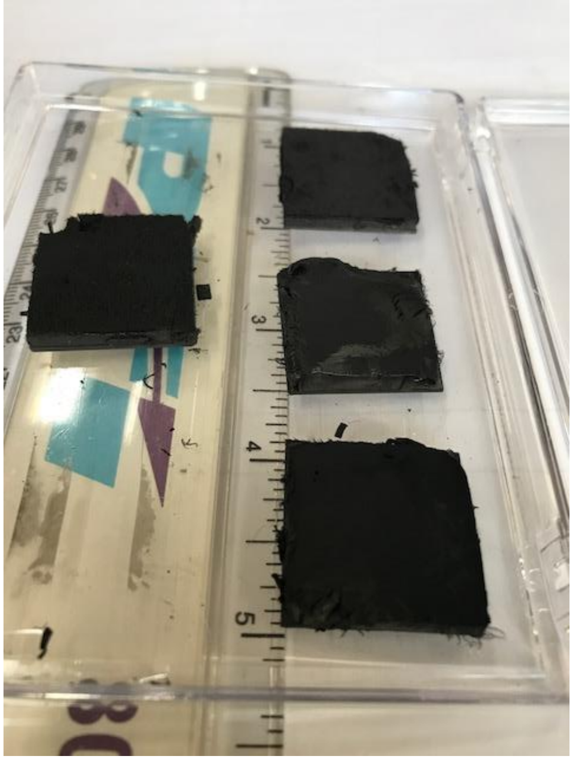


Photo 2. VACNT Arrays, 1" x 1" prior to infiltration

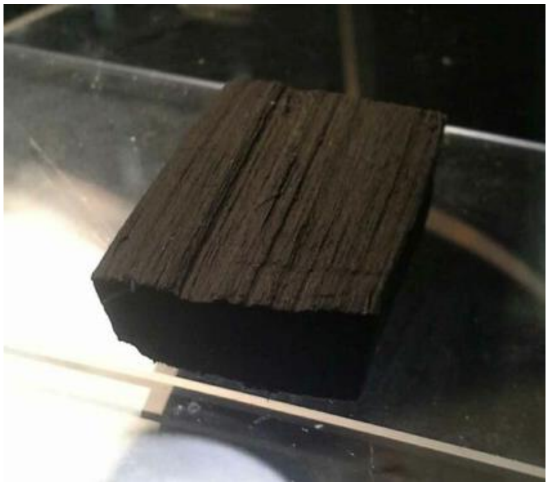


Photo 3. Pre-cut small (1/2") spun array prior to infiltration in Set #6

Photo 4. Large (5.5") Spun Array for Set #7 prior to cutting or infiltration

Photo 5. Photo of Set #7 spun array "End" after cutting out desired samples for CSA 7 and CSA8

PVB infiltration and drying with $scCO_2$ was the chosen method for Set #1. CF Tech continued to use PVB for Set #2 due to the promising mechanical, microscopic, visual and dimension and mass data. After reviewing the polymer infiltrated Set #1 and Set #2 results, and using them as a benchmark for VACNT, CF Tech evaluated other methods and considered the benefits of other polymer and/or infiltration methods, as the initial results were very promising; however, even the starting material appeared far too stiff for the desired use of the final product. The compressive strength and storage modulus both increased with increasing PVB concentration in the infiltration solution as seen in Figure A-1, while the recovery, shown in Figure A-4, was also favorable for many of the PVB reinforced VACNTs.

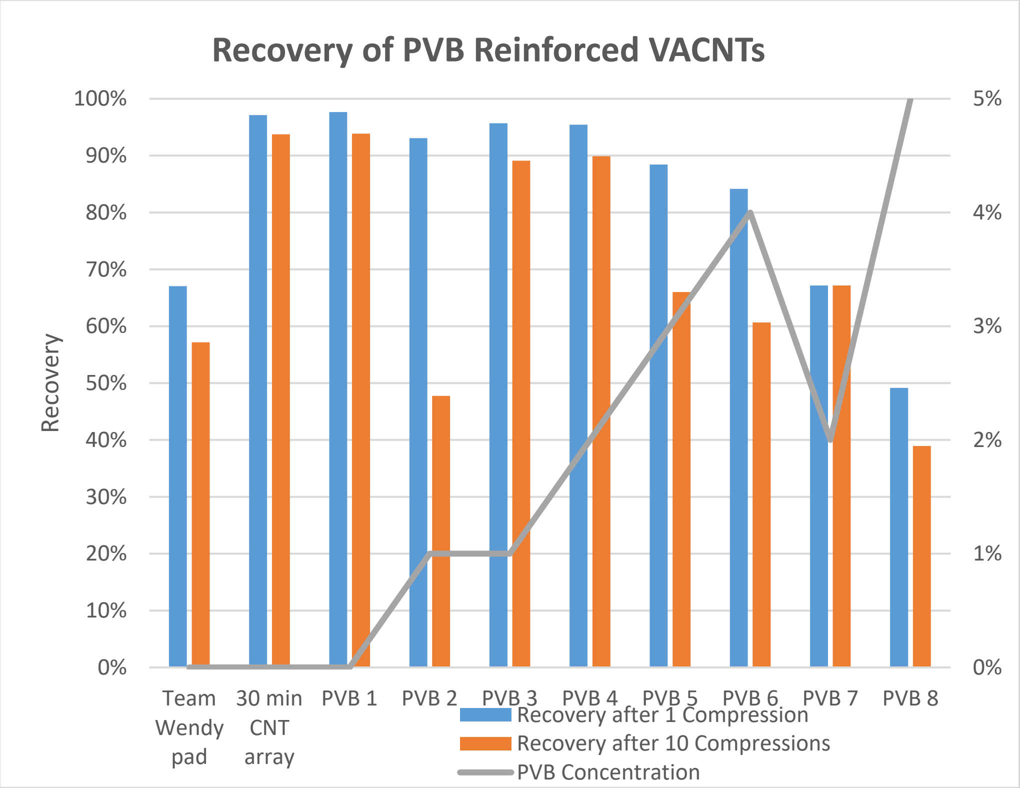


Figure A-4. Recovery of VACNTs with varying PVB solutions

CF Tech engineers discussed with colleagues best practices, experiences and know-how, and existing patents (Steiner I. S., 2014) (Meador, 2016) were explored. Further, communications with CNT–polymer composite experts explored existing methods and recommended polymers. CF Tech also communicated with a PVB polymer expert. CF Tech reviewed CNT aerogel CO_2 drying (Bryning, 2007) (Wang, Jim, Cheng, Hong, & Zhang, 2017), including solvents of interest, gelling materials, drying needs, methods and procedures.

New methods were tried with Sets #3 and 4 which included another CNT form, spun arrays in Set #3, and another infiltration method (aerogel process) and polymers (polyimide “PI” and polyurea “PU”) in Set #4. Set #3 is discussed below with spun arrays. Set #4 procedure was to infiltrate the VACNT with monomer and oligomer, and polymerize and crosslink them in the VACNT, forming a sol-gel, and then drying using CO_2 to enmesh the CNT in an aerogel like formation. To perform Set# 4 aerogel style CNT, new equipment was setup, drying equipment was modified, and a gelling and washing station was setup in a chemical fume hood. CF Tech found that the aerogel product in Set #4 although it had good mechanical properties, as seen in

Figure A-5, was unsatisfactory due to their poor recovery in compression testing as seen in Figure A-6.

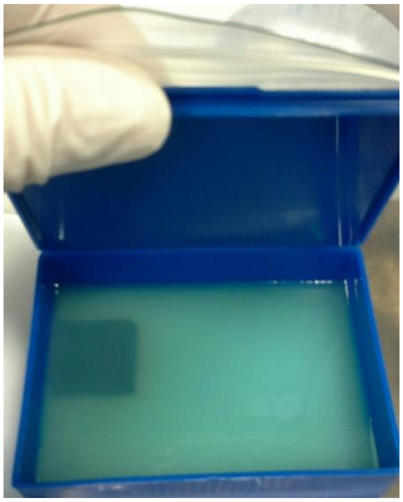


Photo 6. 1" VACNT soaking in gelling solution during Set #4

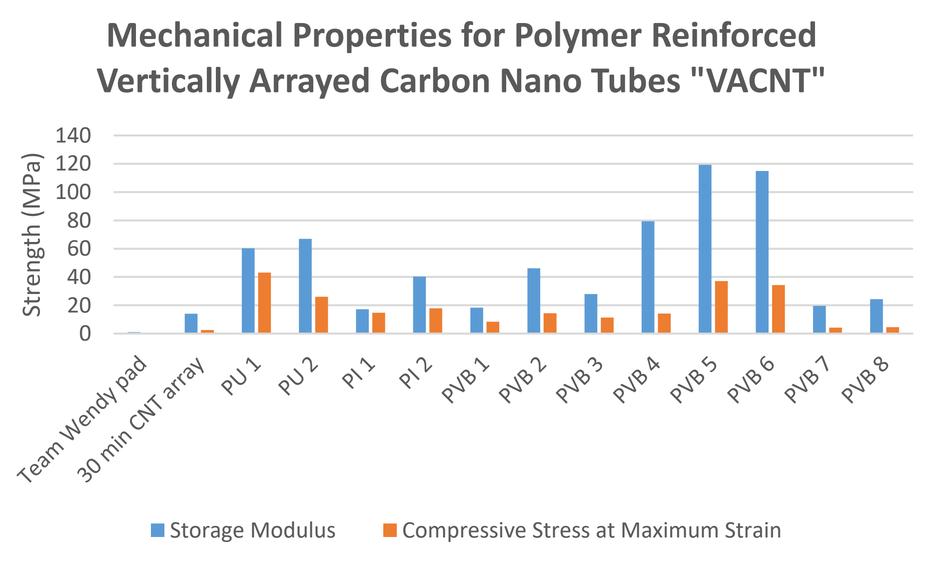


Figure A-5. Comparison of strength with various polymers

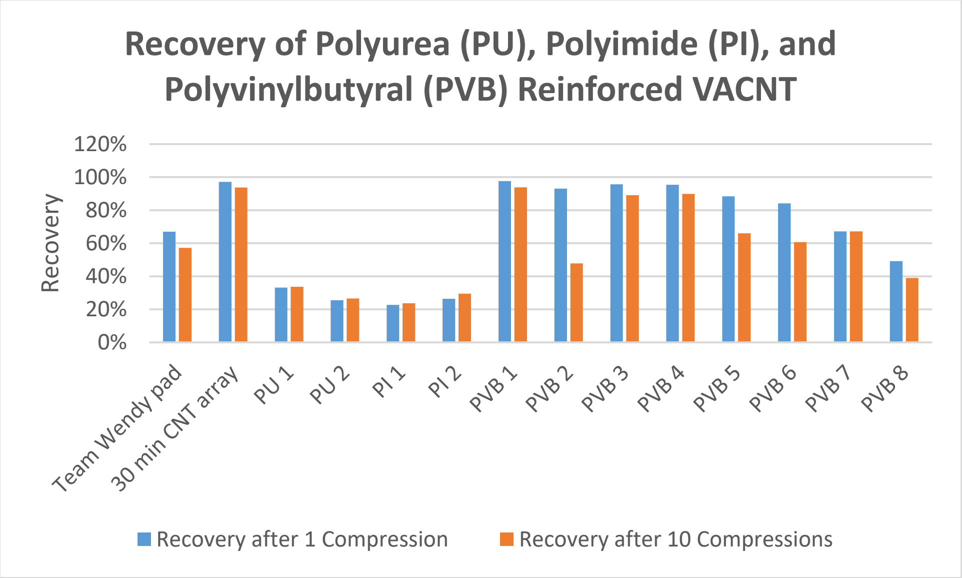


Figure A-6. Comparison of recovery with various polymers

PVB infiltration of the spun array (Set #3) showed promise, but as the VACNTs were too strong, the spun arrays were not strong enough, as seen in Figure A-7.

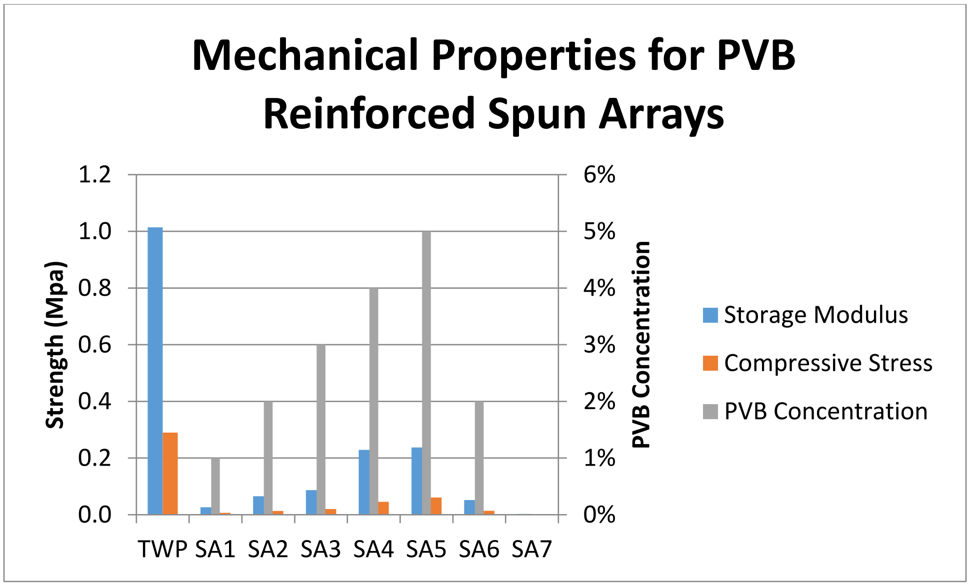


Figure A-7. Strength Comparison of Spun Arrays with TWPs

The differences in the spun arrays in PVB concentration and array density provided a range of mechanical properties, and regression analysis was used to project density and PVB concentration that would get strength closer to TWP. The next set of experiments tested methods of increasing the spun array foam to the target density and then infiltrating and drying it while maintaining the density. CF Tech evaluated other methods of cutting and compressing the spun arrays to make a more uniform starting material and increasing the strength by increasing original density of the infiltrated materials. CF Tech compressed the array in Set #5 prior to and during infiltration, which appeared to have been favorable. Set #6 continued with spun arrays, compressed to greater densities. The results were encouraging, as seen in Figure A-8 and A-9, with mechanical properties comparable to TWPs and excellent recovery.

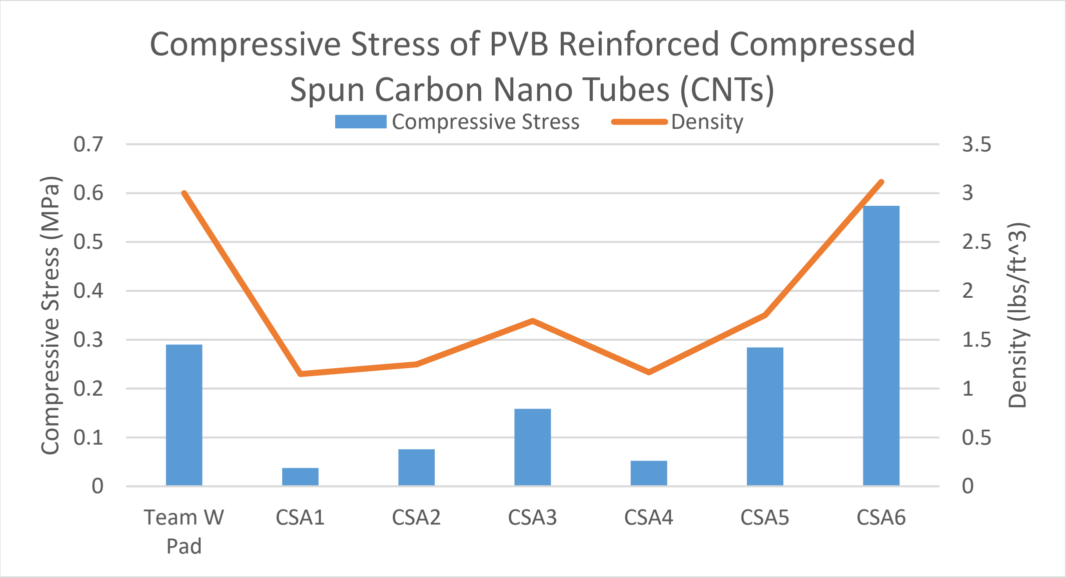


Figure A-8. Compressive Strength of Compressed Spun CNTs compared with TWP.

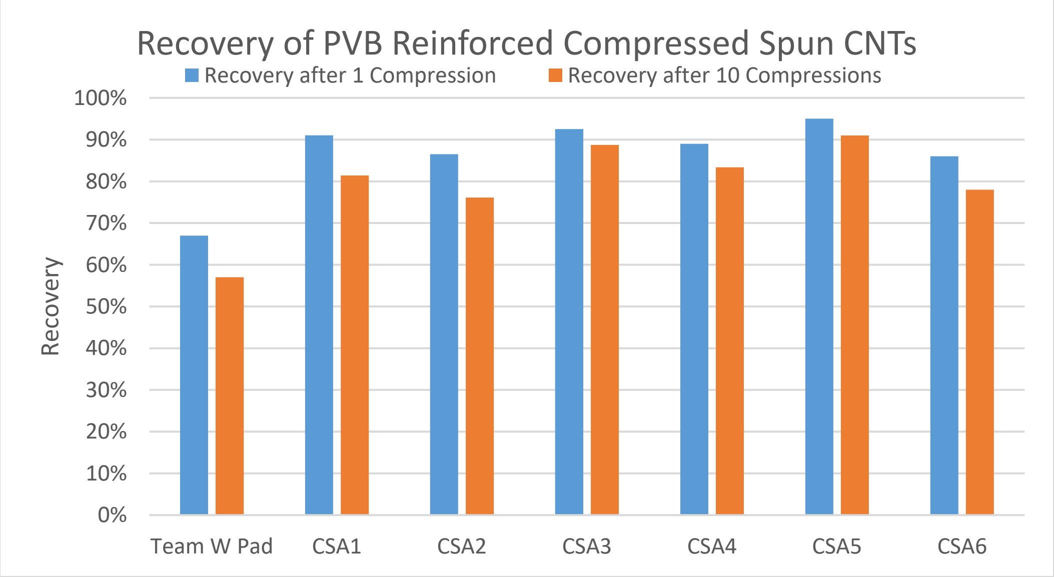


Figure A-9. Recovery of Compressed Spun CNT arrays (CSAs).

Final Set #7 required cutting of spun arrays, and also compressing and testing at larger scale. Based on appearance and feel of the Set #5 and Set #6 samples, this PVB infiltrated CSA material seemed to have improved properties over TWPs. Improvements include lower weight, better recovery and better temperature stability while maintaining strength similar to Team Wendy. Results from NSSC testing confirmed the improved temperature stability of the compressed CNT over the TWP. The DMA temperature testing of the Team Wendy Hard Pad and CF Tech Array CSA1 from Set #5 are shown in Figures A-10 and A-11. The noise in Figure

A-11 is assumed to be the result of the uneven dimpled surface of CSA1, as seen in Photo 7. The CNT spun arrays have lower stiffness, and less compressive strength and resistance than the VACNTs (which before processing with polymers already exceeded the Team Wendy material stiffness by an order of magnitude). When compressed to about 1/2 the density of the TWP and polymer reinforced, the spun arrays have similar compressive strength to the Team Wendy individual components, and about half the strength of the Team Wendy composite pad. However, the CSA has significantly better recovery, 76–89% after 10 cycles vs. 50–57% for Team Wendy after 10 cycles.

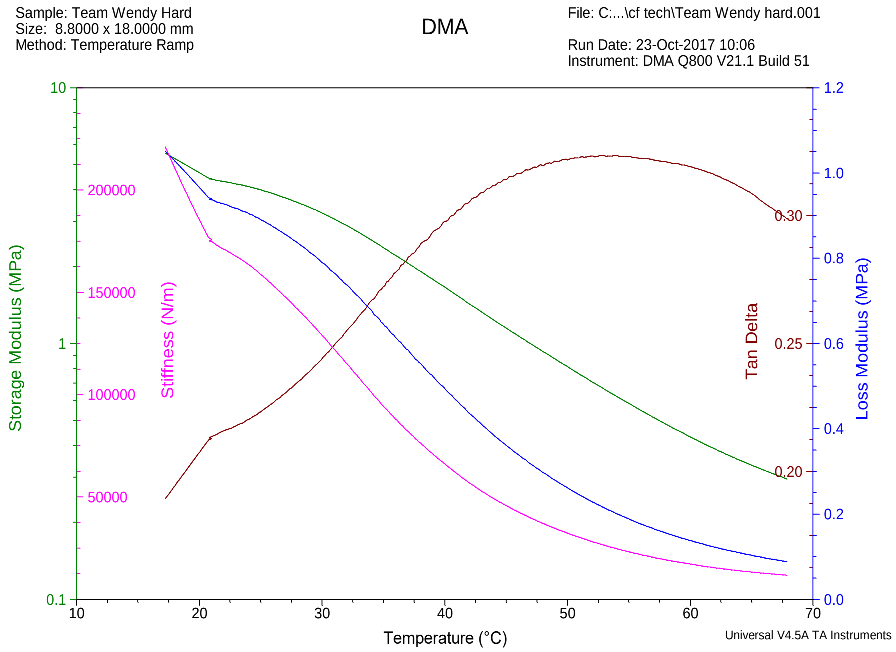


Figure A-10. NSSC DMA testing results of Team Wendy Hard Pad

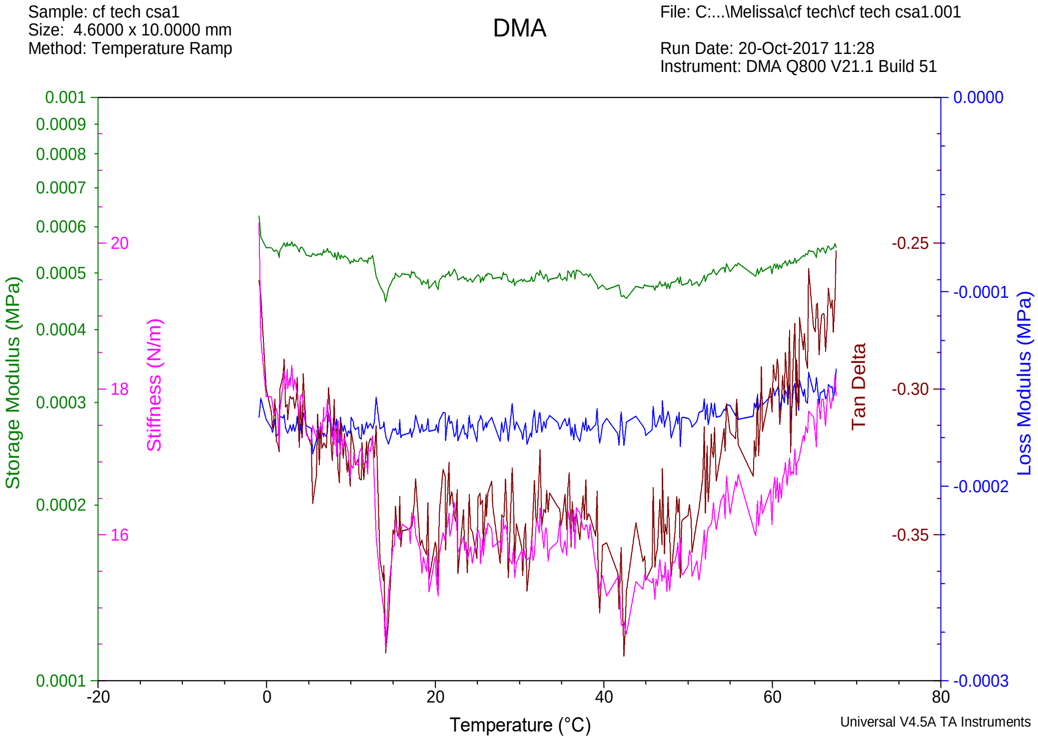


Figure A-11. NSSC DMA testing results of CF Tech CSA1 from Set #5. The noise in the data is presumed due to the uneven surface of the array, as seen in Photo 7

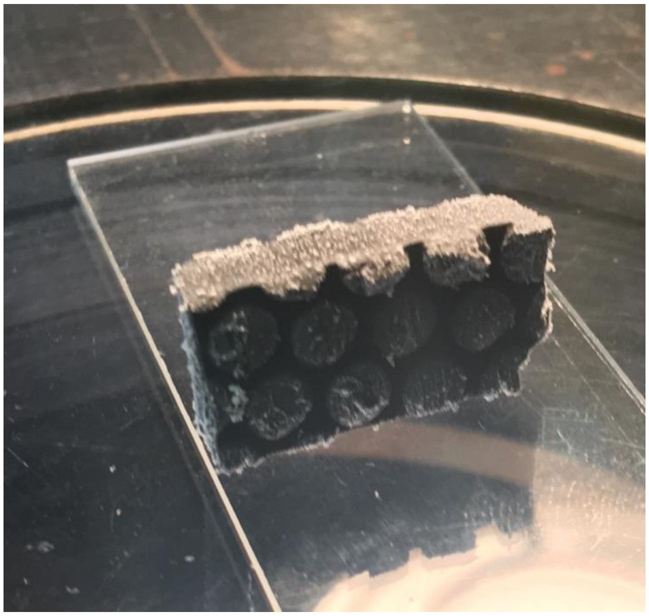


Photo 7. CSA1 post Polymer infiltration and $scCO_2$ drying

The final set, Set #7, experimental procedure was to duplicate, with larger CNT parts, the conditions for the highest performance sample from Sets 5 and 6, which was sample CSA6.

Unfortunately, the spun array received from NCSU was not pre-cut. The array was received as an approximately 5.5" x 2" x 1.5" mound, as compared to the laser cut material received and used in Set #6. Cutting the Set #7 array into large test pieces required CF Tech to manufacture plastic holders with cutting slits. Without any practice material, CF Tech attempted to cut the starting material into two neat 2" x 2" test pieces with target finished thickness of 0.75" after processing and trimming. Unfortunately, the cutting process did significant damage to the material including flaking, separating and peeling of the piece. The edges did not cut easily and the in-house cutting resulted in jagged and lopsided starting pieces. The first of these two pieces, CSA8, was compressed to a density of 0.021 g/ml, and infiltrated with a PVB in ethanol solution of 5% similar to that of CSA6. NSSC testing of CSA8 included impact velocity testing of an anvil at 17 feet per second (fps). The goal of this test was to maintain less than 150Gs at 17 fps. CSA8 peak acceleration was 295Gs, failing the test. NSSC was able to get these results quickly. CF Tech went back to the lab and infiltrated and dried CSA7 with 3% PVB solution and compression to a density of 0.026 g/ml (actual was 0.0257 g/ml). CSA7 measured peak acceleration was 280Gs, a slight improvement, but also failing the test. These large thick parts, CSA7 & 8, appeared to be significantly more brittle than the other CSA samples. Much longer solvent exchange and drying times were required with the thick samples, and it is speculated that more of the plasticizier may have been extracted during the increased drying time, and may have resulted in a lower glass transition temperature and more brittle material.

Sub - Task 2. Name: Design Fixtures.

Over the course of the experiments, a variety of fixtures were created, modified, expanded, duplicated and improved. Initial internal discussion focused on mold materials and potential styles to use and mold sizes. These discussions were more fruitful after receiving the arrays. CF Tech selected a plastic mold for experimental set up of 1" x 1" VACNT and prepared them for use during infiltration. The drying fixture was fabricated from stainless steel weigh boats, and was loaded with one to four arrays per vessel. Early sets used four fixtures, stacked on top of each other inside the drying vessel. Later sets were more advanced, were made of perforated stainless steel sheet, stainless wire cloth, and polytetrafluoroethylene (PTFE) mesh coatings to avoid sticking to the fixture and to produce flat, smooth surfaces. The last tests included fixtures that could be tightened to compress the arrays in order to increase their density, during infiltration and drying. The last test had all of these features, but was expanded to compress the large substrate to a 2" x 2" x 0.75" test material.

Glass laboratory jars were used during solution preparation (heating and dissolving polymer in solvent). The arrays were infiltrated and aged in these jars. A second fixture design was used in the vacuum oven, prior to determining vacuum drying was unnecessary.

Set #4 required new infiltration containers and a new fixture was made for the solvent/polymer gel, to allow the VACNT to be immersed in the solution, and then to keep the VACNT fully immersed during gelling and solvent exchange. After five washes with fresh laboratory grade acetone over 3 days, these gels remained submerged for a few more days in the infiltration containers. These CNT aerogels were placed in the Set #1 style sample holders for insertion into the pressure vessel.

Sets #5, 6, and 7 required new styles of fixtures that could be used to compress the array, and maintain compression during submerged infiltration and during drying inside the pressure vessel. The Set #5 fixture was fabricated from stainless perforated plate, which caused dimpling in the CSA. Set #6 required a second fixture, which was designed and fabricated in similar fashion to Set #5 but with two separable, yet stackable parts in order to infiltrate the arrays in two separate solutions, 2% and 5%, but to stack during drying within the pressure vessel. A layer of fine Teflon mesh was placed between the perforated plate and the array to prevent dimpling and adhesion of the array to the stainless steel. Although there was minor peeling, the polymers and arrays usually separated more easily from the Teflon sheet than from the stainless steel wire cloth and perforated sheet.

Set #7 required additional fixtures for cutting the large spun array. CF Tech followed the instruction of NCSU, using equipment that was available in the laboratory and shop, and fabricating a plastic cutting template and holder. A large CNT section measuring approximately 2" x 2" was cut from a full sized spun array. In order to cut the array, a plastic plate was cut to approximately the size of the array, and two slits spaced 2 inches apart were cut into the plate to guide the razor knife during cutting while compressing the spun array. The plastic sheet was then pressed down on the array to compress it by about 70%, and a razor blade was inserted into the slits and used to cut the array. After a 2" x 2" square section had been prepared, it was measured and weighed. Calculations were then made to determine how much the array should be compressed in order to attain a density of .021 g/mL. In order to compress the sample, a staging system capable of fitting into a pressure vessel was constructed. The staging system consisted of two perforated stainless steel sheets covered with teflon mesh supported by four threaded rods, with spacers fabricated from tubing on each rod setting the gap between the screens. The spacer tubing was cut to a length equal to the desired thickness of the CNT array. The CNT sample was placed on the bottom screen, and the top screen was pushed down, with the rods compressing the CNT until the top plate contacted the spacer. The top screen was then held down with nuts on each of the threaded rods. The Set #7 large arrays each required their own fixture and had to be dried individually, as only one at a time fit in the vessel.

Sub - Task 3. Name: Infiltrate and dry VACNT arrays per Sub-Task 1.

PVB, EtOH, CO_2 and DME were procured from CF Tech inventory. The first set of polymer infiltration experiments with PVB was tested with two polymer solvents and delivery methods, with EtOH solvent at atmospheric pressure, and with DME, a liquefied gas, solvent at elevated pressure, in both cases using $scCO_2$ to “dry” the array after infiltration.

Based on the measured density of the arrays as received, and the target maximum product density of 4 lb/ft^3, the estimated concentration of PVB in EtOH was calculated to be approximately 2% by mass to reach the target. The first set of experiments tested infiltration with PVB dissolved in ethanol at concentrations of 1 and 2%, and with PVB dissolved in DME at low concentration.

CF Tech employees met with the Army on 8/25/2017 and hand-delivered the first set of results: four small arrays from the preliminary tests, and Set #1, four 1” x 1” PVB infiltrated arrays for analysis.

PVB, EtOH and CO_2 were procured from CF Tech inventory for Sets #2 and 3. Experimental Sets #2 and 3 used PVB in EtOH solvent and dried in $scCO_2$ pressures and temperatures. VACNT and spun arrays were infiltrated in Sets #2 and 3 respectively. PVB concentrations of 1%-5% were studied, and included one duplicate test sample. CF Tech employees met with the Army rep on 9/8/2017 and hand delivered the second set of samples: four 1” x 1” PVB infiltrated arrays for analysis. CF Tech employee John M. Moses traveled to Natick and met with Army reps, at their facility on 9/22/17, delivering the third set of VACNTs and witnessing some preliminary mechanical testing of the Set #3 spun arrays on site at the laboratory.

NMP, DMBZ, EPDA, TAPM, Et3N and acetone were procured for Set #4. Set # 4 consisted of cutting a 2" square VACNT into four individual squares, two polyurea aerogel reinforced VACNTs and two polyimide aerogel reinforced VACNTs were made. CF Tech employees met with the NSSC team lead on 10/5/2017 and hand delivered the Set #4 samples for analysis. PVB, EtOH and CO_2 were procured from CF Tech inventory for Set #5. The Set #5 infiltration experiment used PVB in EtOH solvent and dried in $scCO_2$ pressures and temperatures. The spun arrays were carefully cut, measured and compressed prior to saturation and infiltration in Set #5. A PVB concentration of 2% in ethanol was selected. CF Tech employees met with the NSSC team lead on 10/20/2017 and hand-delivered the Set #5 samples for analysis.

Set #6 spun array materials were received from the client on 10/30/2017, the dimensions and mass were measured and density and compression to meet target density calculated. The materials received were two small cube-like spun arrays, which were infiltrated with the prepared solutions of 2% and 5% PVB in EtOH solvent and dried in $scCO_2$ pressures and temperatures and delivered to NSSC on 11/6/17 for analysis.

Set #7's CSA8 attempted to duplicate 8113-1-6-CSA6, which was the 5% PVB compressed to 0.021 g/mL, in a larger size. After receiving the peak acceleration test results from NSSC, CF Tech infiltrated and dried a second Set #7 array, CSA7 to 3% PVB in EtOH, and compressed it to 0.0257 g/mL. These large samples required additional time drying in $scCO_2$ before all of the EtOH was collected, greater than was used in CSA1-CSA6. CSA8 consisted of two halves when it was placed into the staging. It was possible to neatly sandwich them together, one on top of the other, and when it was removed from the extractor, the sample was firmly glued together in one solid piece, by the PVB. Visually, CSA8 and CSA7 had very little PVB on the outer surface of the sample; there were no major conglomerations or web-like coatings as with previous samples. The sample was very lightly adhered to the teflon screens, making it easy to pull off without leaving behind any layers of CNT fibers, as was more of a struggle, losing layers with CSA5 and CSA6.

CF Tech PI John M. Moses was in regular communication with the client regarding experimental planning, testing, analysis and results.

The infiltration and drying procedure is detailed within Appendix 2. All drying was performed in a CF Tech manufactured 500 cc MAWP 5,000 psi @ 200 °F standard DurOLok pressure vessel. The DurOLok vessel is a quick opening, patented vessel system able to be opened in less than 1 min. As seen in Figure 3, the system has two DurOLok Vessels, a sight gage separator, gas meter, double pipe heat exchangers, electric heaters and all necessary plumbing, fittings, valves and measurement instruments.

Sub - Task 4. Name: Evaluate mechanical and electron microscopy analysis from Sub - Task 3 results.

Results were received in September for Sets #1 and 2, mechanical and microscopic. CF Tech reviewed the results and images and decided to take a different approach going forward; mainly, to use low compressive strength spun arrays for Set #3, and, for Set #4, an aerogel infiltration to compare results for a less stiff result.

Mechanical and microscopic results were received in October for Sets #3, 4 and 5. CF Tech reviewed the results and images and decided, with concurrence by NSSC personnel, to use only the spun arrays and the PVB polymer for the remainder of the planned experiments. The VACNTs are too stiff, and the aerogels were too brittle; the PVB infiltration provided good recovery after compression, and the compressed spun array increased strength, comparable to the Team Wendy benchmark, while PVB infiltration maintained the compressed dimensions after drying with CO_2 and release from the drying fixture.

Set #6 results were very good, the 5% PVB sample, CSA6, compressed sample hit the storage modulus mark, of falling within the 0.3-0.6 MPa and the recovery after 10 compression cycles was better than the TWP. The NSSC team was impressed by the look, feel, and mechanical results.

Set #7 results were disappointing. CSA7 and CSA8 both failed the <150Gs peak acceleration when an anvil was dropped on them at 17 fps. Both samples appeared more brittle that their Set #6 counterparts and cracked and broke apart under the force of the impact. Set #7 did not receive temperature, microscopic or storage modulus testing prior to the completion of the program.

NSSC provided SEM microscopic images for the majority of the delivered samples. They are shown in Appendix 1.

Summary of Results and Conclusions

CF Tech was able to produce a product with favorable qualities (CSA6) within the time and budget allowed. CF Tech recommends that the spun array infiltration method be further tested in order to provide a superior solution with improved performance and durability for soldier helmets compared to the currently used Team Wendy foam helmet padding.

The cut and compressed spun array, infiltrated with a 5% PVB EtOH solution and dried with $scCO_2$ provides the desired strength, 0.3-0.6 MPa, capacity across the desired temperature range, and lower weight profile required by NSSC for soldier safety in helmet padding. During the larger peak acceleration tests, the 3% PVB array fared slightly better than the 5%. CF Tech recommends additional measures to fabricate the Set #7 sized spun array, with the properties of the Set #6 materials, and presumably with significantly improved peak acceleration testing. There is excellent potential for providing superior helmet padding.

During Set #7, due to the diffusion resistance of the thick CSA, to remove all of the EtOH in the sample, significantly more CO_2 was pumped through the vessel, compared to the thinner samples. There is a possibility that the samples became brittle due to the excess CO_2 required for solvent exchange, and that the plasticizer may have been extracted from the PVB. It was also observed that when the extractor was opened, there was a layer of PVB that coated the bottom of the vessel. The feet of the staging were glued in place, and a gentle pull was necessary to get the staging free.

CF Tech does not recommend using the VACNT for the helmet padding due to its naturally occurring high strength and stiffness. However, there may be other applications that could take advantage of the excellent properties of the PVB reinforced VACNT.

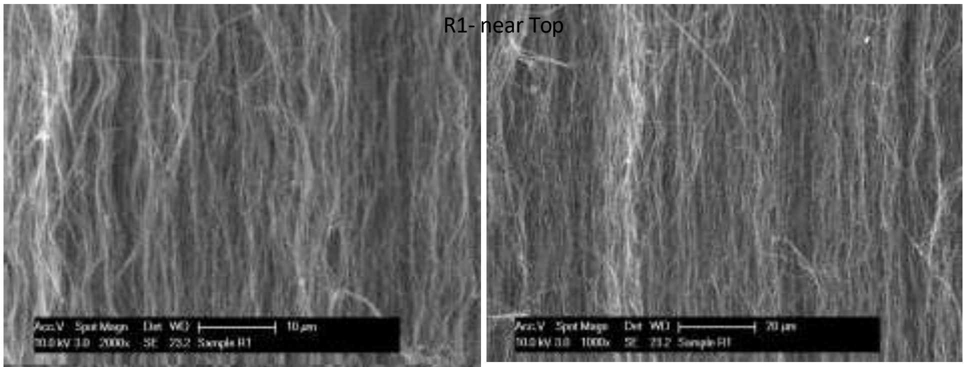
Project Conclusions:

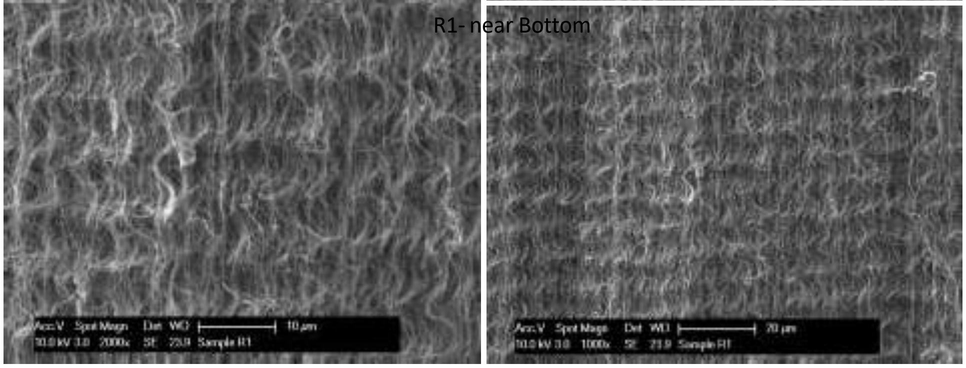
- $scCO_2$ does not damage the array and is a favorable drying agent.
- 2-5% PVB in EtOH is a favorable solution for infiltration.
- The foam spun arrays are the favorable pre-solution material.

Project Recommendations:

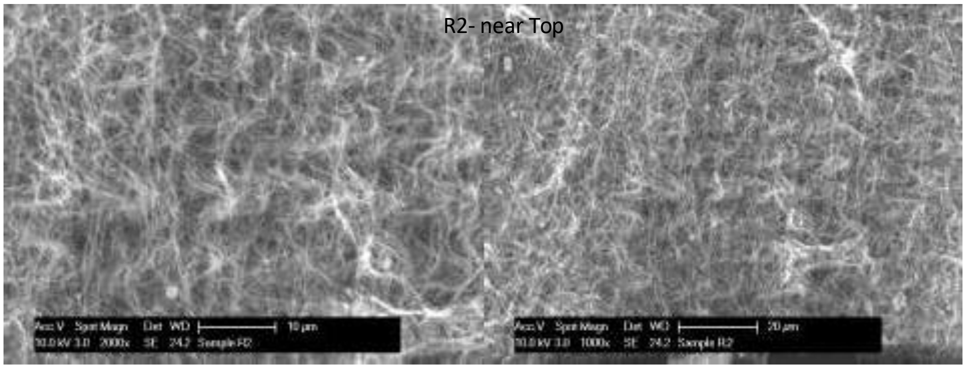
- A faster, more homogenous procedure needs to be developed for the manufacture of spun arrays.
- A procedure needs to be developed for cutting and shaping the spun arrays for testing and measurement quality. The spun arrays arrived in vastly different shapes, sizes, densities and formations and make it hard to quantify results easily. This was partially overcome by compressing the arrays prior to infiltration to provide uniform density.
- Explore other uses of the VACNT, as they are too stiff for helmets, but had excellent results in terms of recoverability, and improved strength, and wide operating temperature range.
- CF Tech does not recommend using monomer and oligomer infiltrations followed by in-situ polymerization of the VACNTs.
- In the future, CF Tech would like to revisit an attempt to procure SWCNTs for a future round of experimental tests, but have not identified a readily available source.
- CF Tech would like to continue this project using NCSU pre-cut spun CNT arrays of equal size, shape and density to confirm and expand upon CSA6 favorable results.

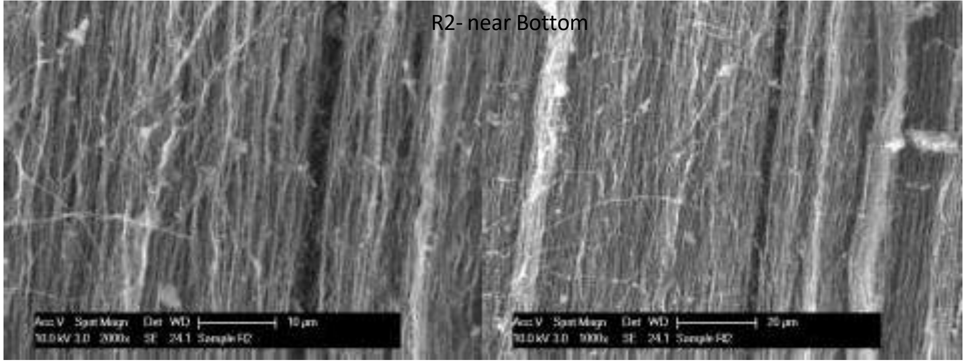
CF Tech report Appendix 1: SEM Images, by NSSC

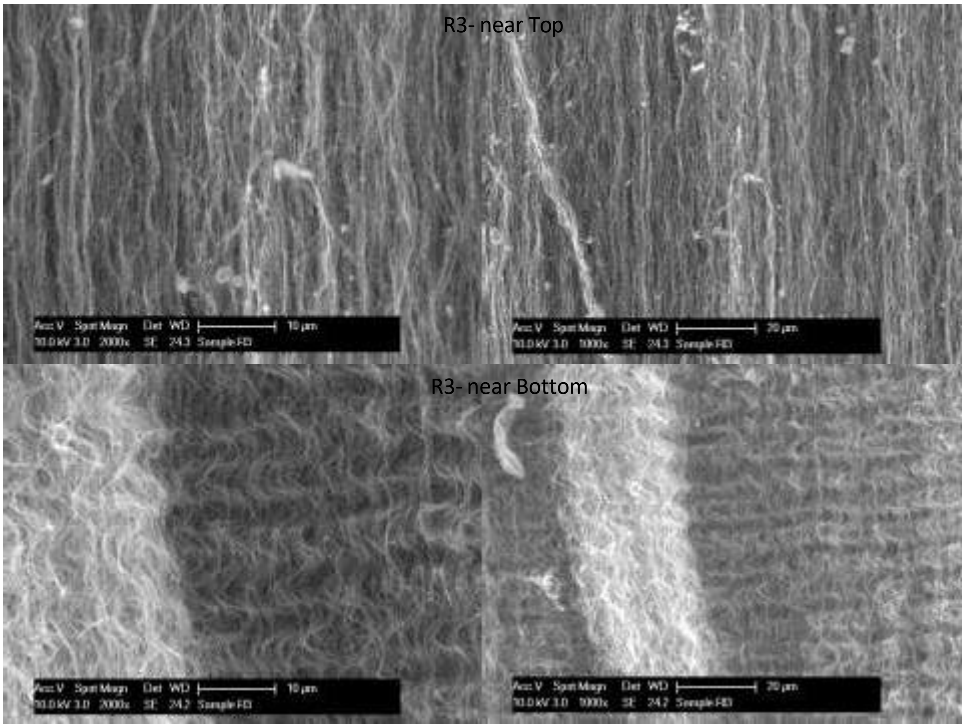

R1- near Top


R1- near Bottom

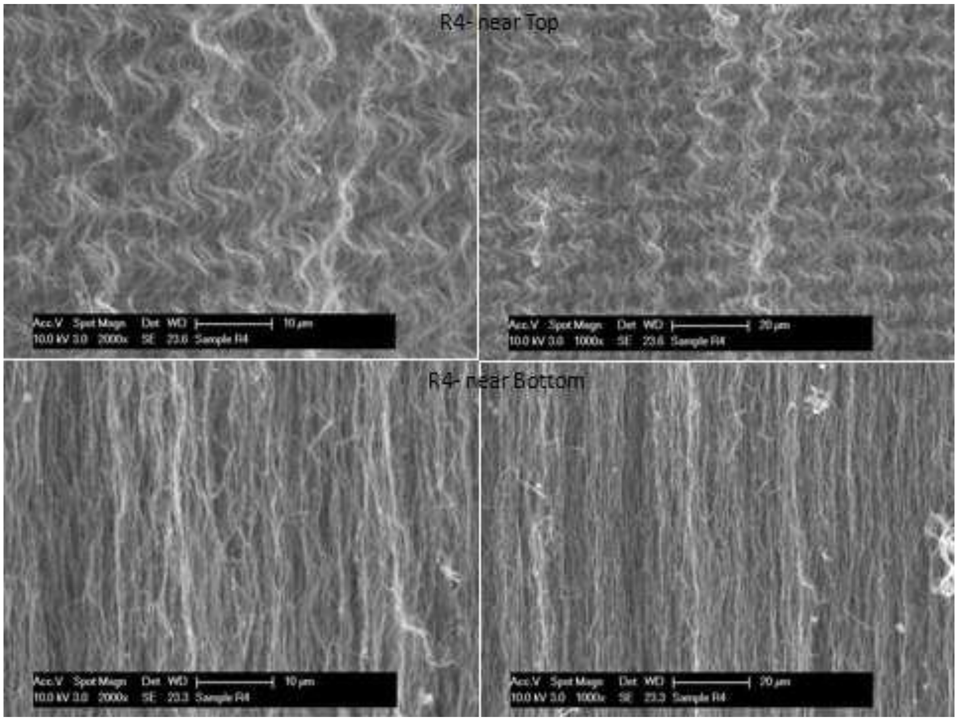
R1


R2- near Top


R2- near Bottom

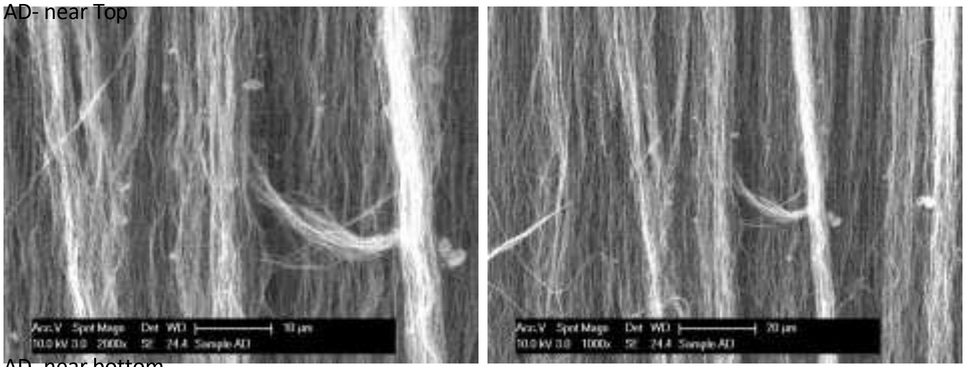

R3- near Top
Acc.V Spot Magn Det WD 10 µm
10.0 kV 3.0 2000x SE 24.3 Sample FD
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1000x SE 24.3 Sample FD
R3- near Bottom
Acc.V Spot Magn Det WD 10 µm
10.0 kV 3.0 2000x SE 24.2 Sample FD
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1000x SE 24.2 Sample FD

R3

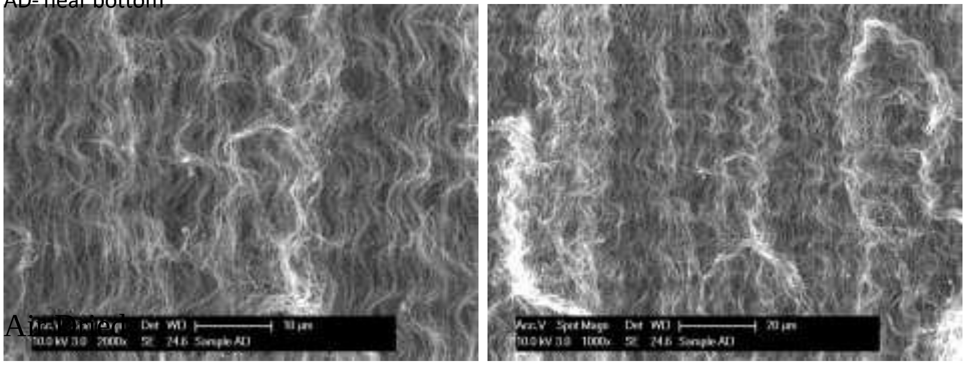

R4- near Top
Acc.V Spot Magn Det WD 10 µm
10.0 kV 3.0 2000x SE 23.6 Sample R4
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1000x SE 23.6 Sample R4
R4- near Bottom
Acc.V Spot Magn Det WD 10 µm
10.0 kV 3.0 2000x SE 23.3 Sample R4
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1000x SE 23.3 Sample R4

R4

AD- near Top

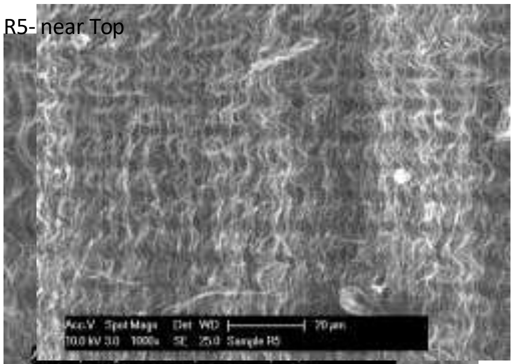


AD- near bottom

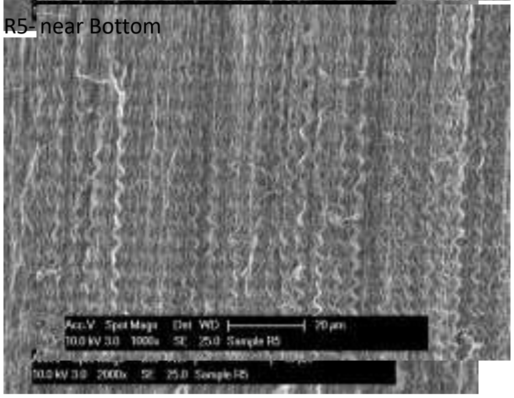


Air Dried

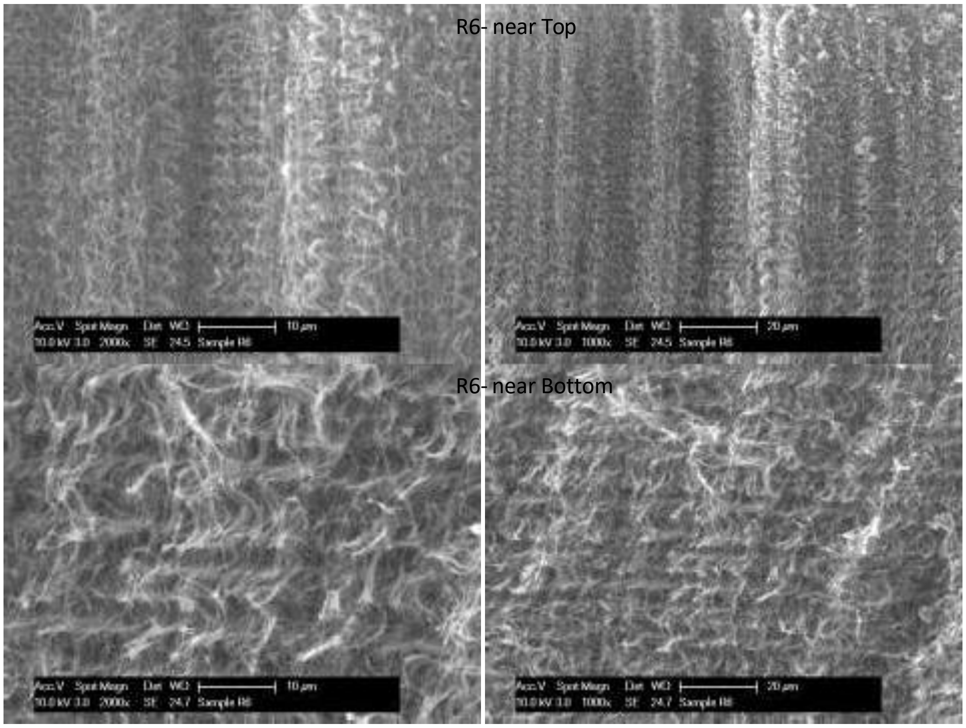
R5- near Top



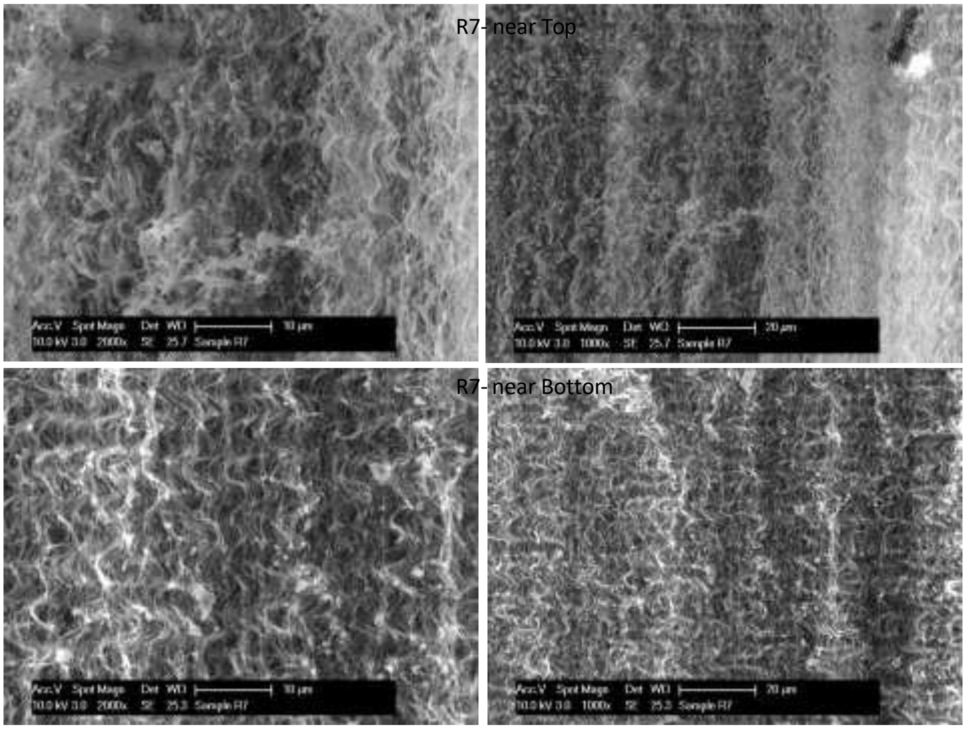
R5- near Bottom



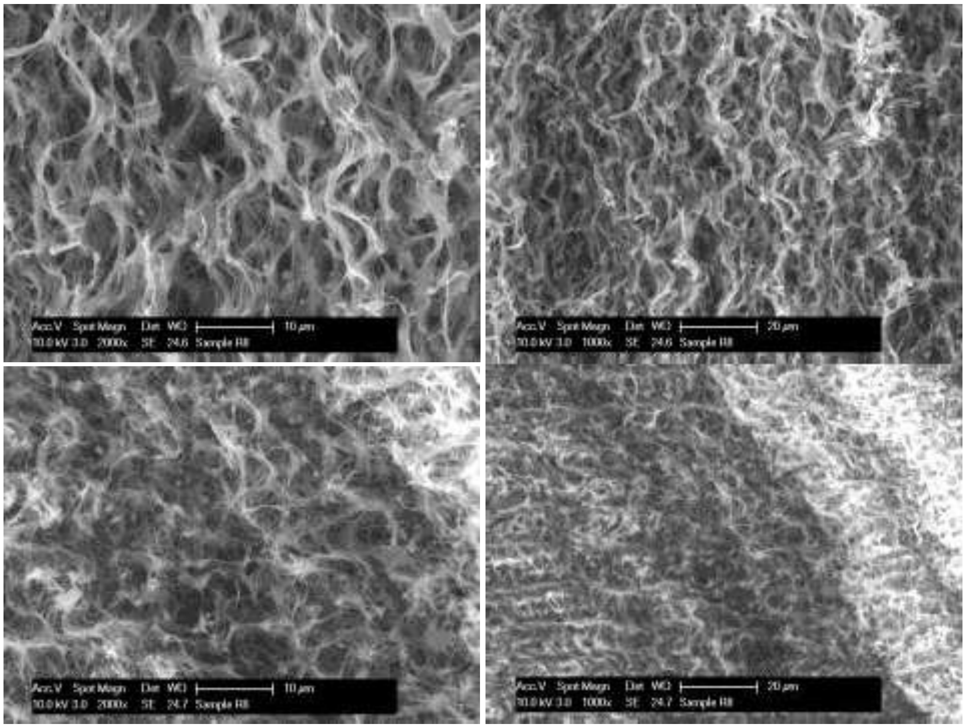
R5


R6- near Top
R6- near Bottom
Acc.V Spot Magn Det WD 10 μm
10.0 kV 3.0 2000x SE 24.5 Sample R6
Acc.V Spot Magn Det WD 20 μm
10.0 kV 3.0 1000x SE 24.5 Sample R6
Acc.V Spot Magn Det WD 10 μm
10.0 kV 3.0 2000x SE 24.7 Sample R6
Acc.V Spot Magn Det WD 20 μm
10.0 kV 3.0 1000x SE 24.7 Sample R6

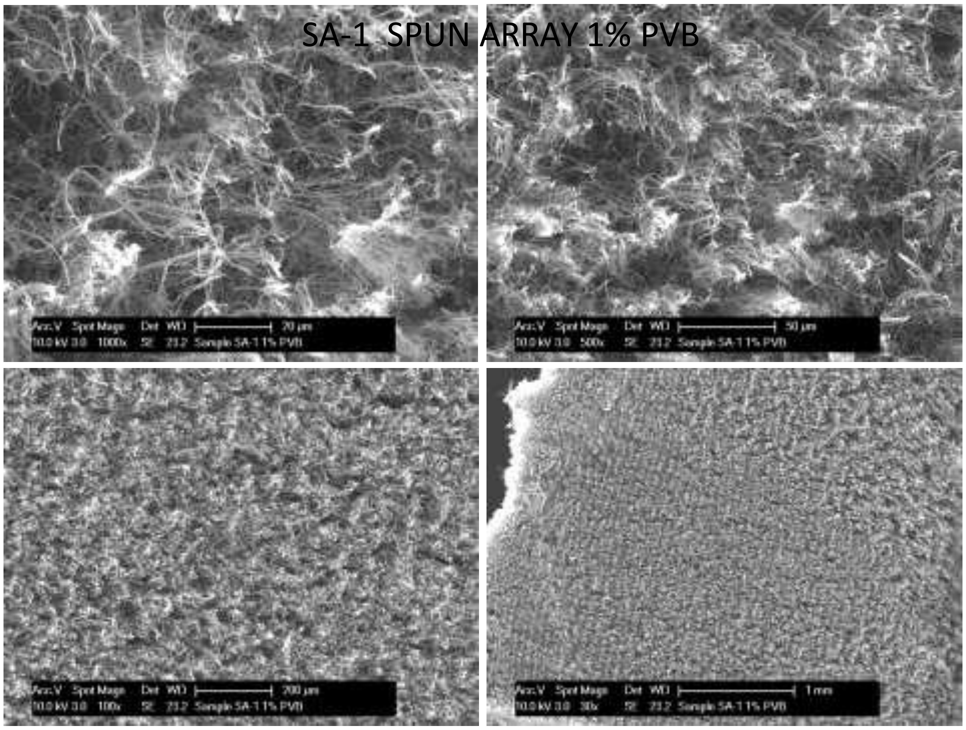
R6


R7- near Top
R7- near Bottom
Acc.V Spot Magn Det WD 10 μm
10.0 kV 3.0 2000x SE 25.7 Sample R7
Acc.V Spot Magn Det WD 20 μm
10.0 kV 3.0 1000x SE 25.7 Sample R7
Acc.V Spot Magn Det WD 10 μm
10.0 kV 3.0 2000x SE 25.3 Sample R7
Acc.V Spot Magn Det WD 20 μm
10.0 kV 3.0 1000x SE 25.3 Sample R7

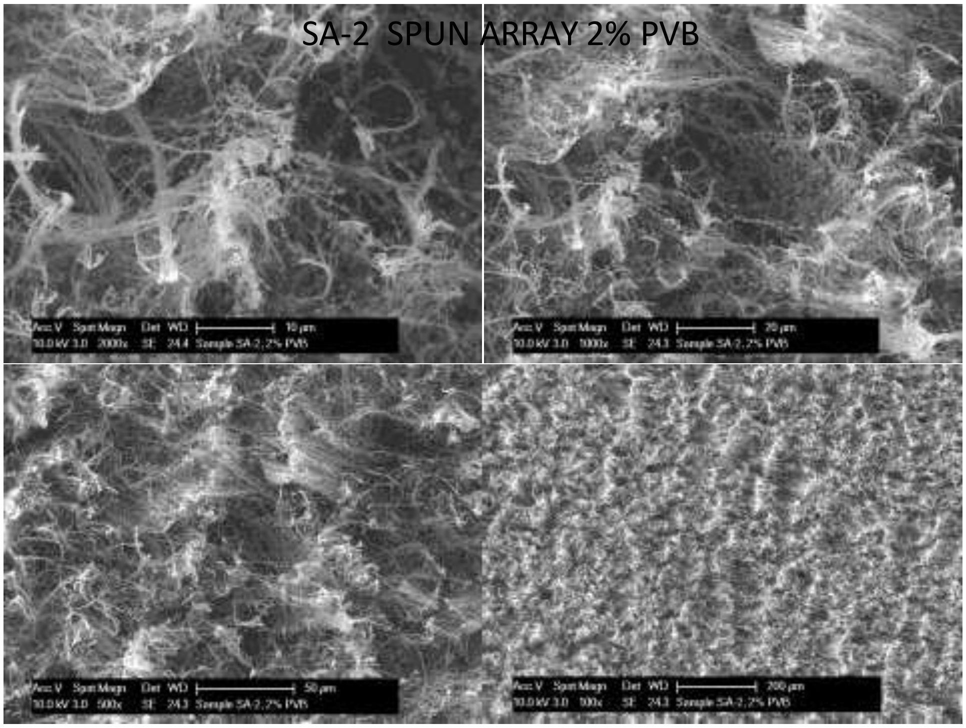
R7


Acc.V Spot Magn Det WD 10 µm
10.0 kV 3.0 2000x SE 24.6 Sample R8
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1000x SE 24.6 Sample R8
Acc.V Spot Magn Det WD 10 µm
10.0 kV 3.0 2000x SE 24.7 Sample R8
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1000x SE 24.7 Sample R8

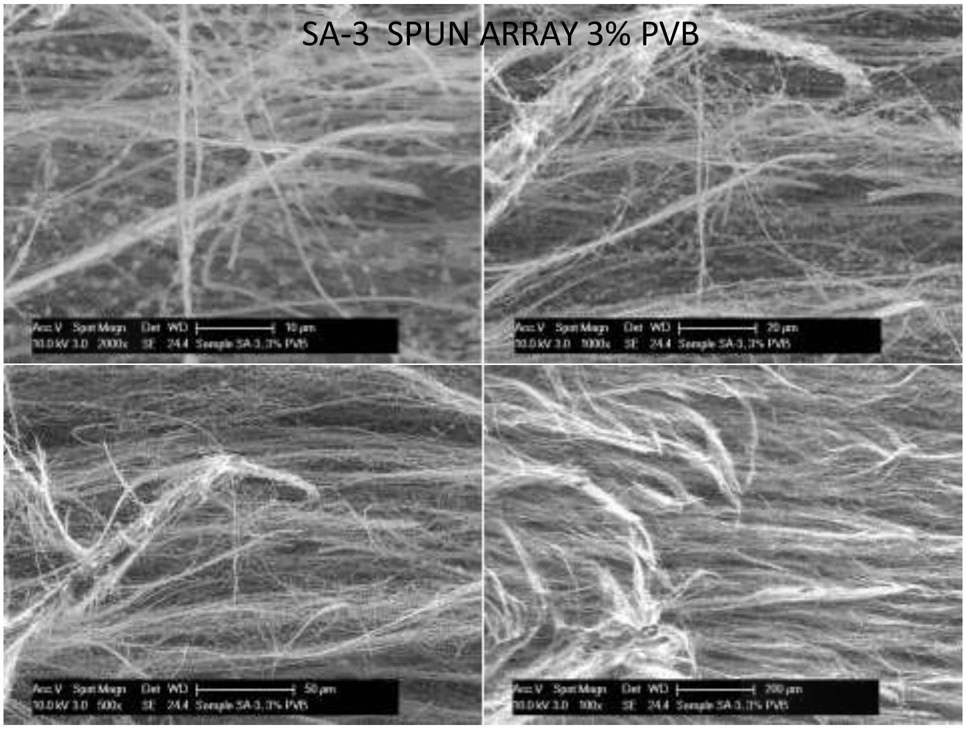
R8


SA-1 SPUN ARRAY 1% PVB
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1000x SE 23.2 Sample SA-1 1% PVB
Acc.V Spot Magn Det WD 50 µm
10.0 kV 3.0 500x SE 23.2 Sample SA-1 1% PVB
Acc.V Spot Magn Det WD 200 µm
10.0 kV 3.0 100x SE 23.2 Sample SA-1 1% PVB
Acc.V Spot Magn Det WD 1 mm
10.0 kV 3.0 30x SE 23.2 Sample SA-1 1% PVB

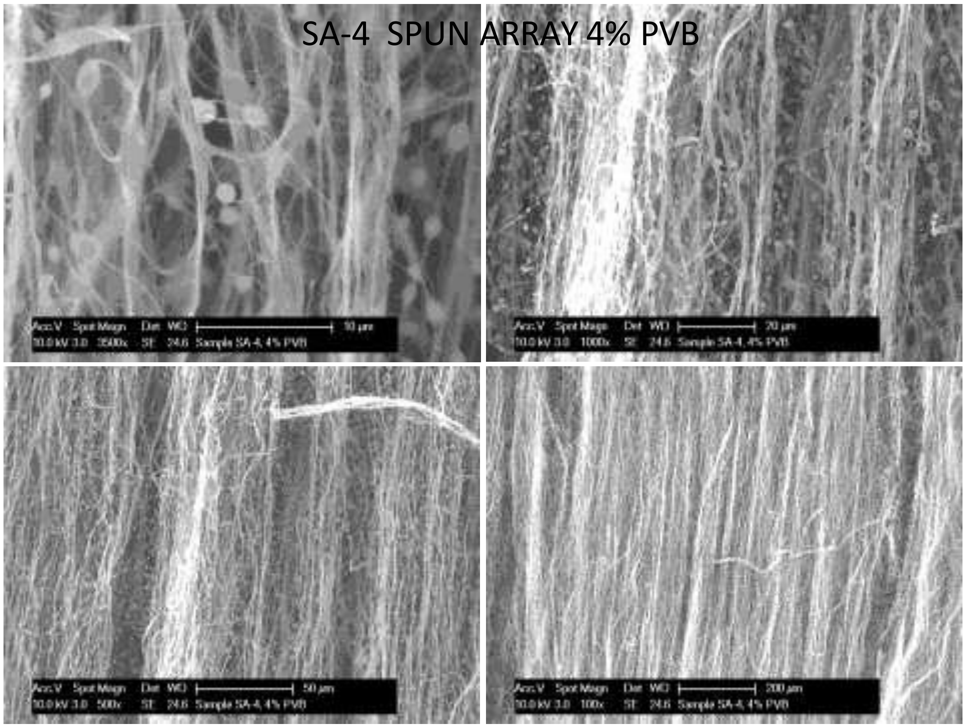
SA1


SA-2 SPUN ARRAY 2% PVB

SA2

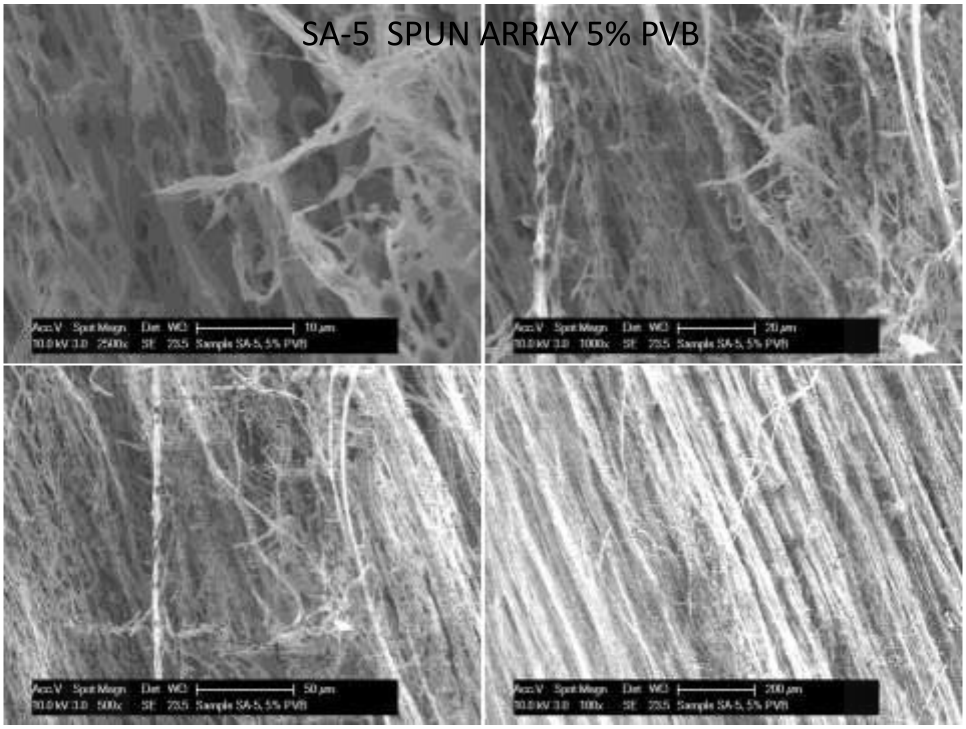

SA-3 SPUN ARRAY 3% PVB

SA3



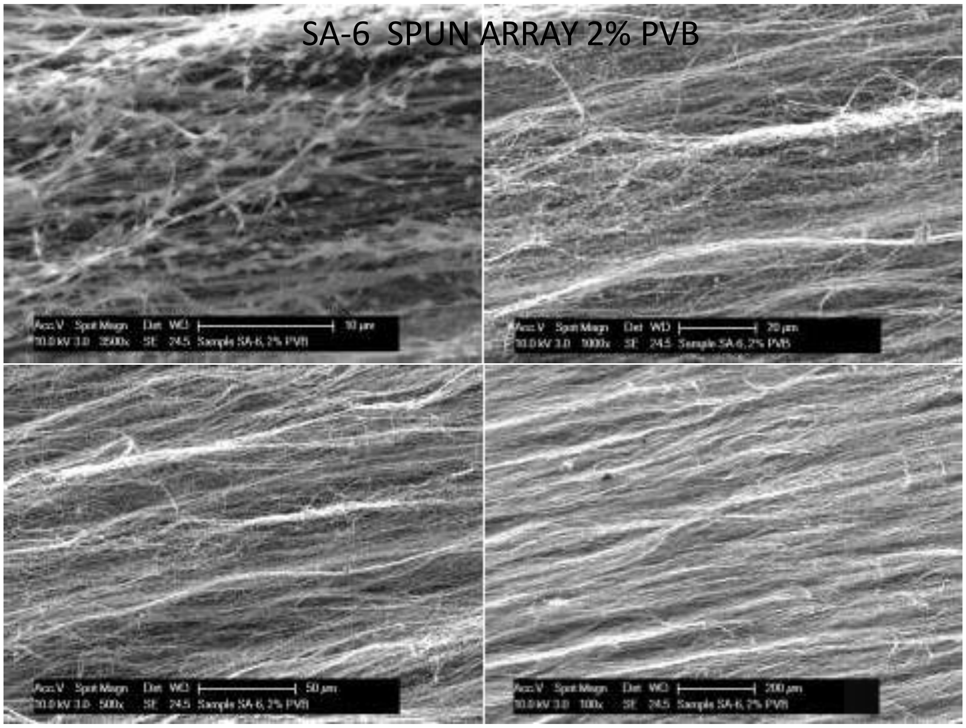
SA-4 SPUN ARRAY 4% PVB

SA4

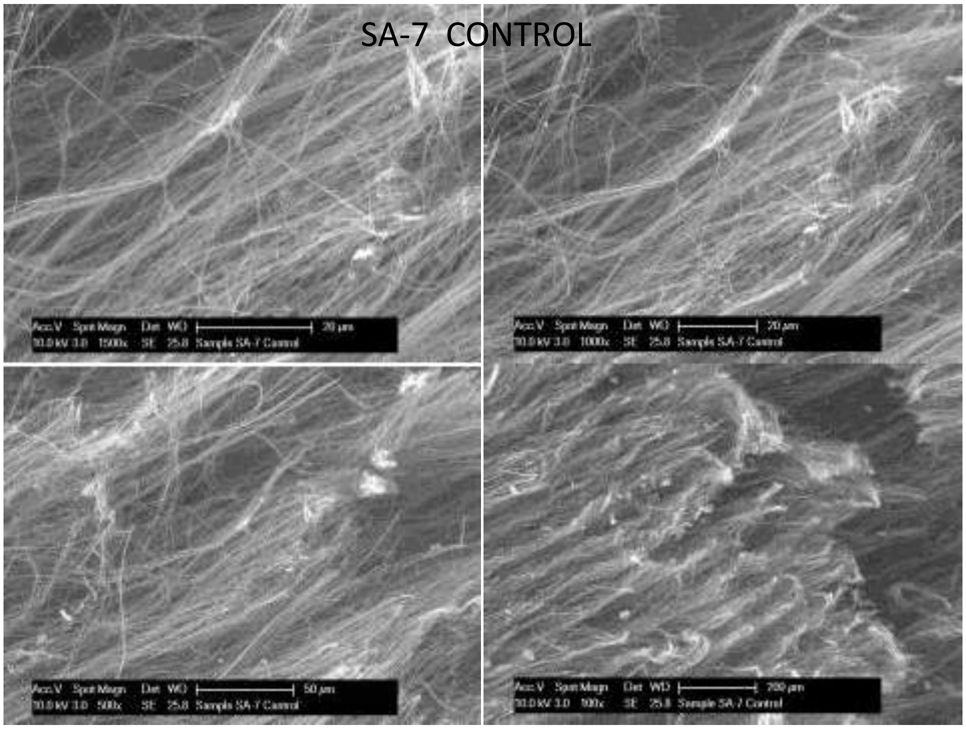


SA-5 SPUN ARRAY 5% PVB

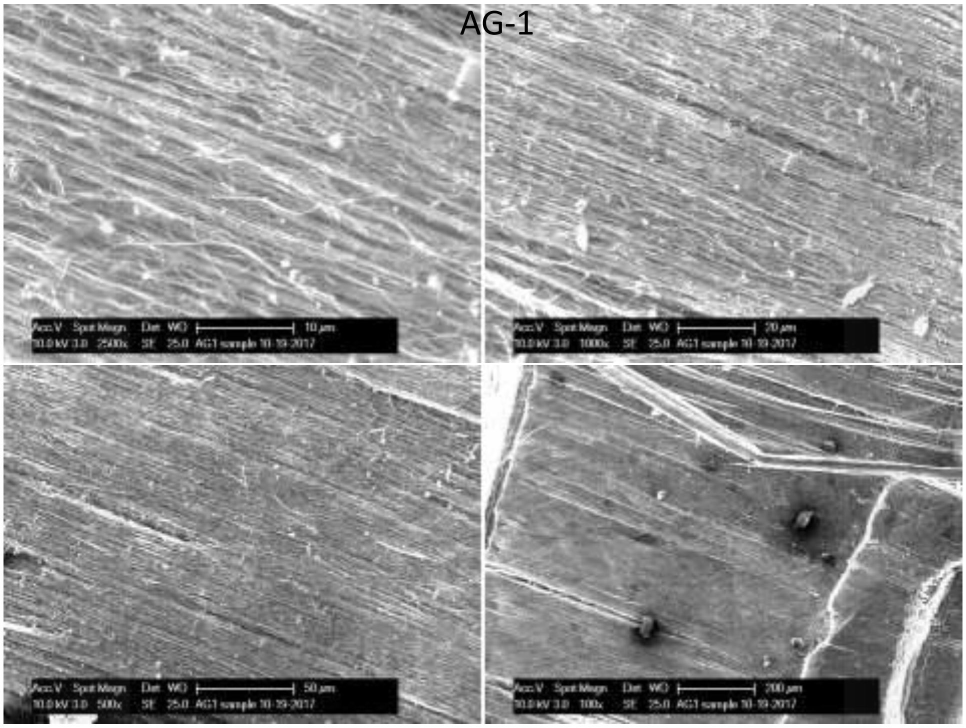
SA5


SA-6 SPUN ARRAY 2% PVB
Acc.V Spot Magn Det WD 10 µm
10.0 kV 3.0 3500x SE 24.5 Sample SA-6, 2% PVB
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1000x SE 24.5 Sample SA-6, 2% PVB
Acc.V Spot Magn Det WD 50 µm
10.0 kV 3.0 500x SE 24.5 Sample SA-6, 2% PVB
Acc.V Spot Magn Det WD 200 µm
10.0 kV 3.0 100x SE 24.5 Sample SA-6, 2% PVB

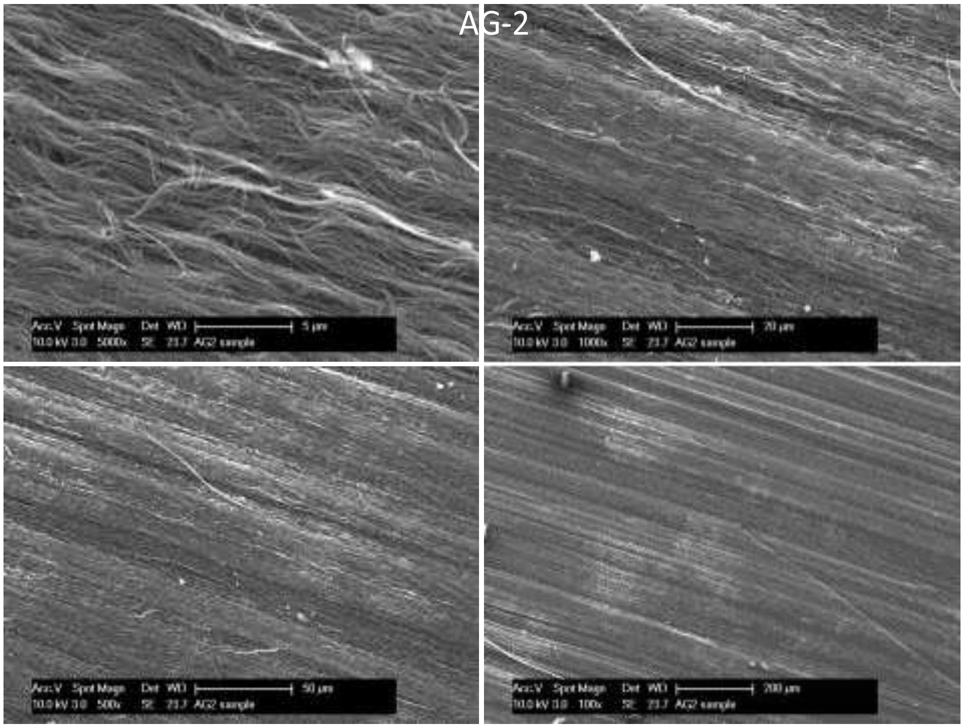
SA6


SA-7 CONTROL
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1500x SE 25.8 Sample SA-7 Control
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1000x SE 25.8 Sample SA-7 Control
Acc.V Spot Magn Det WD 50 µm
10.0 kV 3.0 500x SE 25.8 Sample SA-7 Control
Acc.V Spot Magn Det WD 200 µm
10.0 kV 3.0 100x SE 25.8 Sample SA-7 Control

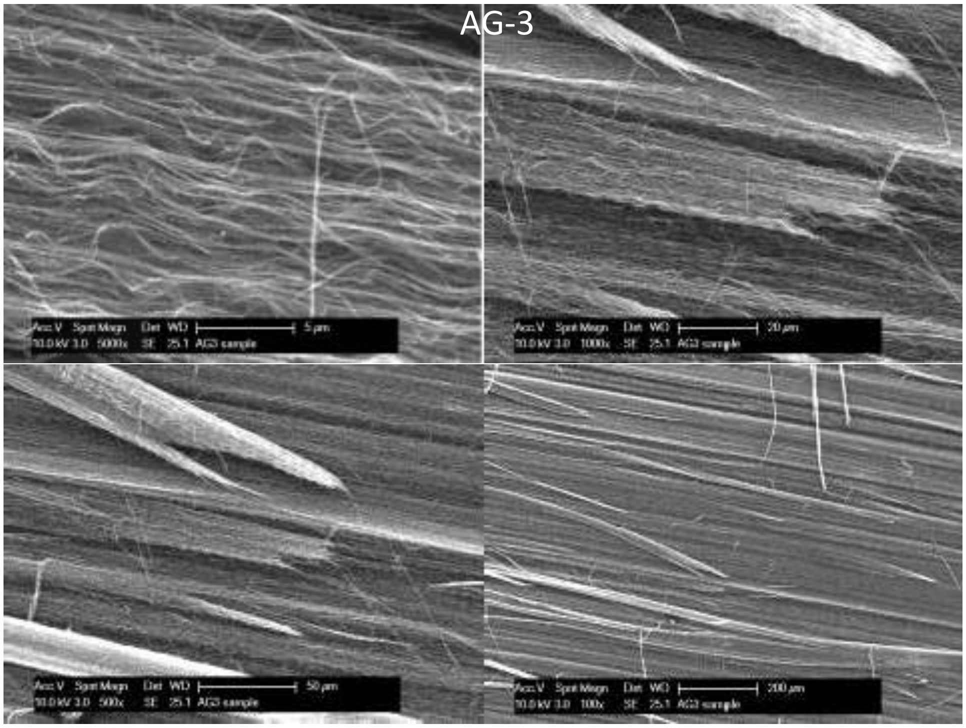
SA7


AG-1
Acc.V Spot Magn Det WD 10 µm
10.0 kV 3.0 2500x SE 25.0 AG1 sample 10-19-2017
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1000x SE 25.0 AG1 sample 10-19-2017
Acc.V Spot Magn Det WD 50 µm
10.0 kV 3.0 500x SE 25.0 AG1 sample 10-19-2017
Acc.V Spot Magn Det WD 200 µm
10.0 kV 3.0 100x SE 25.0 AG1 sample 10-19-2017

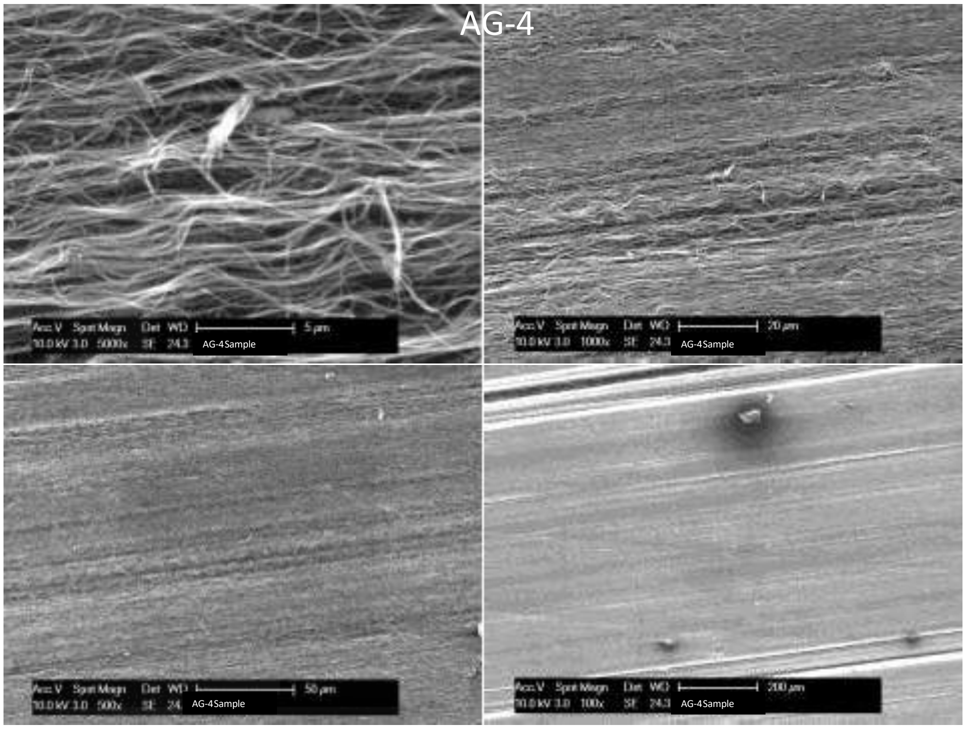
AG1


AG-2
Acc.V Spot Magn Det WD 5 µm
10.0 kV 3.0 5000x SE 23.7 AG2 sample
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1000x SE 23.7 AG2 sample
Acc.V Spot Magn Det WD 50 µm
10.0 kV 3.0 500x SE 23.7 AG2 sample
Acc.V Spot Magn Det WD 200 µm
10.0 kV 3.0 100x SE 23.7 AG2 sample

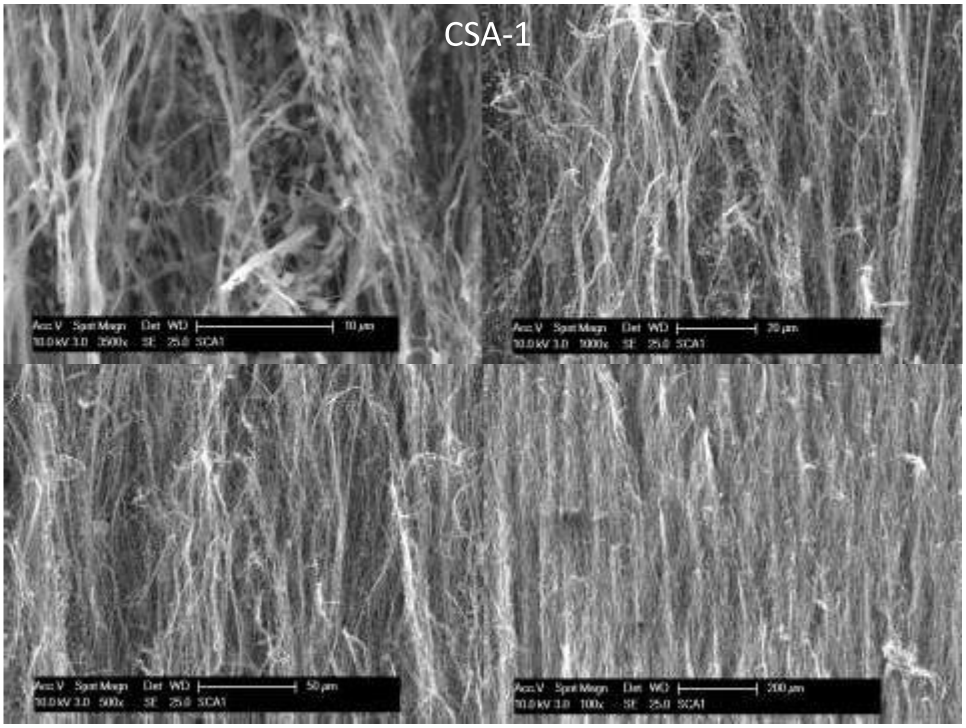
AG2


AG-3
Acc.V Spot Magn Det WD 5 µm
10.0 kV 3.0 5000x SE 25.1 AG3 sample
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1000x SE 25.1 AG3 sample
Acc.V Spot Magn Det WD 50 µm
10.0 kV 3.0 500x SE 25.1 AG3 sample
Acc.V Spot Magn Det WD 200 µm
10.0 kV 3.0 100x SE 25.1 AG3 sample

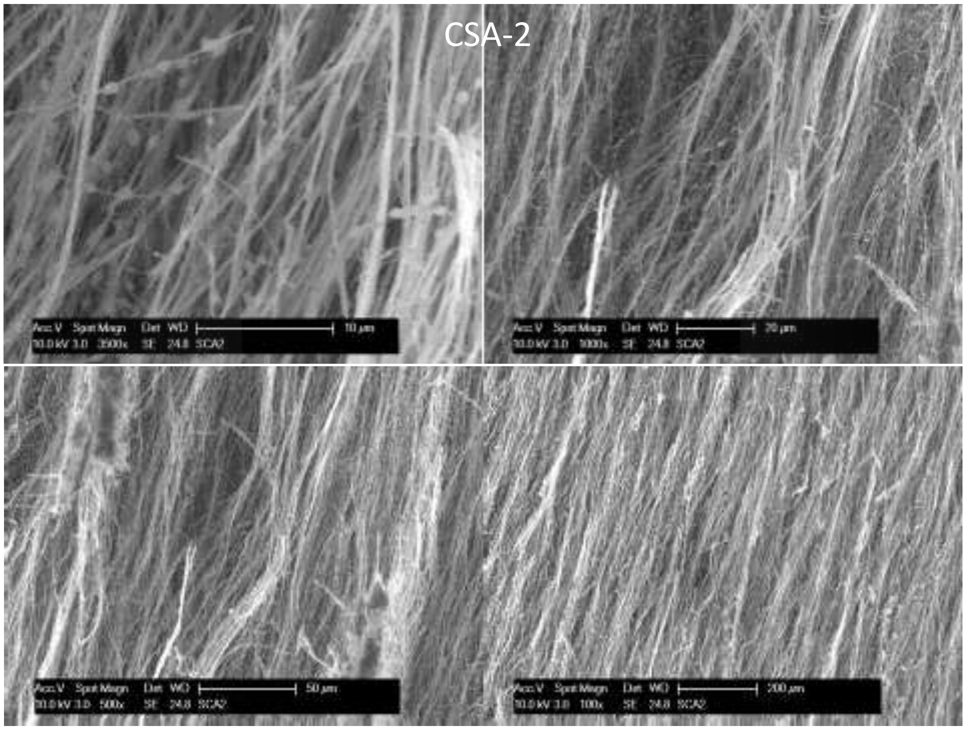
AG3


AG-4
Acc.V Spot Magn Det WD 5 µm
10.0 kV 3.0 5000x SE 24.3 AG-4Sample
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1000x SE 24.3 AG-4Sample
Acc.V Spot Magn Det WD 50 µm
10.0 kV 3.0 500x SE 24. AG-4Sample
Acc.V Spot Magn Det WD 200 µm
10.0 kV 3.0 100x SE 24.3 AG-4Sample

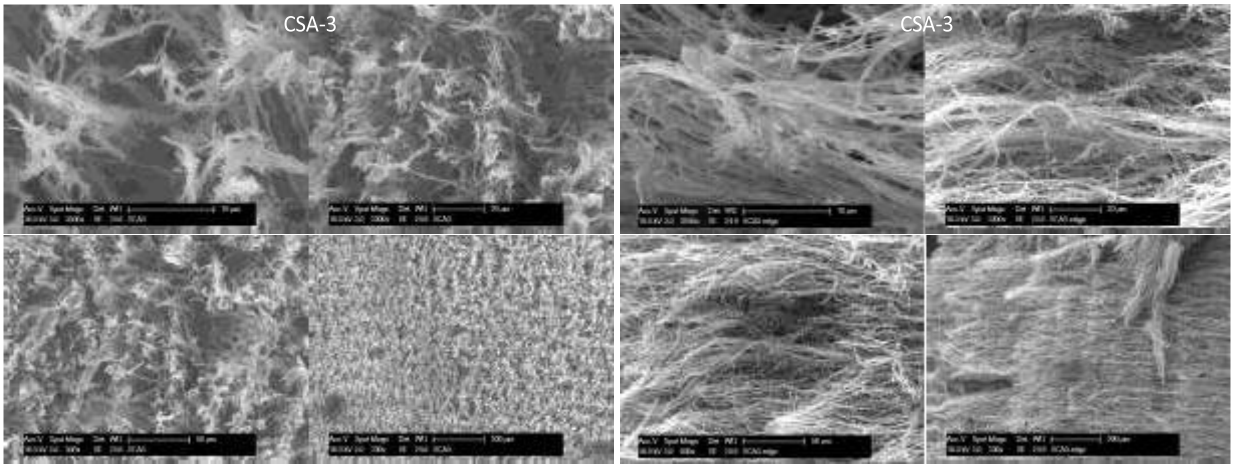
AG4


CSA-1
Acc.V Spot Magn Det WD 10 µm
10.0 kV 3.0 3500x SE 25.0 SCA1
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1000x SE 25.0 SCA1
Acc.V Spot Magn Det WD 50 µm
10.0 kV 3.0 500x SE 25.0 SCA1
Acc.V Spot Magn Det WD 200 µm
10.0 kV 3.0 100x SE 25.0 SCA1

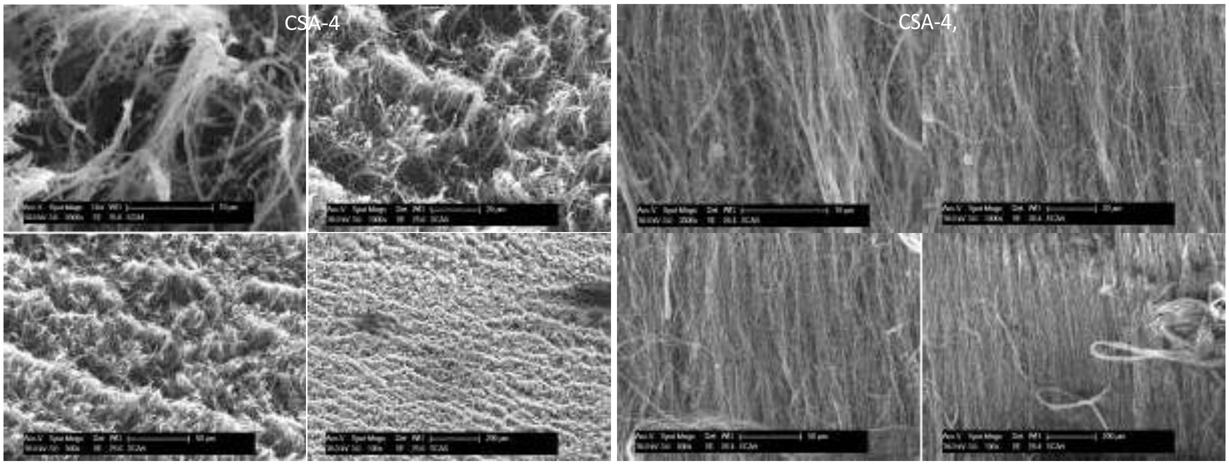
CSA1


CSA-2
Acc.V Spot Magn Det WD 10 µm
10.0 kV 3.0 3500x SE 24.8 SCA2
Acc.V Spot Magn Det WD 20 µm
10.0 kV 3.0 1000x SE 24.8 SCA2
Acc.V Spot Magn Det WD 50 µm
10.0 kV 3.0 500x SE 24.8 SCA2
Acc.V Spot Magn Det WD 200 µm
10.0 kV 3.0 100x SE 24.8 SCA2

CSA2



CSA3



CSA4

CF Tech report Appendix 2: Standard Operating Procedure

STANDARD OPERATING PROCEDURE

Project:	8913
Client:	US Army Natick Labs
Contract:	584786
Period of Performance:	July 25, 2017 - November 30, 2017

Material #1: Vertically Aligned Carbon Nanotube Array (VACNT)
Step #1: Measurements:
Dimensions for vertical carbon nanotube arrays were obtained by using a Bosch & Lomb ND6315 analytical microscope. Measurements were made by aligning a bottom corner of the array with the edge of the field of view. A starting measuring point was recorded and the field of view was moved across the array until the edge was aligned with the opposite corner of the array. Features of array samples were noted as best as possible so that measurements could be conducted from the same position after processing. Samples were then weighed using a Mettler H80 scale capable of measuring up to 4 decimal places.

Step #2: Infiltration Preparation with Polymer:
In preparation for infiltrating arrays with PVB, a hot water bath was assembled using a hot plate and a stainless steel tray filled with water. Temperature was monitored with a bi-metal thermometer, and the bath was heated to between 140-150°F. In order to infiltrate arrays with PVB, solutions of varying percentages were prepared by weight. Sections of PVB were cut from a larger sheet and then weighed based on the desired concentration of the solution. Ethanol was weighed by pouring it into a jar on a tared A&D digital scale.

The PVB sections were then diced into small pieces before being placed into the jar filled with the ethanol. Jars containing ethanol and PVB were placed in the water bath and allowed to heat for several minutes before being taken out again. The jars were then hand shaken in a vortex like motion for approximately 3-4 minutes before being placed back in the bath. Intervals of soaking and shaking were repeated until solid PVB was no longer visibly remaining at the bottom of the jar.

Note: A stir bar was considered in lieu of shaking, but it was decided that the PVB was too viscous for this to work successfully.

Once the PVB had fully dissolved, the temperature of the solution in the jar was recorded with an analog thermometer. Arrays were immersed in the solution when the temperature read between 120-130°F. Solutions containing the arrays were taken out of the water bath and left to cool to room temperature, with arrays left in solution for timespans ranging from 18 hours to five days.

Note: R3&4 soaked for 18 hours, R5&6 soaked for four days, R7&8 soaked for five days

Note: As the project progressed, it was decided that better results were achieved when array soak time did not exceed 24 hours. This was only put into practice with the spun arrays.

Alternate Step #2: Infiltration Preparation with Aerogel-Like Sol-Gelling:

Vertical arrays infiltrated with aerogel were prepared with the assistance of associates from Aerogel Tech. Two aerogel formulations were utilized, one consisting of a polyimide base, and the other a polyurea base. In order to achieve infiltration of the CNT arrays, each array was individually placed in a separate casting box. Casting boxes consisted of polypropylene plastic and were approximately 6" x 4" x 2" with tight fitting lids. Aerogel mixture was poured over the arrays in the boxes, with enough gel poured to submerge the arrays just below the surface. Two CNT arrays were submerged in the polyimide aerogel, and two were submerged in the polyurea aerogel.

Following the pouring of the gel, casting boxes were placed in sealed plastic bags along with a dish of acetone. The following day, after an approximately 24-hour period, the CNT arrays were cut out of the cured aerogel, along with approximately equally sized, in this case, 1x1" squares of aerogel. Polyurea infiltrated arrays and gel sections were placed in the same Tupperware container, whilst polyimide infiltrated arrays and gels shared a separate container. Both sets of samples were then covered with laboratory grade acetone.

A total of four acetone washes were conducted by pouring acetone at a 6:1 by mass ratio into the containers. Washes were done over the course of two days, with washes performed at approximately 3-5 hour intervals each day. During washes, the arrays and pure aerogels were placed in a shallow dish of acetone and sealed in a plastic bag. The contents of the Tupperware containers were then dumped into a waste beaker. Following the final wash, samples were left submerged in acetone for a duration of six days before being placed in the extractor.

Step #3: Infiltration:

For each run, the infiltrated arrays were placed in the extractor on top of a small piece of staging cut from a perforated metal sheet. The extractor used was a CF Tech manufactured Standard DurOLok pressure vessel measuring 2.875” ID x 4.75” IL with a total volume of 500cc. Once the extraction vessel was sealed, it was pressurized to cylinder pressure, approximately 900 psi, and CO_2 was allowed to flow through the system. CO_2 typically passed through the extractor for 90-120 minutes, with temperatures falling within a range of 18-26 °C. The extractor was then isolated from flow and the heating unit for the vessel was turned on. CO_2 in the extractor was brought to supercritical conditions by increasing the temperature to a minimum of 45 °C*, which in turn raised the vessel pressure to over 2,000psi. After temperatures began to exceed 45 °C, the outlet valves for the extractor were opened and the vessel was slowly depressurized to the separator, and flow was measured by cracking open the separator outlet valve, allowing system CO_2 to flow through the gas meter. For the duration of the run, a system log was kept in which the extractor pressure and temperature were recorded every 5 to 10 minutes. Readings were also taken from the gas meter and the cylinder so that flow rate and total CO_2 usage could be monitored. As soon as the top closure was removed from the extractor, samples were taken out and measured using the same methods prior to drying, as in Step #1.

* For patent reasons, temperature and pressure were brought to just below supercritical conditions for aerogel infiltration samples, see Patents referenced (Steiner I. S., 2014) (Meador, 2016).

STANDARD OPERATING PROCEDURE

Project	8913
Client	US Army Natick Labs
Contract	584786
Period of Performance	July 25, 2017 - November 30, 2017

Material #2: Carbon Coated CNT Spun Foam Arrays

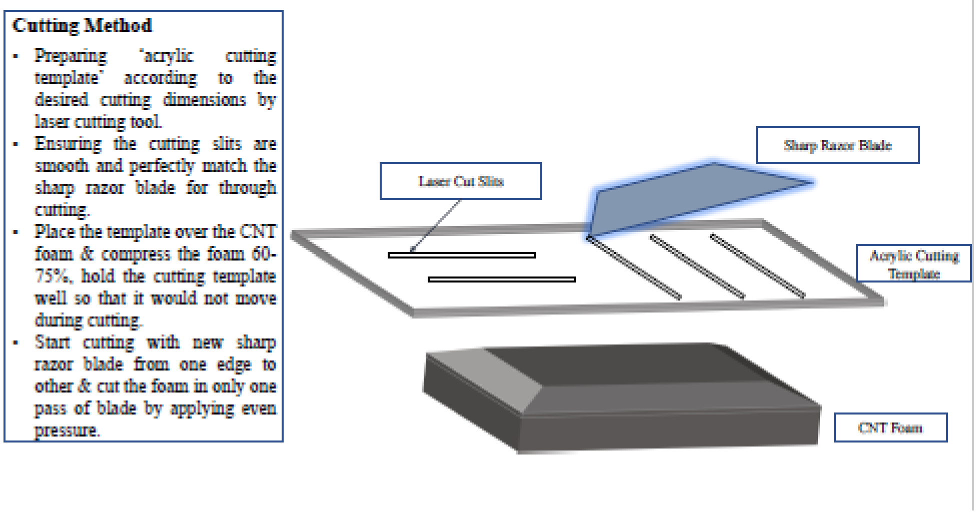
Step #1: Measurements:

Over the duration of the project, carbon coated nanotube foam was acquired in several different forms. Foam that originated from the end and middle section of full sized CNT spun arrays had a tendency to separate into layers, splitting apart along the horizontal axis, as shown in Photo 1. Separated layers were selected from the material and a razor blade was used to cut away small four-sided sections. Cuts were made in the same direction as the grain of the CNT fibers, as it was easier to separate compared to trying to cut across the grain. Even so, cutting through the foam often required pressing down on the razor blade until it made contact with the cutting surface. Trying to adjust the height of foam samples proved to be more difficult than cutting the foam length-wise. The best method that was utilized was to "shave" the foam sections with a razor blade, in effect peeling of thin strands of CNT fibers. This had to be done gently, as the foam sections were prone to having CNT fibers cling together and peel off in thick layers.

Photo 1: End of a Spun CNT Array

The largest samples were sourced from a fully intact spun array, see Photo 2, instead of a single cross section. Two large foam squares measuring approximately 2x2" were cut from the spun array. In order to cut the sections, per instructions shown below in Photo 3 from NCSU, a stiff plastic sheet was cut to approximately the size of the array, and two slits were cut through the middle using a saw blade. Slits were spaced two inches apart in order to create a CNT section of the aforementioned size. The plastic sheet was then pressed down on the array to compress it to about 70%, and a razor blade was inserted into the slits and used to cut the array.

Photo 2: Fully Intact Spun Array



Cutting Method

- Preparing 'acrylic cutting template' according to the desired cutting dimensions by laser cutting tool.
- Ensuring the cutting slits are smooth and perfectly match the sharp razor blade for through cutting.
- Place the template over the CNT foam & compress the foam 60-75%, hold the cutting template well so that it would not move during cutting.
- Start cutting with new sharp razor blade from one edge to other & cut the foam in only one pass of blade by applying even pressure.

Photo 3: Spun Array cutting Method, by NCSU

After shaping the CNT foam samples, dimensions were obtained by using a Bosch & Lomb ND6315 analytical microscope. Measurements were made by aligning a bottom corner of the array with the edge of the field of view. A starting measuring point was recorded and the field of view was moved across the array until the edge was aligned with the opposite corner of the array. Due to the non-uniform shapes of the first samples, it was decided that multiple dimensional measurements would be taken for future foam samples. Sketches of the samples were also drawn so that a visual starting point for measurements could be established. Samples were then weighed using an analytical scale measuring up to 4 decimal places.
Note: Larger samples were measured on the A&D digital scale

Step #2: Infiltration Preparation with Polymer:

In preparation for infiltrating arrays with PVB, a hot water bath was assembled using a hot plate and a stainless steel tray filled with water. Temperature was monitored with a bi-metal thermometer, and the bath was heated to between 140-150 °F. In order to infiltrate arrays with PVB, solutions of varying percentages were prepared by weight. Sections of PVB were cut from a larger sheet and then weighed based on the desired concentration of the solution. Ethanol was weighed by pouring it into a jar on a tared A&D digital scale.

The PVB sections were then diced into small pieces before being placed into the jar filled with the ethanol. Jars containing ethanol and PVB were placed in the water bath and allowed to heat for several minutes before being taken out again. The jars were then hand shaken in a vortex like motion for approximately 3-4 minutes before being placed back in the bath. Intervals of soaking and shaking were repeated until solid PVB was no longer visibly remaining at the bottom of the jar. Solutions that were not used immediately were stored in a fume hood with the lid tightly sealed.

Excluding samples SA1-7, all of the spun arrays were compressed prior to infiltration. The first samples to be compressed were samples CSA1-4, with all of them compressed to half of their original height. Heights for following samples were based off of the pre-infiltration density of the best performing sample. With a target density established, calculations were made to determine the height an array would need to be in order to reach a specific density. In order to compress the samples, staging systems capable of fitting into a 2.875” ID pressure vessel were constructed. Each staging system consisted primarily of two perforated metal screens supported by four threaded rods, with small pieces of tubing on each rod creating a gap between the screens. Tubing was cut from ¼” ID piping using a pipe cutter, and a Vernier caliper was used to measure the height of the cut pieces. CNT samples were placed on the bottom screen, and the top screen was slid down the rods until it rested on top of the tubing

Note: To ensure that the samples would be less likely to stick to the screen, a piece of Teflon cloth was placed between the screens and the samples.

The top screen was then held down with nuts on each of the threaded rods. After the CNT samples were compressed between the screens, the staging systems were submersed in PVB/EtOH solutions with a temperature ranging from 130 to 140 °F. Smaller compressed foam samples were left to soak for approximately 24 hours. One of the compressed 2”x 2” samples was left to soak for approximately 12 hours, and the other was given a soak time of approximately 48 hours. A longer soak time was chosen for the second 2”x 2” to ensure that infiltration was successful.

Note: Samples SA1-7 were dropped straight into solution, with a soak time of approximately 1 week.

Step #3: Infiltration:

The extractor used was a CF Tech manufactured Standard DurOLok pressure vessel measuring 2.875” ID x 4.75” IL with a total volume of 500cc. Once the extraction vessel was sealed, it was pressurized to cylinder pressure, approximately 900 psi, and CO_2 was allowed to flow through the system. For the smaller CNT foam sections, CO_2 typically passed through the extractor for 90-180 minutes, with temperatures falling within a range of 12-25 °C. The larger 2”x 2” arrays required longer run times, with flow occurring for durations of over five hours*. A pneumatic mixer was turned on during flow to increase diffusion of CO_2 in the extractor. Additionally, an alternate outlet hose was attached to the sight gauge for the purpose of detecting any EtOH odor. Once flow was stopped, the heating unit for the extraction vessel was turned on. CO_2 in the extractor was brought to supercritical conditions by increasing the temperature to a minimum of 40 °C, which in turn raised the vessel pressure to over 2,000psi. After temperatures began to exceed 40 °C, the outlet valves for the extractor were opened and the vessel was slowly depressurized to the separator, and flow was measured by cracking open the separator outlet valve, allowing system CO_2 to flow through the gas meter.

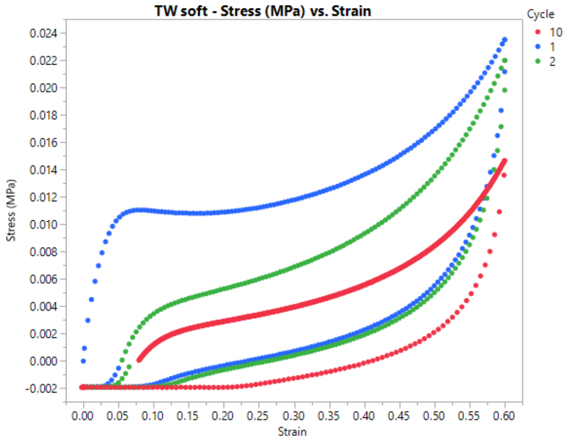
For the duration of the run, a system log was kept in which the extractor pressure and temperature were recorded every 5 to 10 minutes. Readings were also taken from the gas meter and the cylinder weight so that flow rate and total CO_2 usage could be monitored. As soon as the top closure was removed from the extractor, samples were taken out and measured using the same methods prior to drying, as in Step #1.

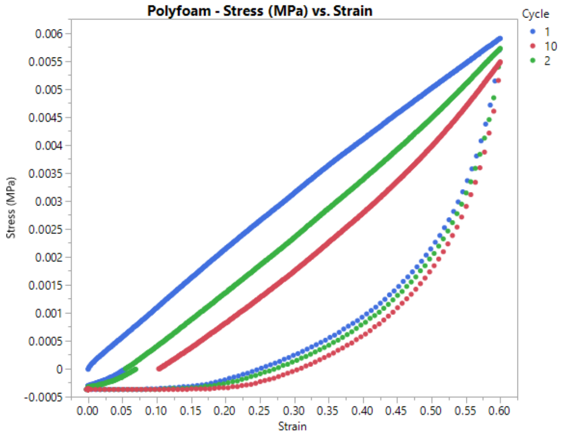
* CO_2 cylinders, must be siphon tube with liquid CO_2 for the duration of the scCO_2 drying cycle. Due to the extractor pressure and temperature readings taken during the runs, there is reason to believe that liquid CO_2 was not being drawn from the cylinder for the entire duration of each run. For the larger samples (Set #7), the samples were temporarily soaked in liquid CO_2 inside the vessel; due to these circumstances, in the future, it may not be necessary for the larger samples to dry as long.

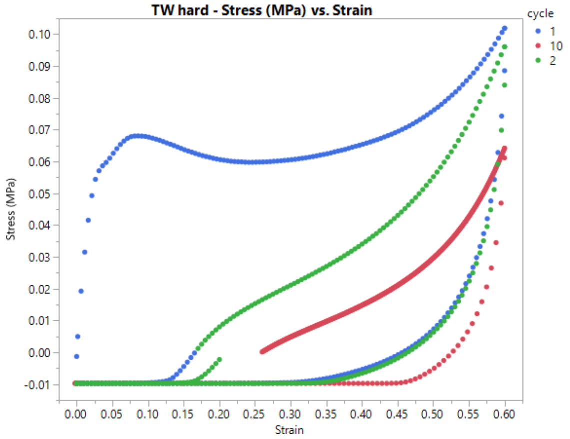
References

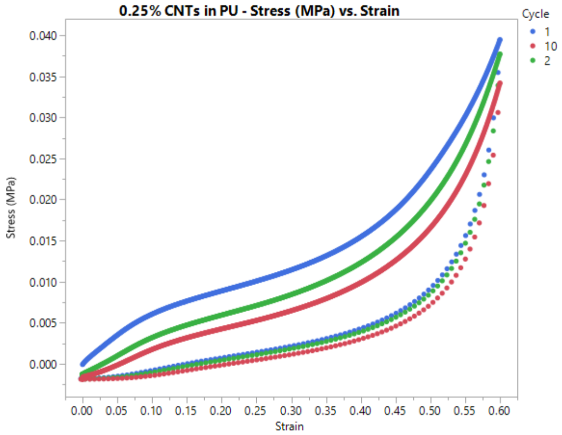
Antunes, M., & Velasco, J. I. (2014). Polymer-Carbon Nanotube Nanocomposite Foams. In V. Mittal, *Polymer Nanotube Nanocomposites* (pp. 279 - 332). Scrivener Publisher LLC.
Bryning, M. (2007). Carbon Nanotube Aerogels. In M. Bryning, *Carbon Nanotube Networks in Epoxy Composites and Aerogels* (pp. 131-146). Ann Arbor: ProQuest Information and Learning Company.
Charitidis, C., Koumoulos, E., Giorcelli, M., Musso, S., Jagadale, P., & Tagliaferro, A. (2013). Nanomechanical and Tribological Properties of Carbon Nanotube/Polyvinyl Butyral Composites. *Polymer Componsites* , 1950-1960.
DeFelice, J., & Lipson, J. (2014). Polymer Miscibility in Supercritical Carbon Dioxide: Free Volume as a Driving Force. *Macromolecules* , ACS Publications.
Li, Z., Tang, H., Liu, X., Xia, Y., & Jiang, J. (2008). Preparation and characterization of microporous poly(vinyl butyral). *Journal of Membrane Science , 312,* 115-124.
Meador, M. A. (2016). *Patent No. 9434832.* Unites States of America.
Rindfleisch, F., DiNoia, T., & McHugh, M. (1996). Solubility of Polymers and Copolymers in Supercritical CO2. *Journal of Phys. Chem.* , 15581-15587.
Steiner, I. S. (2014). *Patent No. 0287641 A1.* United States of America.
Steiner, I. S. (2014). *Patent No. 2014028641.* United States of America.
Wang, C., Jim, X., Cheng, H., Hong, C., & Zhang, X. (2017). Organic aerogel-impregnated low-density carbon/carbon composites: Preparation, properties and response under simulated atmospheric re-entry conditions. *Materials & Design* , 177-185.
Weng, B., Xu, F., Garza, G., Alcoutlabi, M., Salinas, A., & Lozano, K. (2015). The Production of Carbon Nanotube Reinforced Poly(vinyl) Butyral Nanofibers by the Forcespinning Method. *Polymer Engineering and Science* , 81-87.
(Antunes & Velasco, 2014)

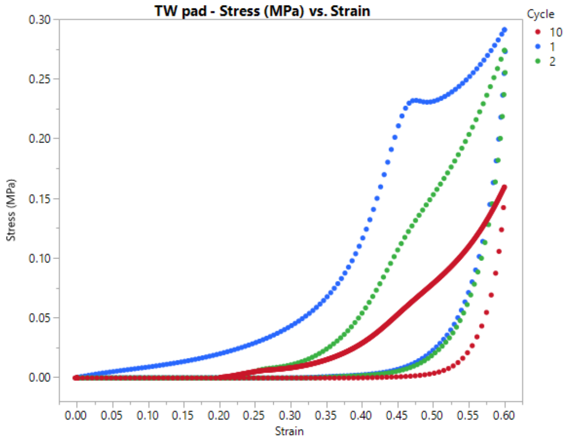
Appendix B

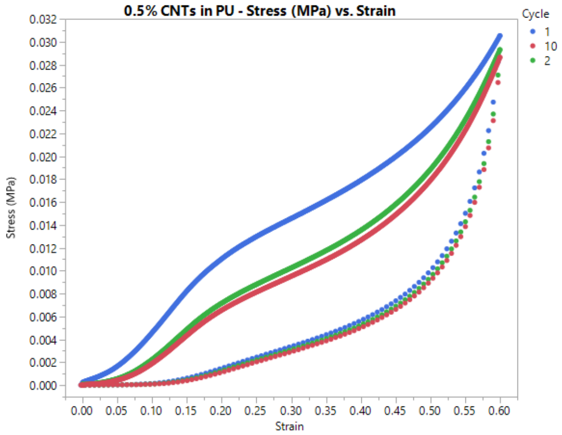

TW soft - Stress (MPa) vs. Strain

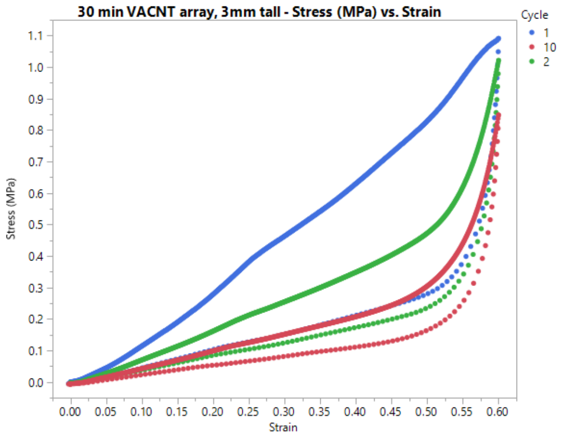

Polyfoam - Stress (MPa) vs. Strain

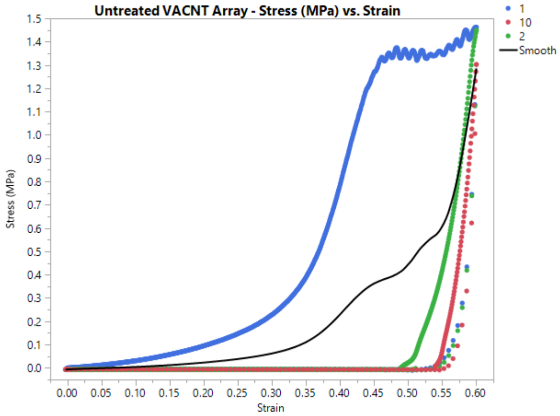

TW hard - Stress (MPa) vs. Strain

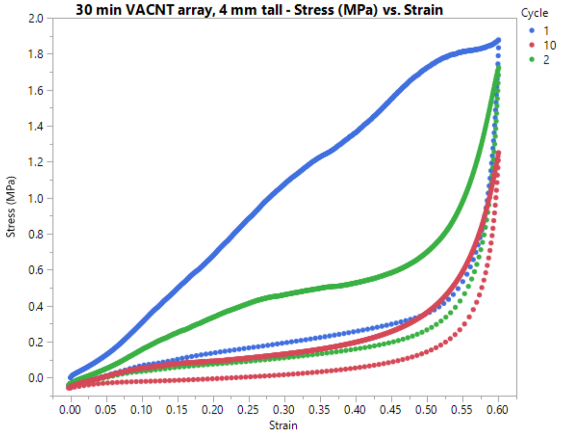

0.25% CNTs in PU - Stress (MPa) vs. Strain

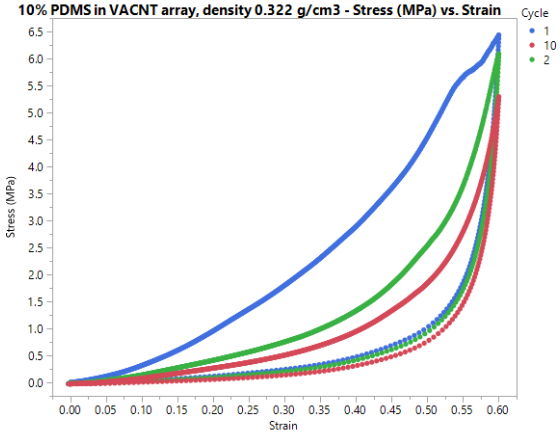

TW pad - Stress (MPa) vs. Strain

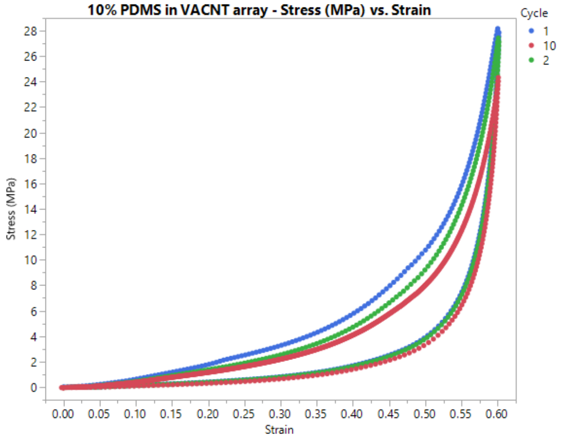

0.5% CNTs in PU - Stress (MPa) vs. Strain

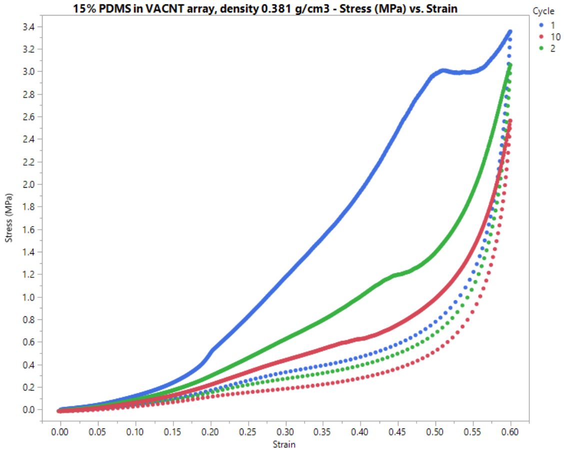

30 min VACNT array, 3mm tall - Stress (MPa) vs. Strain

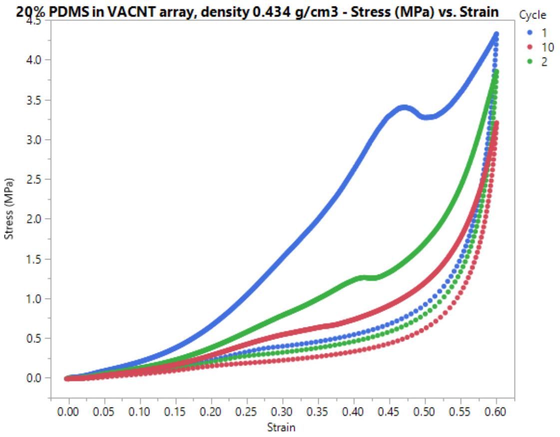

Untreated VACNT Array - Stress (MPa) vs. Strain

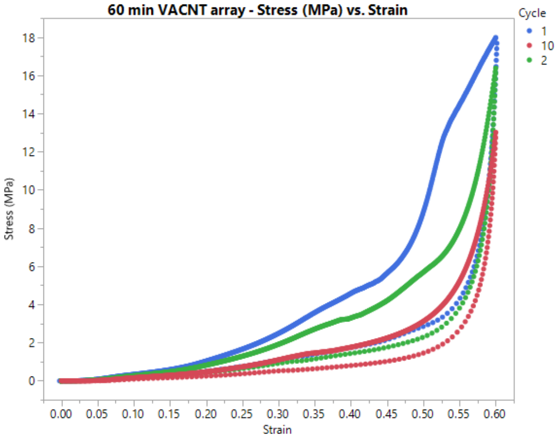

30 min VACNT array, 4 mm tall - Stress (MPa) vs. Strain

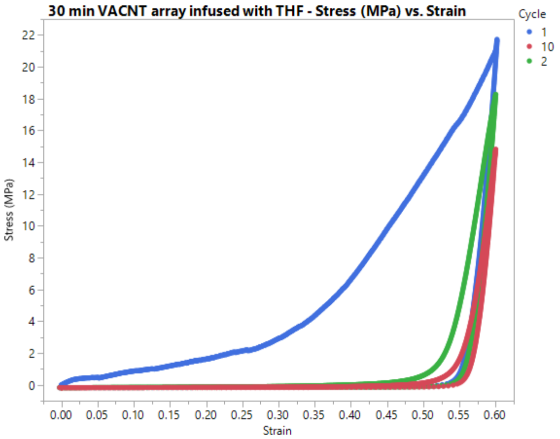

10% PDMS in VACNT array, density 0.322 g/cm3 - Stress (MPa) vs. Strain

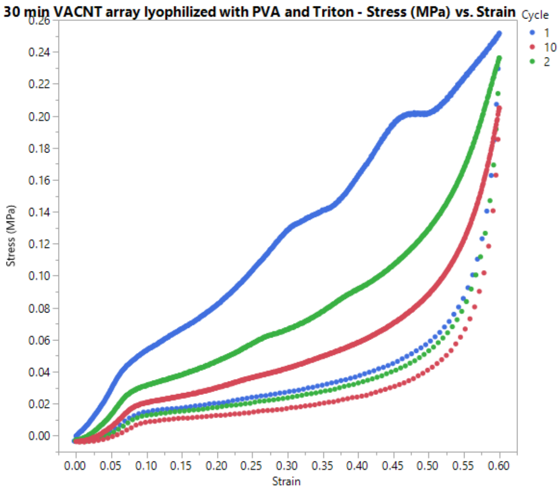

10% PDMS in VACNT array - Stress (MPa) vs. Strain

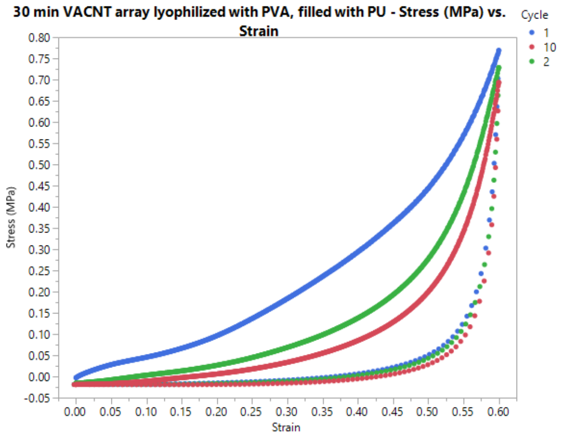

15% PDMS in VACNT array, density 0.381 g/cm3 - Stress (MPa) vs. Strain

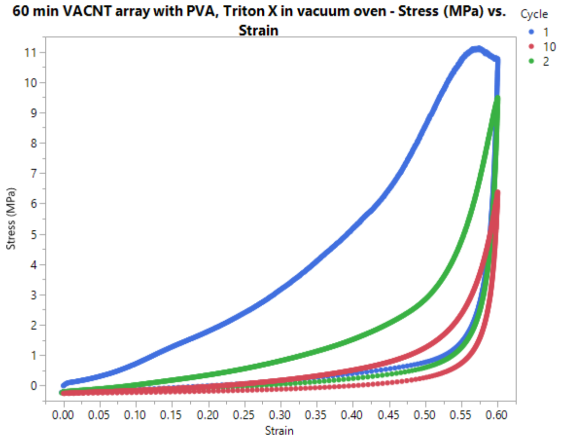

20% PDMS in VACNT array, density 0.434 g/cm3 - Stress (MPa) vs. Strain

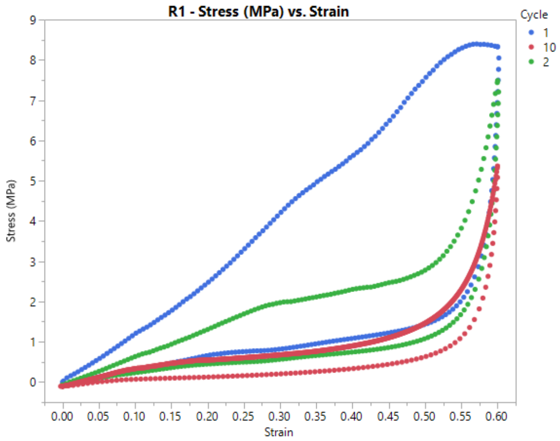

60 min VACNT array - Stress (MPa) vs. Strain


30 min VACNT array infused with THF - Stress (MPa) vs. Strain

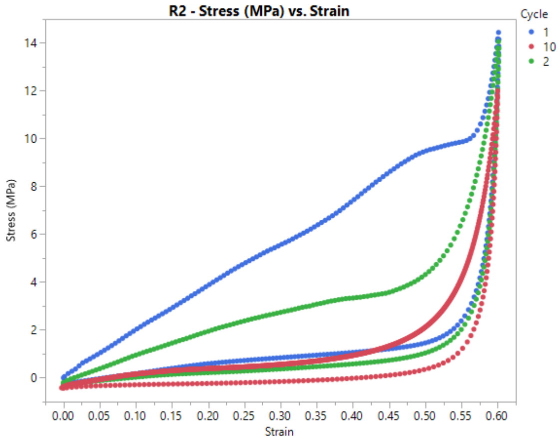

30 min VACNT array lyophilized with PVA and Triton - Stress (MPa) vs. Strain


30 min VACNT array lyophilized with PVA, filled with PU - Stress (MPa) vs. Strain

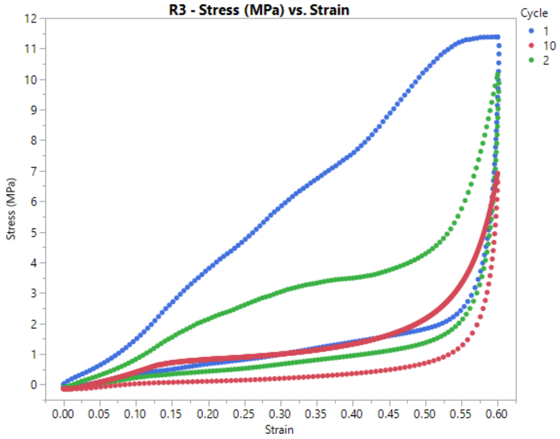

60 min VACNT array with PVA, Triton X in vacuum oven - Stress (MPa) vs. Strain



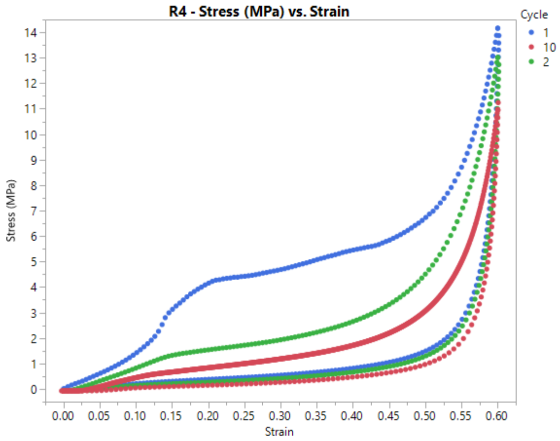
R1 - Stress (MPa) vs. Strain



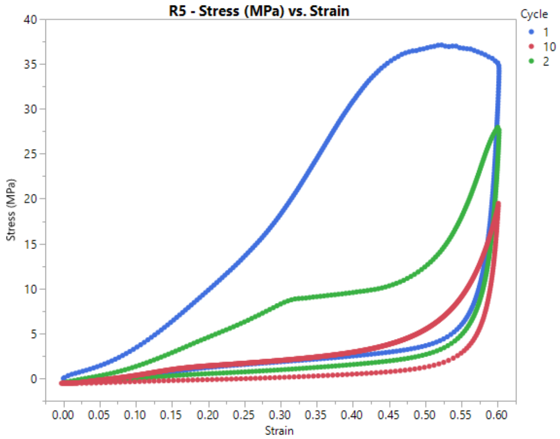
R2 - Stress (MPa) vs. Strain



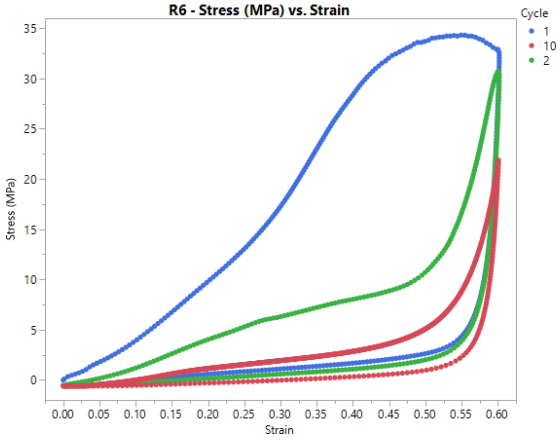
R3 - Stress (MPa) vs. Strain



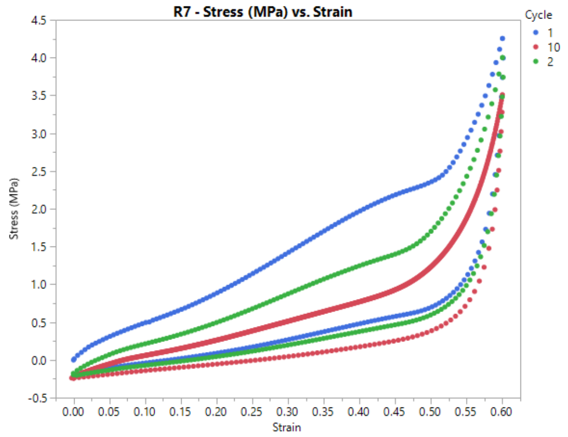
R4 - Stress (MPa) vs. Strain

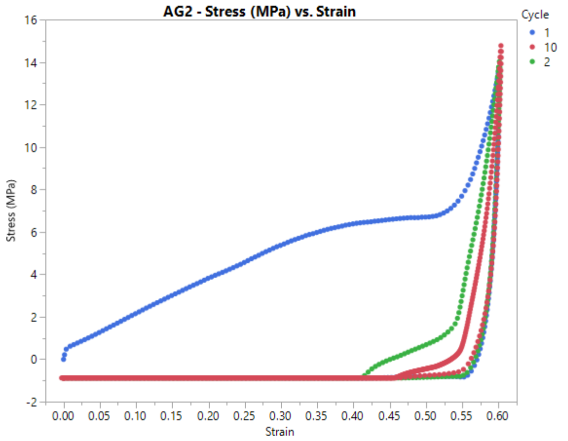


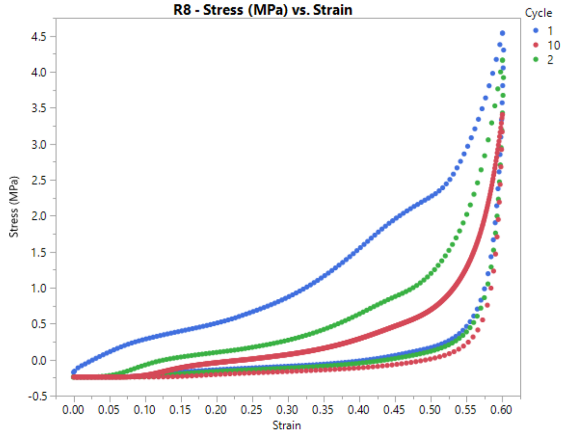
R5 - Stress (MPa) vs. Strain

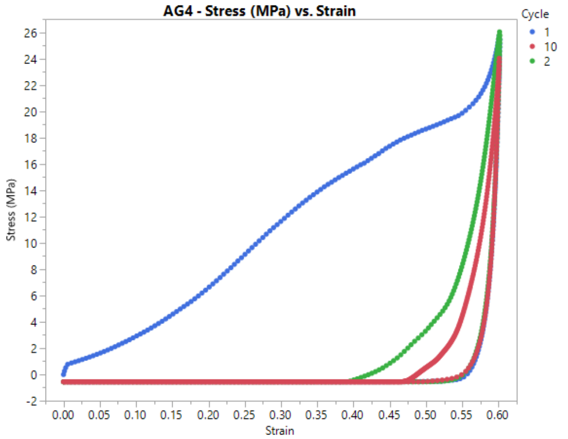


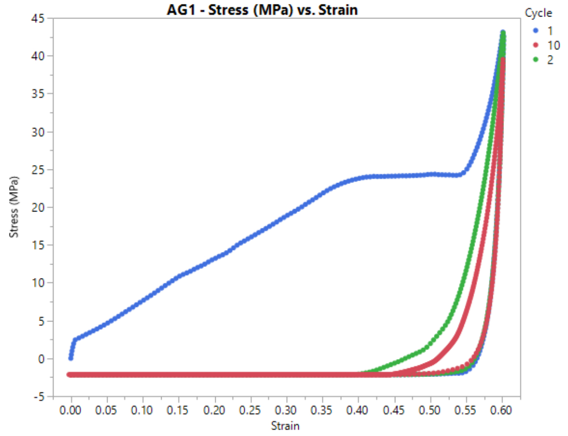
R6 - Stress (MPa) vs. Strain

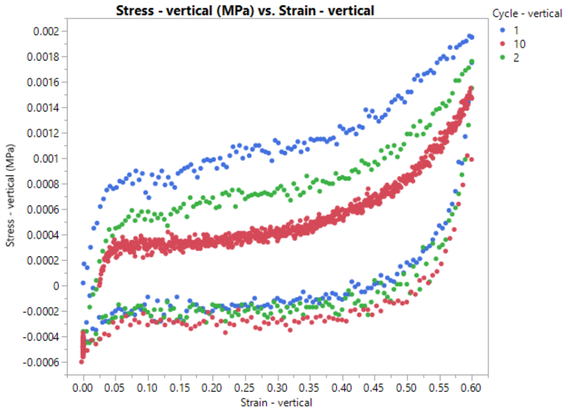

R7 - Stress (MPa) vs. Strain

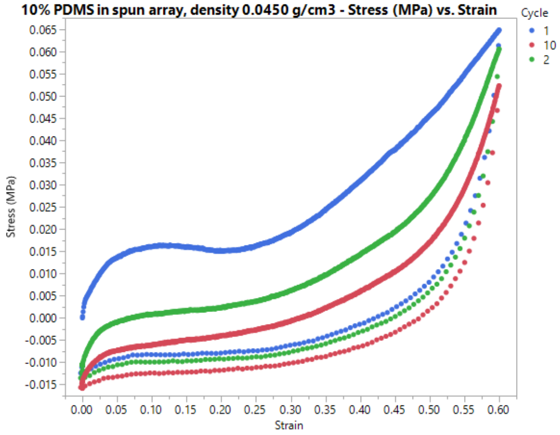

AG2 - Stress (MPa) vs. Strain

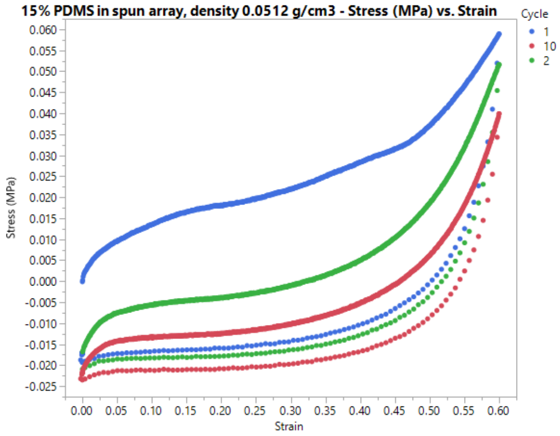

R8 - Stress (MPa) vs. Strain

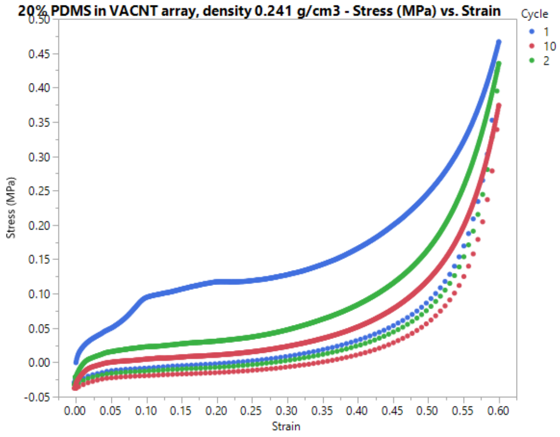

AG4 - Stress (MPa) vs. Strain

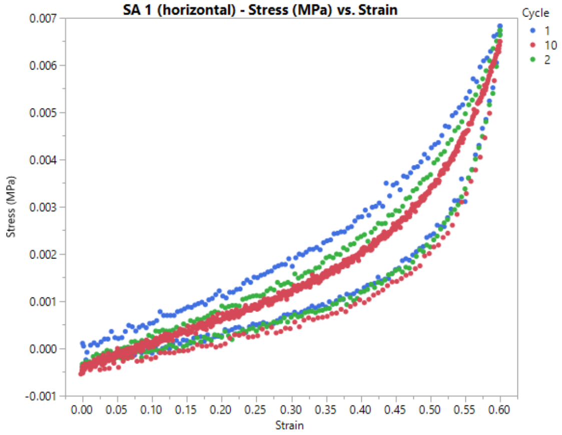

AG1 - Stress (MPa) vs. Strain

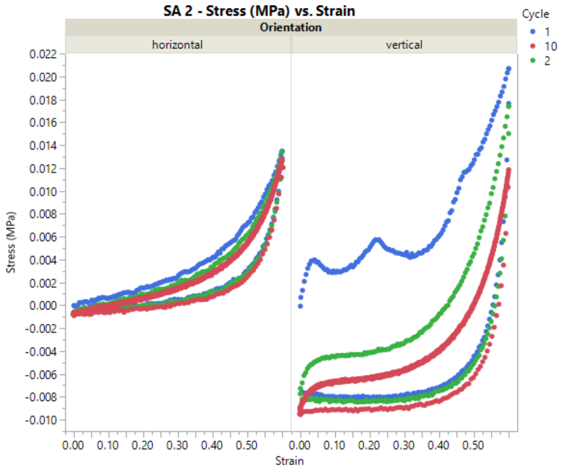

Stress - vertical (MPa) vs. Strain - vertical

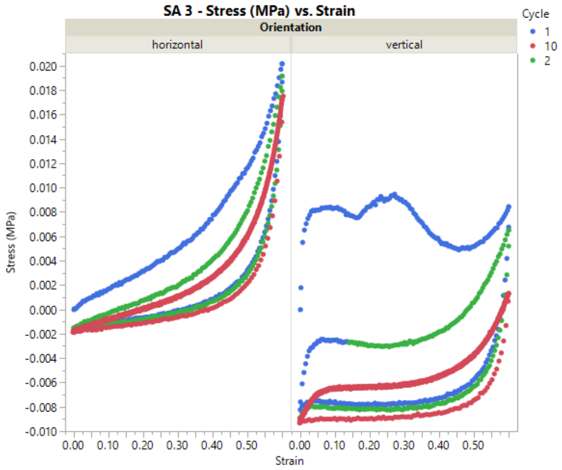

10% PDMS in spun array, density 0.0450 g/cm3 - Stress (MPa) vs. Strain

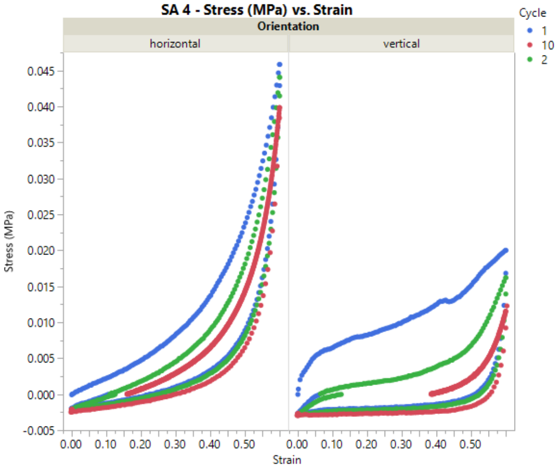

15% PDMS in spun array, density 0.0512 g/cm3 - Stress (MPa) vs. Strain

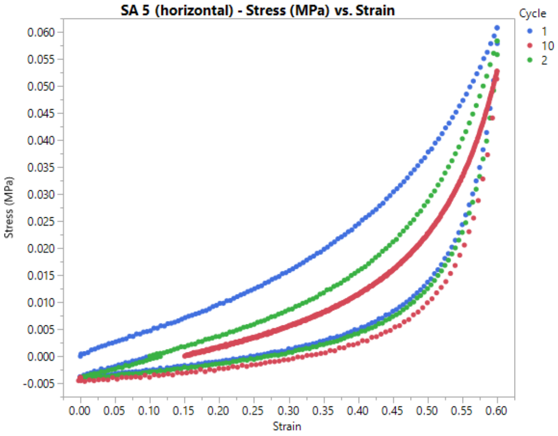

20% PDMS in VACNT array, density 0.241 g/cm3 - Stress (MPa) vs. Strain

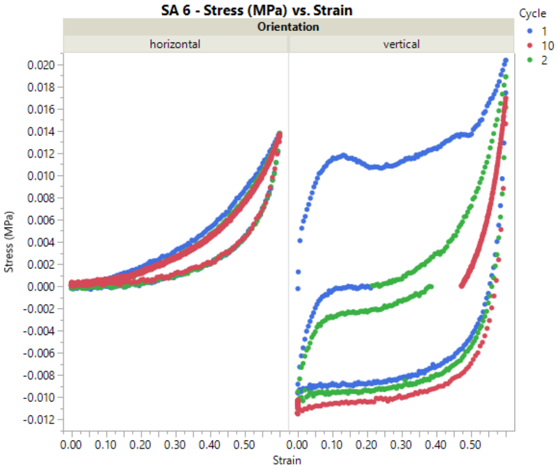

SA 1 (horizontal) - Stress (MPa) vs. Strain

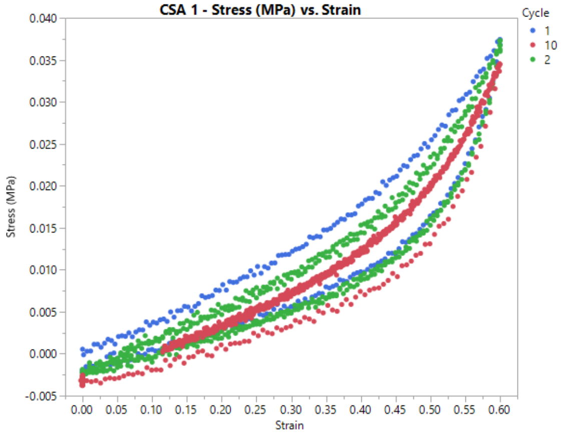

SA 2 - Stress (MPa) vs. Strain

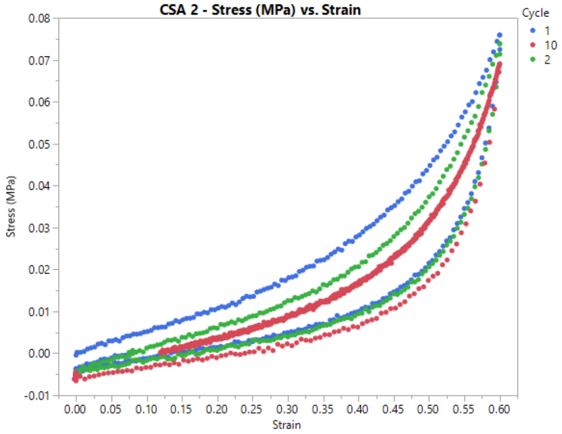

SA 3 - Stress (MPa) vs. Strain

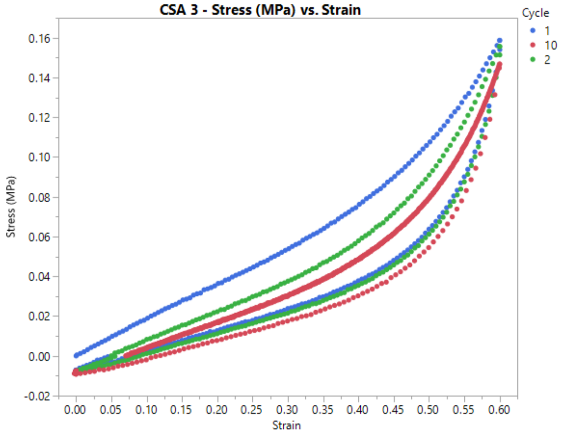

SA 4 - Stress (MPa) vs. Strain

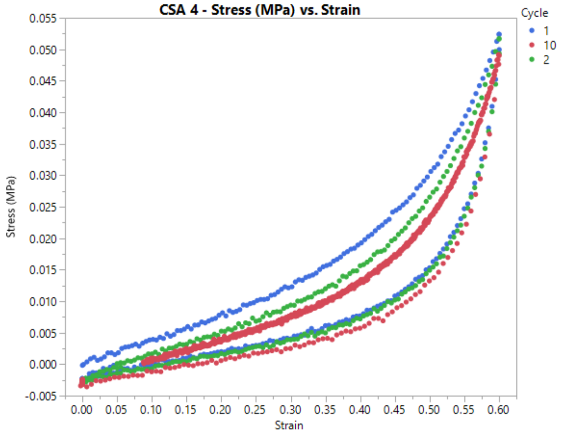

SA 5 (horizontal) - Stress (MPa) vs. Strain

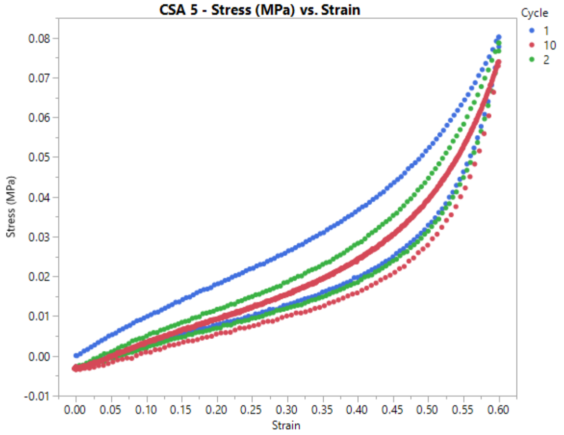

SA 6 - Stress (MPa) vs. Strain


CSA 1 - Stress (MPa) vs. Strain


CSA 2 - Stress (MPa) vs. Strain


CSA 3 - Stress (MPa) vs. Strain


CSA 4 - Stress (MPa) vs. Strain
Stress (MPa)
0.055
0.050
0.045
0.040
0.035
0.030
0.025
0.020
0.015
0.010
0.005
0.000
-0.005
0.00 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50 0.55 0.60
Strain
Cycle
● 1
● 10
● 2


CSA 5 - Stress (MPa) vs. Strain
Stress (MPa)
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0.00
-0.01
0.00 0.05 0.10 0.15 0.20 0.25 0.30 0.35 0.40 0.45 0.50 0.55 0.60
Strain
Cycle
● 1
● 10
● 2