Ultra Lightweight High Pressure Hydrogen Fuel Tanks Reinforced with Carbon Nanotubes

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Applied Nanotech, Inc.

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Project ID #
ST105

Applied Nanotech, Inc.

Overview

Timeline

- Project start date: Aug. 8, 2012
- Project end date: Aug. 7, 2014
- Percent complete: *75-80%*

Budget

- FY13 DOE Funding: $359,593.88
- Planned FY14 DOE Funding: $545,674.12
- Total DOE Project Value: $999,990

Barriers

- Barriers addressed
  - Cost of hydrogen storage tanks;
  - Weight of the storage tanks;
  - Performance of the storage tanks.
- Target
  - Reduce the cost of the hydrogen storage tanks by lowering their weight (>20%) .

Partners

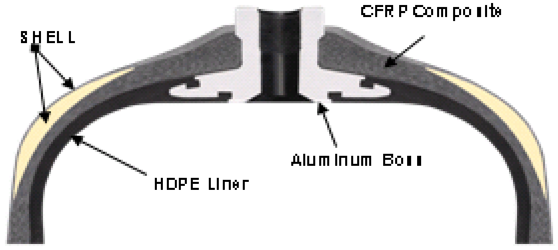
- Hexagon Lincoln – (Subcontractor)
- Prof. Don Paul (University of Texas at Austin) - Consultant

Relevance

Our goal is to make the hydrogen storage tanks stronger, lighter and with better performance through CNT reinforced CFRP composites. As a result, the cost of the hydrogen storage tanks will be significantly reduced while increasing vehicle efficiency.

DOE Barriers

- Cost of hydrogen storage tanks
- Weight of the storage tanks
- Cost of the carbon fiber is too high



Cross-section view of a hydrogen storage tank (CFRP portion occupies 53wt.% of the tank)

Base Materials for CFRP	Price ($/kg)
Neat Epoxy Resin	8.25
Toray T700 Carbon Fiber	33
CNT (1.0 wt.%) Epoxy Resin	11.17
Neat Epoxy Resin + Carbon Fiber (Weight Ratio 3:7)	25.58
CNT (1.0 wt.%) + Neat Epoxy Resin + Carbon Fiber	26.45 (+3.4%)

Hydrogen fuel tank (Composite type IV, 5,000 psi)	Price of Carbon fiber ($)	Price of Resin ($)	Labor & Other Costs ($)	Cost of CFRP Portion ($)	Total Cost of Tank ($)
Baseline	1224.3	131.18	755.52	2111	2727
20% Weight Reduction w/ CNTs	979.44	142.08	755.52	1877.04 (-11%)	2493.04 (-9%)
40% Weight Reduction w/ CNTs	734.58	106.56	755.52	1596.66 (-24%)	2112.56 (-23%)

Based on our careful calculations, the cost for 1 kg of the CNT reinforced epoxy resin is the following based on high volume manufacturing:

Epoxy: $8.25/kg
CNT: $1 ($0.1/g, 10 g will be used in the epoxy assuming 1% loading)
Production cost (including labor): $2

So, the total cost for 1 kg of the CNT (1.0%) reinforced epoxy resin is $11.17 ((0.99x8.25) + (0. 1x10) +2)) making the cost increase of 35% compared to the base epoxy ($8.25/kg). It can be seen that the cost of the CFRP composite increases about 3.4% using 1% CNT reinforcement (including all related production costs of the reinforced epoxy resin). According to a 2010 TIAX report, carbon fiber reinforced polymer accounts for 77% of the total cost of a hydrogen fuel tank. Assuming a 5,000 psi tank, if we can lower the weight by 20% for the CFRP portion using CNT reinforcement, we are able to reduce the cost by at about 9% for the total tank. If we are able to lower the weight of the CFRP portion by 40%, the total cost for a tank can be further reduced by a total of nearly 23% .

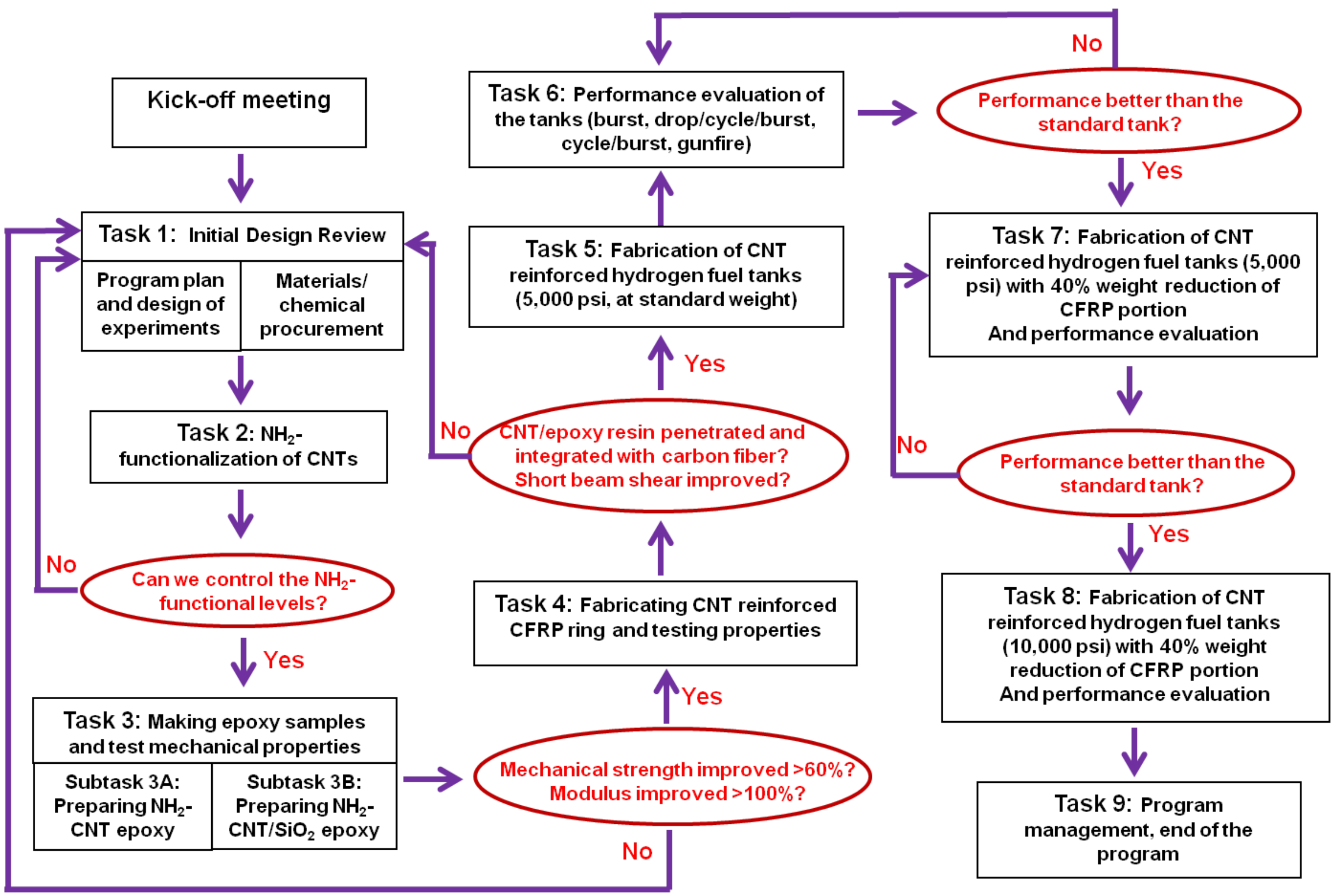
Objectives

#	Objectives
1	Demonstrate that we can further control NH_2-functionalization level of the CNTs with the goal of further improving the mechanical properties of the epoxy matrix. We have achieved this objective.
2	Demonstrate that we can improve the strength by more than 60% and the modulus by more than 100% in the epoxy matrix by reinforcing it with NH_2-functionalized CNTs and SiO_2 nanoparticles. This objective is over 90% completed.
3	Demonstrate that the CNT reinforced epoxy resin can successfully penetrate and integrate with the carbon fibers during the filament winding portion of the CFRP fabrication process. We have achieved this objective.
4	Demonstrate that the 5,000 psi hydrogen fuel tanks with 40% weight reduction of the CFRP portion utilizing CNT reinforcement perform better than the standard tanks based on sophisticated testing including burst, drop/cycle/burst, impact, and gunfire.
5	Demonstrate that the 10,000 psi hydrogen fuel tanks with 40% weight reduction of the CFRP portion utilizing CNT reinforcement perform better than the standard tanks based on sophisticated testing including burst, drop/cycle/burst, impact, and gunfire.

Approach

Reducing the cost of high pressure hydrogen storage tanks - Our approach is to reduce the cost of the high pressure hydrogen storage tanks by lowering their weight. Using CNT reinforcement, we are able to significantly improve the mechanical properties of the carbon fiber/epoxy composite (CFRP) matrix used to construct the tanks with the final purpose being to lower the weight of the CFRP composites while preserving or even increasing the performance of the tanks.

Program Schedule



Milestones

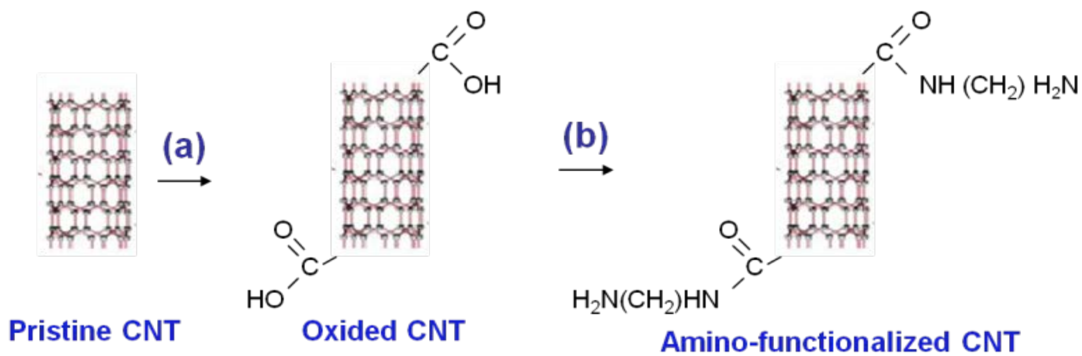
Milestone #	Progress Notes	Timeline
1	Kickoff Meeting	Start of month 1
2	Initial design and material/chemical acquisition complete	Month 1
3	NH_2-functionalization of CNTs at different functional levels complete	Month 4
4	Synthesis and mechanical evaluation of CNT/epoxy and CNT/SiO_2/epoxy complete	Month 6
5	CNT reinforced CFRP ring made and tested, demonstrating that the CNT-reinforced epoxy can fully penetrate the carbon fibers	Month 8
6	Fabrication of CNT reinforced hydrogen fuel tanks (5,000 psi) at standard weight complete	End of Month 11
7	Performance evaluation of the tanks complete	Month 13
8	Fabrication of CNT reinforced hydrogen fuel tanks (5,000 psi) with 40% weight reduction of the CFRP portion complete. Better performance of the tanks achieved	Month 18
9	Fabrication of CNT reinforced hydrogen fuel tanks (10,000 psi) with 40% weight reduction of the CFRP portion complete. Better performance of the tanks achieved	Month 23
10	Final Report Complete - Phase II program completion.	Month 24

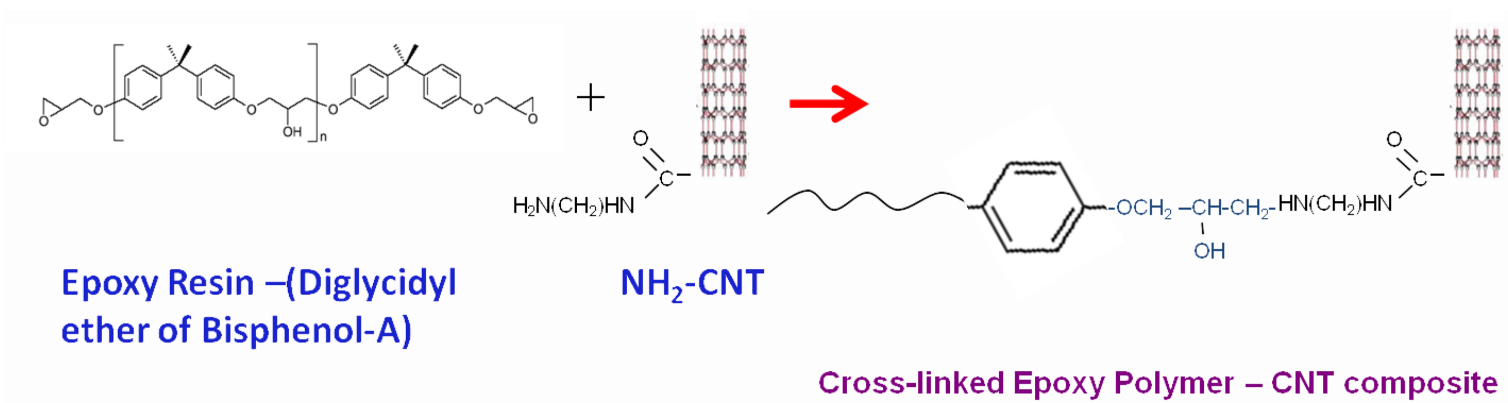
Work Plan/Progress (for the First Year of the Program)

Task	Task Description	Progress/Accomplishments	completion
	Kick-off meeting	Dr. Dongsheng Mao of ANI attended the kick-off meeting organized by the DOE in September, 2012. He also attended the PI/Contractor meeting in Nov. 2012.	100%
1	Initial design review		
	A - Design review	ANI team had a number of meetings at the beginning of the program to discuss the design of experimentation and overall schedule. We also discussed with the subcontractor related to the Statement of Work	100%
	B – Obtain materials and chemicals	All the chemicals and materials were obtained in Sept. 2012 for the 1st year of the program	100%
2	Functionalization of CNTs at different levels	We have prepared enough functionalized CNTs for the next task.	100%
3	Synthesize epoxy samples reinforced with CNTs and SiO_2 nanoparticles	We obtained further improved mechanical properties compared with the achievement obtained in the Phase I program	100%
4	Fabricate CNT reinforced CFRP rings and test properties	We have already tested inter-laminar shear strength for 2 formulations of the CNT and SiO_2 reinforced epoxy resin. Hexagon Lincoln is working on fabrication of additional CFRP rings at this stage. This task will be finished in early May, 2013. This task is proceeding as planned.	80%
5	Fabricate CNT reinforced tanks (5,000 psi)	In this task, we will produce a large quantity of the CNT/epoxy resin, fabricate tanks, and test preliminary performance of the tanks. This task is proceeding as planned.	0%
6	Performance evaluation of tanks	In this task, burst, drop/cycle/burst, gunfire, and impact properties of the tanks will be performed. This task is proceeding as planned. A portion of this task will be performed at the beginning of the 2nd year.	0%

Accomplishment and Progress - 1

We were able to control the NH_2-functionalization of the CNTs which can significantly improve the mechanical properties of the epoxy resin used to fabrication hydrogen storage tanks.

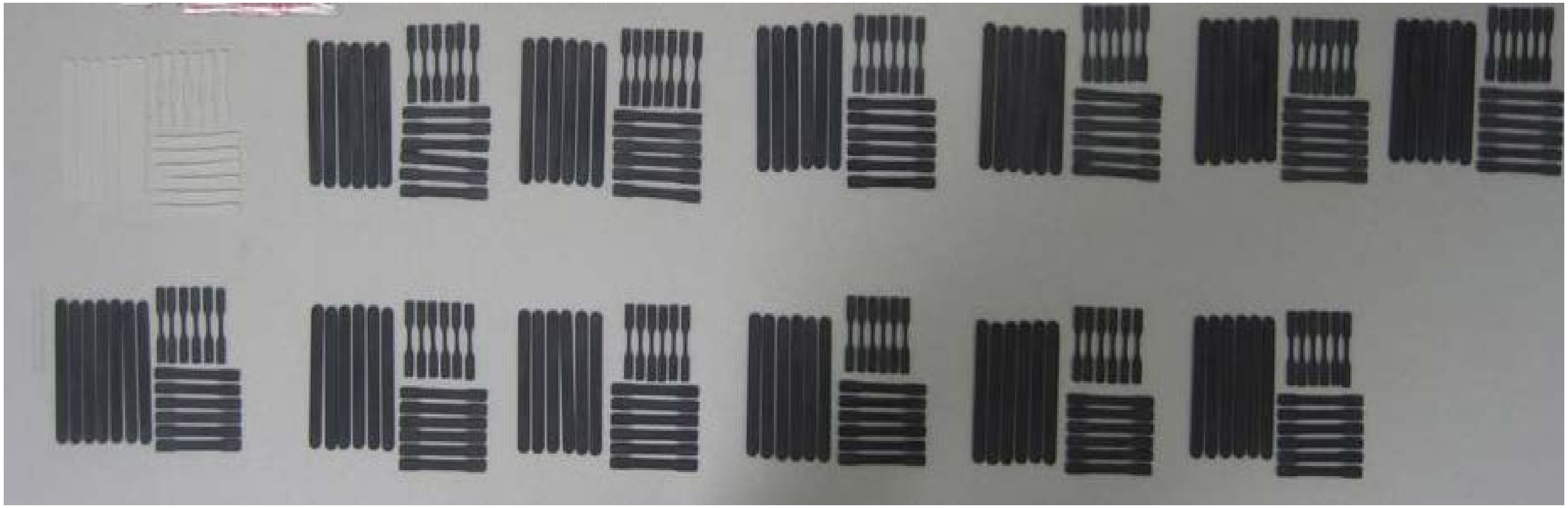




The NH_2-functionalization process is a wet chemical process. During the process, CNTs can be damaged while on the other hand, they will have functional groups attached. It is essential to find an optimized process that can significantly improve the mechanical properties of the epoxy based on NH_2-functionalization.

Accomplishment and Progress – 2

A series of samples were made and tested based on CNT and SiO_2 reinforced epoxy. Based on the results, we have determined the optimized NH_2-functionalization level and loading of the CNTs and SiO_2 in the epoxy matrix.



Accomplishment and Progress - 3

We were able to achieve further improved mechanical properties of the epoxy matrix based on NH_2-functionalized CNTs at optimized functionalization levels. At a CNT loading of 1 wt.% (2 hour treatment), we were able to achieve significantly improved mechanical properties.

Sample #	NH_2 (2 hr) (%)	NH_2 (4 hr) (%)	NH_2 (8 hr) (%)	NH_2 (16 hr) (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Compression strength (MPa)	Compression modulus (GPa)
Neat epoxy					76.7	3.35	106.0	2.54	102.3	2.62
1	0.25				88.7	3.45	115.3	2.70	113.8	2.98
2	0.5				93.3	3.70	127.4	3.88	135.3	3.12
3	1				105.8 (38%↑)	3.88 (16%↑)	148.7 (40%↑)	3.03 (19%↑)	147.7 (44%↑)	3.28 (25%↑)
4	2				90.1	4.01	129.3	4.25	140.3	3.97
5	3				80.4	4.08	117.1	4.58	135.4	4.18
		0.5			87.0	3.62	117.1	2.68	115.8	3.47
		1			96.6	3.78	128.6	3.07	157.0	4.28
		2			89.3	3.87	135.7	3.08	133.3	4.50
		3			83.8	3.80	113.7	2.69	134.6	4.57
6			0.25		80.7	3.53	110.0	2.67	117.8	3.01
7			0.5		87.2	3.68	120.0	2.67	117.8	3.51
8			1		95.6	3.88	124.3	2.98	133.4	4.01
9			2		80.1	3.99	116.0	3.28	127.3	4.50
10			3		78.0	4.23	107.9	3.30	129.5	4.37
				0.5	76.0	3.13	116.3	3.03	118.3	2.68
				1	77.1	3.30	113.2	2.84	114.5	2.78
				2	76.3	3.16	111.2	2.87	108.0	2.87
				3	77.1	3.24	113.4	2.85	106.6	2.87

Accomplishment and Progress - 4

NH_2-CNT and SiO_2 co-reinforced epoxy samples were synthesized and characterized. We were able to achieve further improved mechanical properties. We have already prepared and sent to Hexagon Lincoln a quantity of samples 1 and 3 for CFRP ring fabrication and evaluation.

Sample #	NH_2 (2 hr) (%)	SiO_2 (%)	Tensile strength (MPa)	Tensile modulus (GPa)	Flexural strength (MPa)	Flexural modulus (GPa)	Compression strength (MPa)	Compression modulus (GPa)
Neat epoxy	0	0	76.7	3.35	106.0	2.54	102.3	2.62
1	0.25	2.5	92.3 (20%↑)	3.74 (12%↑)	118.7 (12%↑)	2.97 (12%↑)	121.8 (19%↑)	3.18 (21%↑)
2	0.5	2.5	100.8	4.04	134.0	3.31	150.3	3.41
3	1	2.5	113.7 (48%↑)	4.31 (28%↑)	150.0 (41%↑)	3.48 (37%↑)	163.7 (60%↑)	4.13 (58%↑)
4	2	2.5	87.3	4.28	132.3	3.38	155.3	3.93
5	3	2.5	83.5	4.14	125.1	3.50	133.0	3.90
6	0.25	5	92.5	3.80	118.0	3.05	120.8	3.14
7	0.5	5	97.8	4.01	123.8	3.40	131.8	3.55
8	1	5	101.5	4.11	117.7	3.40	123.0	3.67
9	2	5	90.5	4.30	103.7	3.48	124.0	3.78
10	3	5	76.7	4.38	95.6	3.60	101.8	3.70
11	0.25	12	80.4	4.01	112.6	3.00	119.3	3.04
12	0.5	12	78.5	4.12	115.7	3.08	125.8	3.38
13	1	12	70.3	4.34	107.4	3.35	130.4	3.59
14	2	12	68.8	4.40	99.8	3.77	107.7	3.53
15	3	12	63.3	4.58	87.7	3.60	90.5	3.48

Accomplishment and Progress - 5

The SBS strength of both formulations based on CNT/SiO_2 reinforcement was improved by over 20%. This is a significant achievement. It is also a great improvement from the Phase I result as far as SBS testing is concerned. In fact, the results are comparable to Hexagon Lincoln's standard samples with T800 fiber, which is a stronger but more expensive fiber. The results confirmed that the CNT/SiO_2 reinforced epoxy resin was successfully penetrated in-between the carbon fibers during the filament winding process.

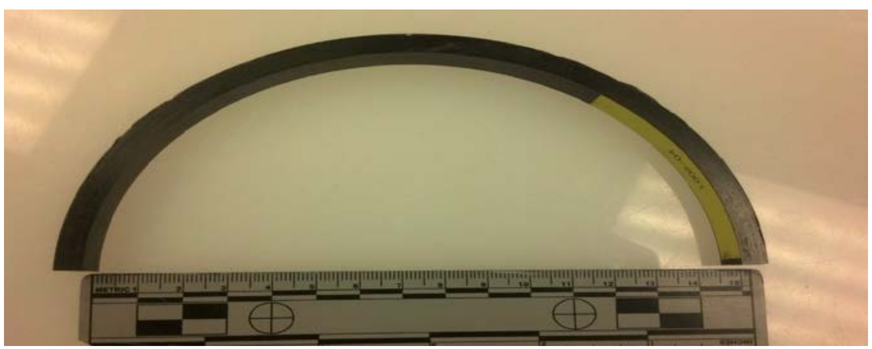
Formulation of CFRP ring*	Viscosity of the epoxy resin (cp)	Viscosity of the resin after adding hardener (cp)	Average shear strength (psi)	Standard deviation	Standard deviation percentage
Standard (epoxy/T700)	3,000	400	7084	79	1.1%
#1 (0.25% NH_2-CNT + 2.5% SiO_2)/epoxy/T700	7,000	800	8508 (20%↑)	171	2.0%
#3 (1.0% NH_2-CNT + 2.5% SiO_2)/epoxy/T700	23,000	2,000	8605 (22%↑)	150	1.7%
Standard (epoxy/T800)	3,000	400	8528	253	3.0%

***Each CFRP ring contains around 58±1% by volume of the carbon fiber.**

Accomplishment and Progress - 6

The impact force of the CFRP rings based on both CNT/SiO_2/epoxy formulations was significantly improved. We tend to believe that the impact tolerance, fracture toughness, stress rupture, cycle fatigue, etc. of the tanks should be improved as well.

Formulation of CFRP ring	Peak force (N)	Peak displacement (mm)
Standard (epoxy/T700)	2045.6	9.037
#1 (0.25% NH_2-CNT + 2.5% SiO_2)/epoxy/T700	2600.5 (27%↑)	10.273
#3 (1.0% NH_2-CNT + 2.5% SiO_2)/epoxy/T700	2275.1 (11%↑)	9.509



CFRP ring: Before and after impact testing

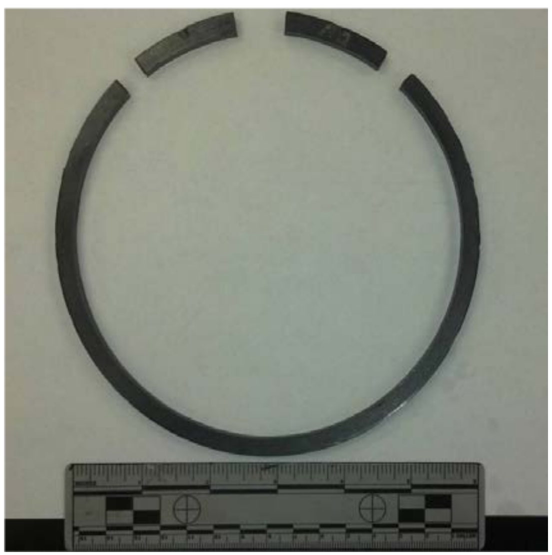
Accomplishment and Progress - 6

The burst strength of the CFRP rings based on CNT/SiO_2/epoxy formulation was not improved. We are at this stage further investigating the reason why the burst strength of the rings based on CNT/SiO_2/ reinforcement was not improved.

Formulation of CFRP ring	Burst strength (psi)
Standard (epoxy/T700)	26532
#1 (0.25% NH_2-CNT + 2.5% SiO_2)/epoxy/T700	25756

Next Key Task

Fabricate and evaluate hydrogen tanks



Continue to fabricate and evaluate the CFRP ring

- CNT reinforced CFRP tanks will be made based on formulation #1. Performance of the tanks will be evaluated;

- In order to better understand the reason why the burst strength of the CFRP rings based on the nano-reinforcement was not improved, ANI will produce the following resins for Hexagon Lincoln to test the burst strength in CFRP form:

  CNT (1.0%)/epoxy
  CNT (0.5%)/epoxy
  SiO_2 (10%)/epoxy
  SiO_2 (5%)/epoxy

Collaboration

Subcontractor: Lincoln Composites

Hexagon Lincoln, manufacturer of the TITAN™ and TUFFSHELL® tanks, is the leading provider of natural gas and hydrogen storage and transport solutions to the alternative fuel vehicle industry.

Hexagon Lincoln's efforts on this Phase II Program:

- Initial Design Review;
- Fabricate CNT reinforced CFRP rings and test properties (shear, impact, burst);
- Fabricate baseline tanks, tanks with CNT reinforcement, tanks with CNT reinforcement at reduced weight and evaluate performance.

Future Work

- ❖ **Continue work to improve the burst strength of the CFRP rings based on nano-reinforcement;**

- ❖ **Move forward to fabricate the 5,000 psi hydrogen fuel tanks with the CNT/SiO_2 reinforcement and evaluate drop/cycle/burst and impact performance;**

- ❖ **Determine how much weight of the CFRP portion of a tank can be reduced based on the results obtained above, fabricate the tanks at reduced weight and evaluate drop/cycle/burst and impact performance.**

- ❖ **Manufacturing**

The final goal of the fourth task will be to establish manufacturing protocols for the ultra light weight hydrogen high pressure fuel tanks demonstrated in the Phase II program.

Summary Slide

Project Summary

Relevance: Our purpose is to make stronger, lighter hydrogen storage tanks with better performance through CNT reinforced CFRP composites. As a result, the cost of the hydrogen storage tanks will be significantly reduced while increasing vehicle efficiency.

Approach: Reducing the cost of high pressure hydrogen storage tanks - Our approach is to reduce the cost of the high pressure hydrogen storage tanks by lowering their weight. Using CNT reinforcement, we are able to significantly improve the mechanical properties of the carbon fiber/epoxy composite (CFRP) matrix used to construct the tanks with the final goal of lowering the weight of the CFRP composites while preserving or even increasing the performance of the tanks.

Technical Accomplishments and Progress: We were able to control the NH_2-functionalization level of the CNTs to significantly improve the mechanical properties of epoxy. We were able to achieve more than 60% improvement in the epoxy matrix of the compression strength and 60% improvement of the compression modulus based on CNT and SiO_2 co-reinforcement. Tensile and flexural properties were also significantly improved (over 40%). Short beam shear strength and impact strength of the CNT/SiO_2 reinforced CFRP rings was significantly improved as well. This confirms that the CNT/SiO_2 reinforced epoxy has successfully penetrated in-between the carbon fibers during the filament winding process.

Proposed Future Research: We need to improve the burst strength of the CNT/SiO_2 reinforced CFRP rings. We need to test the performance of the hydrogen fuel tanks based on the CNT/SiO_2 reinforcement. We also need to understand the correlation between the properties of the CFRP rings and performance of the hydrogen fuel tanks based on the CNT/SiO_2 reinforcement.

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