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: Jun. 17, 2011
- Project end date: Mar. 16, 2012
- Percent complete: *100%*

Budget

- Total project funding
  - DOE share: $149,897
  - Contractor share: $43,760
- Funding received in FY11: $53,953
- Funding for FY12: $95,944

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

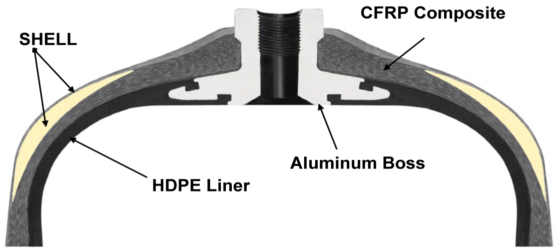
- Lincoln Composites, Inc. – (Subcontractor)

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 61 wt.% of the tank)

Base Materials for CFRP	Price ($/kg)
Neat Epoxy Resin	6
Toray T700 Carbon Fiber	28
CNT (1.0 wt.%) Epoxy Resin	8.94
Neat Epoxy Resin + Carbon Fiber (Weight Ratio 3:7)	21.4
CNT (1.0 wt.%) + Neat Epoxy Resin + Carbon Fiber	22.28 (+4.1%)

Hydrogen fuel tank	Price of Carbon fiber ($)	Price of Resin ($)	Cost of CFRP Portion ($)	Total Cost of Tank ($)
Baseline	392	36	428	713
20% Weight Reduction w/ CNTs	313.6	42.91	356.51 (-17%)	641.51 (-10%)
40% Weight Reduction w/ CNTs	235.2	32.18	267.38 (-38%)	552.38 (-23%)

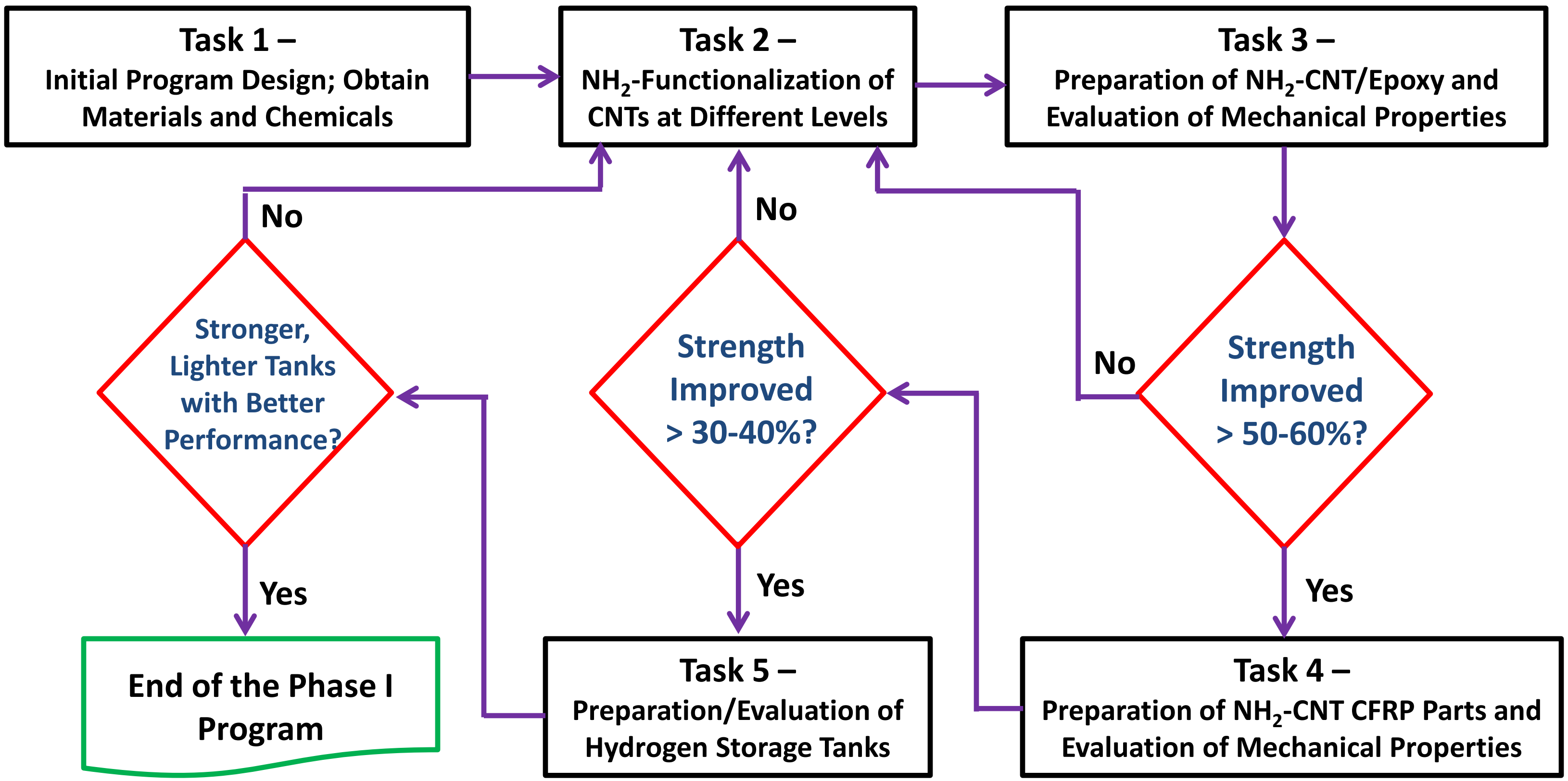
Based on our careful calculations, the cost for 1 kg of the CNT reinforced epoxy resin is the following based on high volume manufacturing:

Epoxy: $6
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 $8.94 ((0.99x6) + (0. 1x10) +2)) making the cost increase of 49% compared to the base epoxy ($6/kg). It can be seen that the cost of the CFRP composite increases about 4.1% using 1% CNT reinforcement (including all related production costs of the reinforced epoxy resin). It is commonly known that carbon fiber accounts for 50-75% of the total cost of a hydrogen fuel tank. Assuming the cost of the carbon fiber is around 60% of 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 least 10% 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% .

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.



Milestones

We focused on 5,000 psi pressure hydrogen storage tanks for this SBIR Phase I.

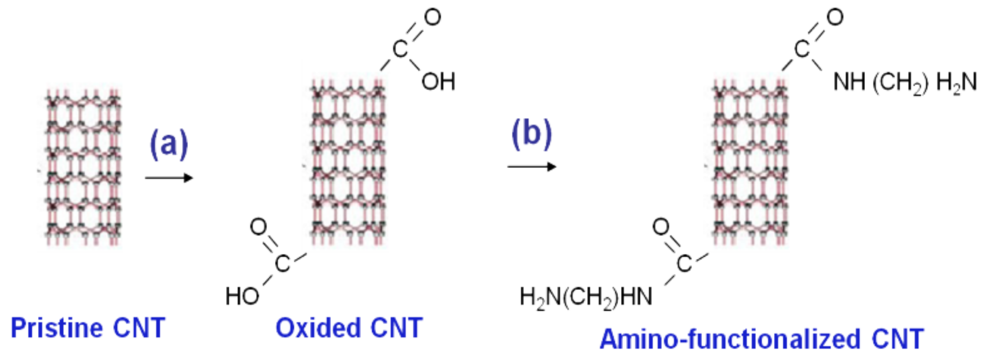
Milestone #	Progress Notes	Timeline
1	Kickoff Meeting	Start of month 1
2	Material/chemical Acquisition Complete	Middle of Month 1
3	NH_2-functionalization of CNTs Complete	Middle of Month 2
4	CNT/epoxy synthesis and strength testing Complete	Middle of Month 4
5	Fabrication of CFRP hydrogen fuel cylinder Complete	Middle of month 8
6	Performance testing of cylinders complete	End of Month 9
7	Final Report Complete	End of month 9 - Phase I Completion

Work Plan/Progress

Task	Task Description	Progress/Accomplishments	completion
	Kick-off meeting	Dr. Dongsheng Mao of ANI attended Hydrogen Storage Tech Team Meeting organized by DOE at the beginning of the Phase I Program	100%
1	Obtain materials/chemicals	Obtained all the necessary materials and chemicals in the first 2 weeks of the program. Received proprietary epoxy resin from subcontractor at the beginning of the program.	100%
2	NH_2-functionalization of CNTs	Prepared enough NH_2-functionalized CNTs at the beginning of the 2^{nd} month for the whole the Phase I Program.	100%
3	Preparation of CNT reinforced epoxy		
	A – Dispersion of CNTs in epoxy	Prepared dispersions of epoxy resin at different loadings of CNTs by the end of the 2^{nd} month.	100%
	B – Specimen preparation	Prepared all the specimens at the end of 3^{rd} month for mechanical testing.	100%
	C – Mechanical testing	Tested mechanical properties of the specimens at the middle of 4^{th} month.	100%
4	CNT reinforced fuel tank		
	A – Prepare CNT/epoxy resin	Prepared over 150 lbs of the CNT reinforced epoxy resins in the middle of the 7^{th} month for hydrogen storage tank fabrication.	100%
	B – Prepare fuel tanks	Fabricated 4 hydrogen storage tanks in the middle of the 8^{th} month.	100%
	C – Performance testing	Tested burst, drop, burst after drop performance of the tanks at the end of the 8^{th} month.	100%
5	Program management	Program finished at the end of the 9^{th} month (Middle of March, 2012)	100%

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 functionalization, CNTs can be damaged although on the other hand they can be attached with functional groups. It is essential to find an optimized process that can significantly improve the mechanical properties of the epoxy matrix based on NH_2-functionalization.

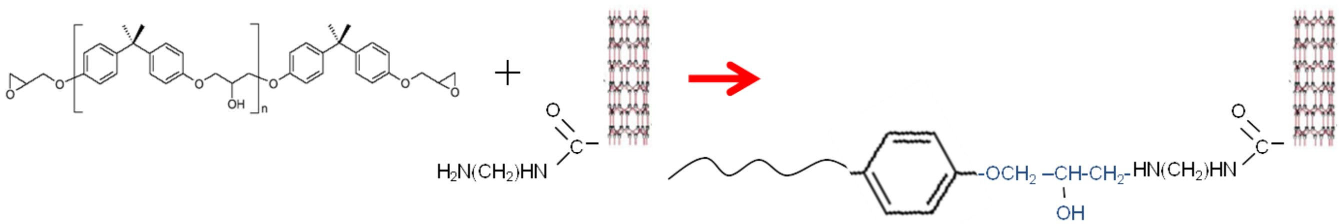
Accomplishment and Progress - 2

Based on 1% loading of the NH_2-functionalized CNTs, we were able to achieve, in the epoxy matrix, more than 50% improvement of the compression strength and 60% improvement of the compression modulus. Tensile and flexural properties were also significantly improved.

Sample #	COOH- (%)	NH_2 (4 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	0.5			79.8	3.49	111.8	2.73	111.3	2.98
2	1			91.8 (20%↑)	3.78 (13%↑)	128.3 (21%↑)	2.93 (15%↑)	138.7 (35%↑)	3.10 (18%↑)
3	2			88.8	3.83	121.7	3.05	122.7	3.08
4	3			85.6	3.79	114.5	2.88	118.5	3.13
5		0.5		87.0	3.62	117.1	2.68	115.8	3.47
6		1		96.6 (26%↑)	3.78 (13%↑)	128.6 (21%↑)	3.07 (21%↑)	157.0 (52%↑)	4.28 (63%↑)
7		2		89.3 (16%↑)	3.87 (15%↑)	135.7 (28%↑)	3.08 (21%↑)	133.3 (30%↑)	4.50 (71%↑)
8		3		83.8	3.80	113.7	2.69	134.6	4.57
9			0.5	76.0	3.13	116.3	3.03	118.3	2.68
10			1	77.1	3.30	113.2	2.84	114.5	2.78
11			2	76.3	3.16	111.2	2.87	108.0	2.87
12			3	77.1	3.24	113.4	2.85	106.6	2.87

Accomplishment and Progress – 2 (Cont.)

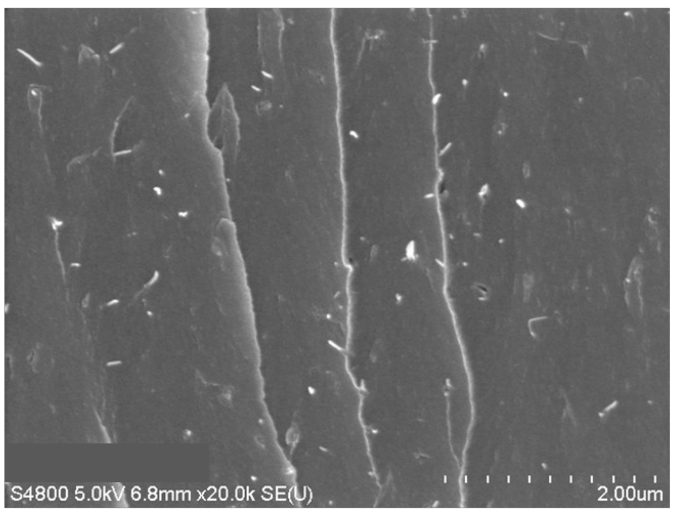
Covalent bonding between NH_2-functionalized CNTs and the epoxy matrix can be formed. The dispersion of the NH_2-functionalized CNTs in the epoxy matrix is excellent.



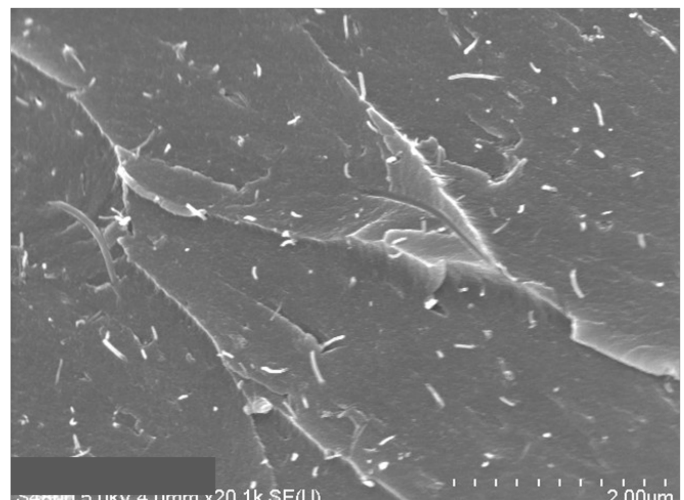
Epoxy Resin –(Diglycidyl ether of Bisphenol-A)

NH_2-CNT

Cross-linked Epoxy Polymer – CNT composite



Flexural surface of NH_2-CNT (1.0%)/Epoxy



Flexural surface of COOH-CNT(1.0%)/Epoxy

Accomplishment and Progress - 3

Hydrogen storage tanks were made without any problem using a filament winding process based on NH_2-CNT (1.0%) reinforced epoxy resin.

Glass fiber layer being wound with CNT reinforced epoxy

After the CNT reinforced epoxy resin was smoothed on the surface

Accomplishment and Progress – 3 (Cont.)

Performance of 5,000 psi hydrogen storage tanks with CNT reinforcement:

4 standard tanks and 4 tanks with CNT reinforcement were fabricated using the same amount of epoxy/carbon fiber (i.e. same weight of the tanks). The burst pressure of the CNT reinforced tanks was significantly lower compared to baseline values. Also, the pressure cycle performance was significantly lower compared to baseline values. Because of the viscosity increase of the CNT reinforced epoxy resin compared with the neat epoxy, the CNT reinforced epoxy resin did not penetrate and adhere to the carbon fibers. This lack of penetration of the resin, and subsequent degradation in ability to transfer pressure loads uniformly through the laminate, explains why burst and cycle values were low.

Cross section of laminate with CNT reinforced resin

Cross section of standard laminate

After burst test: Hydrogen storage tank reinforced with CNTs

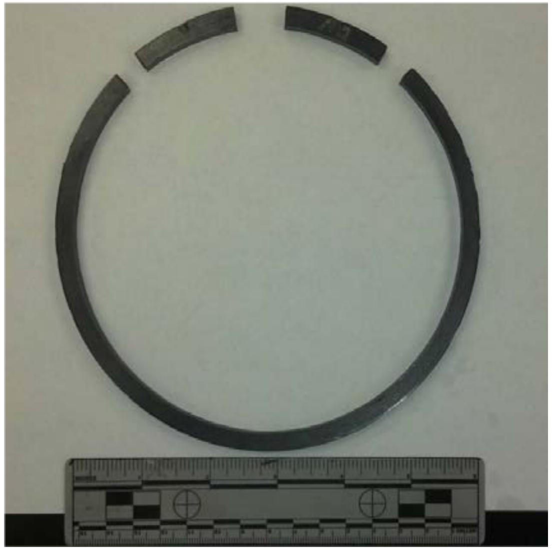
SN	Resin	Pressure (psi)	Failure location
1763-001	CNT/epoxy	8,724	Mid-cylinder
1763-003	CNT/epoxy	10,693	Mid-cylinder
1764-001	Standard	13,718	2” port
1764-003	Standard	15,363	2” port

Results of burst tests of the tanks (standard and with CNT reinforcement)

SN	Resin	Cycles completed	Pressure at burst after cycle (psi)	Failure location
1763-002	CNT/epoxy	419	N/A	Mid-cylinder
1763-004	CNT/epoxy	864	N/A	Mid-cylinder
1764-002	Standard	15,000	12,954	2” port
1764-004	Standard	15,000	12,778	2” port

Results of cycle test of the tanks (standard and with CNT reinforcement)

Accomplishment and Progress – 3 (Cont.)



CFRP rings made in the Phase I program

Results of the CFRP rings (with or without CNT reinforcement):

- Viscosity of the epoxy resin plays a large role in the fabrication of the CFRP composite when using a filament winding process;
- At a CNT loading of 0.3%, the CFRP ring could be made with full penetration of the epoxy in-between the carbon fibers, thus improving the result of the short beam shear test;
- When a 5% loading of the surfactant was added to the CNT (0.3%)/epoxy, the short beam shear was not decreased but the viscosity was significantly decreased;
- In the Phase II program we will add a low loading of a surfactant into the CNT reinforced epoxy to lower the viscosity. We are confident that the hydrogen fuel tanks can be fabricated with the epoxy matrix fully integrated with carbon fiber.

Base resin for the CFRP ring	Viscosity of the resin (cp)	Viscosity of the resin after adding hardener (cp)	Void by volume %	Shear strength of the laminates (psi)	Shear modulus of the laminates (psi)
Standard	3,000	400	<5.0	8615	272,000
1.0% NH_2-functionalized CNT	29,000	3,200	>20.0	192	188,000
0.75% NH_2-functionalized CNT	22,000	2,200	~8.0	7383	300,000
0.5% NH_2-functionalized CNT	14,000	1,500	~7.5	8437	571,000
0.3% NH_2-functionalized CNT	9,000	800	5.0	9138	468,000
0.3% NH_2-functionalized CNT with 5% of surfactant	2,500	300	<5.0	9078	473,000

Collaboration

Subcontractor: Lincoln Composites

Lincoln Composites, 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.

Lincoln Composites' efforts in this Phase I Program:

- 4 standard tanks were fabricated;
- 4 tanks with CNT reinforcement were fabricated;
- Burst 2 baseline tanks and 2 tanks reinforced with CNTs;
- Drop, cycle, and burst the remaining tanks;
- CFRP rings with and without CNT reinforcement were made to see the quality of the CFRP composites.

We were not able to achieve hydrogen fuel tank with reduced weight in the Phase I program during to the viscosity increase of the CNT reinforced epoxy resin. However extra work was done by Lincoln Composites in the Phase I how to solve the viscosity issue of the CNT reinforced epoxy resin in order to for it to be penetrated in-between the carbon fibers. ANI/Lincoln Composites used a surfactant to lower the viscosity of the CNT reinforced epoxy and checked the mechanical performance of the CFRP ring, very promising results were achieved. We firmly believe that the viscosity issue can be resolved. In the Phase II program, one of our focuses is for ANI/Lincoln Composites to find better ways to fabricate the tanks. We may use a surfactant to lower the viscosity of the matrix and improve the wetting between the CNT reinforced epoxy and the carbon fibers. Another approach is to increase the temperature of the CNT reinforced resin to lower the viscosity of the matrix.

Future Work

❖ **Optimize the formulation of the functionalized-CNT/epoxy based upon Phase I results.**

The goal of the this task will be to optimize the formulation of the functionalized-CNT/epoxy resin that was used as proof-of-concept of the hydrogen fuel tank in the Phase I program. Mechanical properties of both functionalized-CNT/epoxy and functionalized-CNT/reinforced CFRP composites will be evaluated. Based on the achievement of this Phase II task, ANI will be able to build hydrogen fuel tanks with further improved performance.

❖ **Improve the processing for fabricating hydrogen storage tanks using CNT reinforced epoxy that wasn't solved in the Phase I Program**

The goal of this task will be to optimize the fabrication process to allow CNT reinforced epoxy resins to be fully penetrated and integrated with carbon fiber during the filament winding process as the viscosity of the CNT reinforced epoxy and its surface tension are higher than the control epoxy. Surfactants or wetting agents may be used. Another way is to increase the tank fabrication temperature to lower the viscosity of the CNT reinforced epoxy resin.

❖ **Continue to focus on the 5,000 psi pressure hydrogen storage tanks initially before moving to higher pressure tanks (for example 10,000 psi tanks)**

The goal of this task will be to figure out how to fabricate 5,000 psi pressure hydrogen storage tanks with high performance CNT reinforced epoxy resin. In this way, we can lower the expense with lower risk. After all issues are resolved and we see better performance of the 5,000 psi tanks. We then move to higher pressure tanks.

❖ **Evaluate the performance of the hydrogen fuel tanks**

We tested hydrostatic burst and drop/cycle/burst of the 5,000 psi tanks in the Phase I Program. The goal for this task will be to conduct more sophisticated tests of the 5,000 psi hydrogen fuel tanks fabricated in the Phase II Program. Further qualification tests, including burst, cycle/burst, drop/cycle/burst, and gunfire, will be performed. Light weight hydrogen storage tanks will be made (purpose – greater than 24% weight reduction compared with the standard tank due to 40% weight reduction of the CFRP portion). These lighter weight tanks will be tested. These results will be documented and considered as very important information upon manufacturing of the new products using the technology developed in the Phase II Program.

❖ **Move to higher pressure hydrogen storage tanks**

The goal of this task will be to fabricate some lighter weight higher pressure (at least 10,000 psi) hydrogen storage tanks based on the results achieved with lighter weight 5,000 psi hydrogen storage tanks. Their performance will be evaluated and documented.

❖ **Manufacturing**

The 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 the hydrogen storage tanks stronger, lighter and with better performance through CNT reinforced CFRP composite. 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 purpose being to lower 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 50% improvement in the epoxy matrix of the compression strength and 60% improvement of the compression modulus. Tensile and flexural properties were also significantly improved. We need to modify the filament winding process to fabricate high quality hydrogen storage tanks with CNT reinforced epoxy due to its higher viscosity compared with the control epoxy. Based on the Phase I result, we firmly believe we are able to achieve the target in the Phase II program.

Proposed Future Research: Continue to improve the mechanical properties of the epoxy matrix using functionalized CNTs; optimize the fabrication process of the hydrogen storage tanks; test the performance of the tanks with CNT reinforcement in more sophisticated ways; license the technology to hydrogen fuel tank manufacturers, set up a subsidiary or joint venture for manufacturing CNT reinforced epoxy resin; commercialize the technology.

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