2013 DOE Hydrogen and Fuel Cells Program Review

Low-cost Integrated Nanoreinforcement for Composite Tanks – “LINCT” (SBIR Phase I)

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NextGen Aeronautics

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Project ID # ST109

Overview

Timeline

- Start date: **November 2012**
- End date: **August 2013**
- Percent complete: ***35%***

Barriers

- Barriers addressed
  - **Durability/Operability**
  - **System Weight and Volume**
  - **System Cost**

Budget

- Total project funding
  - DOE share: **$149,949**
  - Contractor share: **$0**
- Funding received in FY12: **$149,949 (Fully Funded)**
- Funding for FY13: **N/A**

Partners

- **Subcontractors**
  - **Precision Nanotechnologies (PNT), Nanofiber process and reinforcement developer**
  - **Hexagon Lincoln, Inc., Tank developer**
- **US Army, collaborator**
- **Project lead: NextGen Aeronautics (NextGen), integrator**

Relevance, Phase I

During Phase I:

• Improve nanofiber fabrication and demonstrate on-line manufacturing control towards maximized material property benefits and minimized time required for nanofiber insertion

• Show quantitative trends in damage-resistance improvements such as interlaminar toughness, shear strength, and burst strength to demonstrate improved durability and potential for reducing tank weight and volume

DOE Barrier	NextGen Team's Phase I Goal
Durability/ Operability	Demonstrate improved durability—example, increase in Mode I and Mode II interlaminar toughness by 10% and 30% respectively
System Cost	Correlate improved durability with lower factors of safety (2.25 to 2.00), leading to less carbon needed and associated lower costs while balancing impact on on-line deposition of nanofibers during filament winding
System Weight and Volume	Demonstrate the potential for selective nanofiber reinforcement such as outer layers in thick-walled tanks and other complex shapes

Relevance, Phase II

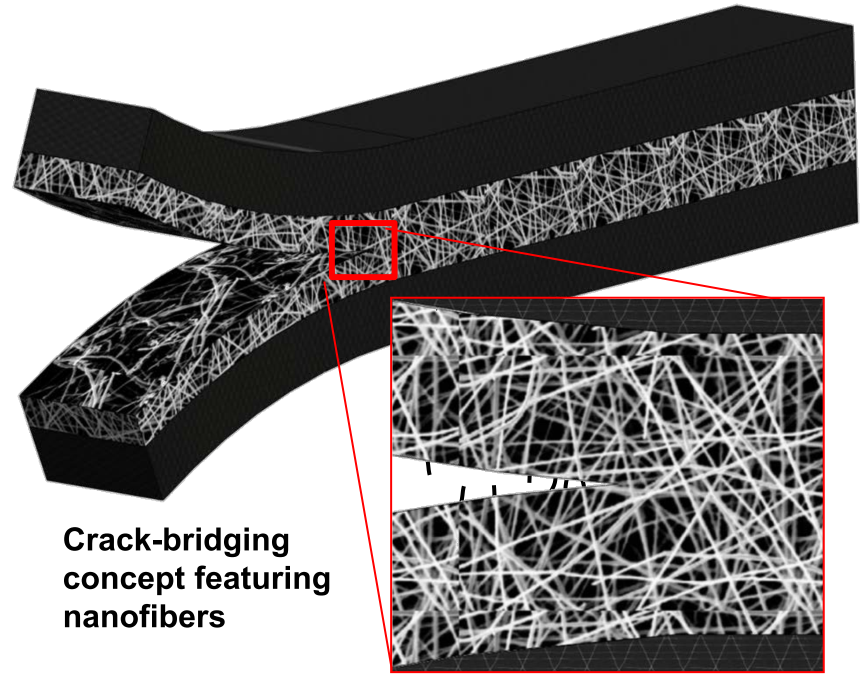
During Life of Project: Improved damage-resistant and -tolerant tanks will facilitate using less fiber at increased pressures leading to lighter tanks, decreased volume and reduced system costs due to the reduction in tank fiber needed

FCT Program Hydrogen Storage Objective	NextGen Team's Phase II Goal
Development of composite additives that will result in composite gas cylinders that exceed the performance of today's T700 cylinders--i.e., Reduce H2 Storage Cost to meet the 2017 H2 Storage Cost of $12/kWh	After identifying performance metrics, the team will continue to use T700 to fabricate 700 bar tanks and demonstrate 25% high-volume cost savings

FCT Program Objective	NextGen Team's Phase II Contribution
Improve durability equivalent to 150,000 miles of driving for automotive fuel cell systems by 2017	Demonstration of reduced hydrogen storage tanks costs will contribute to this objective
	Demonstration of tank durability well over 150,000 miles of driving supports future fuel cell durability
	Indication of this technology for complex geometries will support 2020 gge goals for conformal tanks

Approach, innovation

- Strength
  - Nanofibers reinforce resin sharing load with carbon fiber
  - Nanofibers increase resin modulus improving load transfer between composite layers
- Impact resistance
  - Cracks are arrested toughening laminate by increasing resistance to energy propagation and crack-bridging (shown)
  - Nanofibers change dynamic properties of resin to respond to impact



Crack-bridging concept featuring nanofibers

- State of the art (SOA) approaches include matrix, fiber, and their combinations*
- LINCT innovation uses PAN nanofibers
  - Continuous form of PAN nanofibers is optimal for energy dissipation
  - Treated as articles rather than nanoparticles mitigating health concerns
  - Inexpensive top-down manufacturing process can be on-line or by hand
  - Ultrafine PAN nanofibers recently demonstrated ultrahigh strength and toughness**

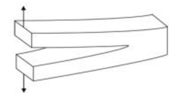
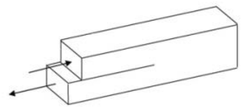
*VanderVennet et al. 2011

** ACS Nano 2013 (highlighted in Nature)

Approach, addressing barriers

- Our goal: Demonstrate both improved damage resistance and tolerance (i.e., damage resistance after impact) by developing nanofiber fabrication and on-line delivery with filament winding and associated tank materials
- Our approach: Reinforce composite hydrogen storage tanks by selective delivery of optimized nanofibers
  - System Weight and Volume: Fiber reinforced polymer composites have high specific strength. However, layered characteristic of laminates and conventional manufacturing gives rise to a low interlaminar strength. *We will address these weaknesses by improving interlaminar and shear strength.*
  - Durability/Operability: Damage growth will be eliminated or slowed by introducing continuous nanofiber reinforcement in very thin interlaminar layers. *The unique continuous nanofibers extend energy dissipation when compared to other nano additives.*
  - System Cost: Projected on-line nanofiber placement will minimally change the filament winding process and will have potentially low impact on costs, but increased savings will be in selective reinforcement placement resulting in optimally structured tanks using minimal carbon fiber. *We will show lower costs by demonstrating reducing carbon fiber quantities required.*

Approach, by metric

Addresses What	Phase I metric	Milestone /Task	Status	Phase II metric
Durability/ Operability	**(1a)** 10% improvement in Mode I Interlaminar Toughness using CH2 representative tank materials Double Cantilever Beam (DCB), Mode I  **(1b)** 30% improvement in Mode II Interlaminar Toughness using CH2 representative tank materials End Notched Flexure (ENF), Mode II 	Milestone 1 through 3 Tasks 1 and 2	25%	20% improvement in Mode I Interlaminar Toughness using CH2 tanks materials 60% improvement in Mode II Interlaminar Toughness using Ch2 tank materials
System Cost H_2 Storage Objective	**(3)** Successful demonstration of (a) controlled high-rate process and (b) concurrent nanofiber deposition with CH2 filament winding process on a 700 bar tank, demonstrating 5% reduction in costs subtracting added winding time increase from reduced carbon fiber costs. **700 bar tank** 	Milestone 4 through 6 Tasks 2 through 5	30%	Quantitative study demonstrating validity of 25% reduction in costs for a 700 bar tank system
Durability/ Operability System Cost System Weight and Volume	**(2)** 10% improvement in Burst Strength of 240 bar tank when compared with unreinforced 240 bar tanks. For high-pressure tanks, shear strength may improve laminate strength.  **240 bar tank**	Milestone 7 Task 6	10%	30% Improvement in Burst-after-Impact Strength of 240 bar and/or 700 bar tanks. If shown, a reduction of 2.25 to 2.0 stress ratio would be supported.

Approach, by milestones

No.	Milestone	Timeline
1	Phase I requirements established	March 2013 ✓
2	G_{IC} of 10% improvement shown with CH_2 tank materials indicating improved controlled high-rate nanomanufacturing process	April 2013
3	G_{IIC} of 30% improvement shown with CH_2 tank materials with improved controlled high-rate nanomanufacturing process	May 2013
4	Nanofiber-deposition attachment ready for Hexagon Composites	June 2013
5	Concurrent manufacturing process verified on 240 bar tank	June 2013
6	Concurrent manufacturing process verified on 700 bar commercial winder	July 2013
7	240 bar tanks have been tested and meet 10% improvement	July 2013

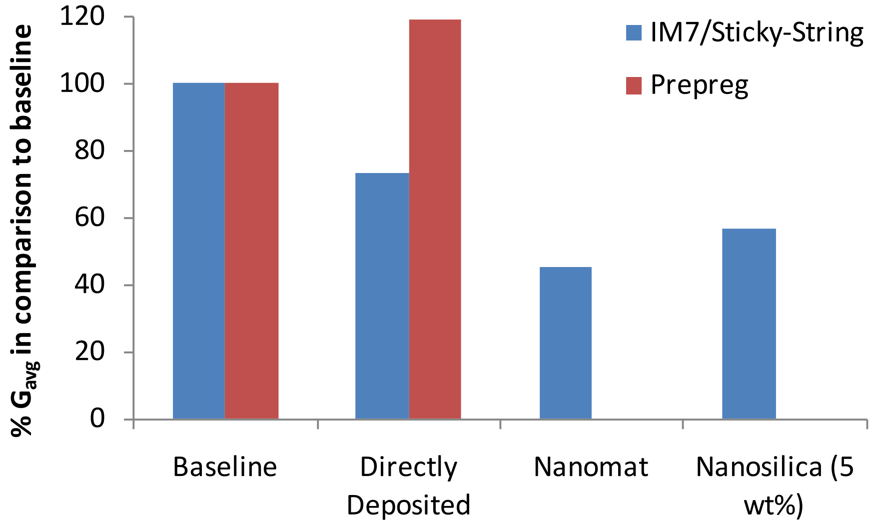
Accomplishments, previous

Previous work: The team has previously shown improvement in fracture toughness

Improvements in both Mode I and Mode II interlaminar fracture toughness have been previously demonstrated in an Army program using prepreg:

– G_{IC} showed improvement of 18.9% (shown for "Directly Deposited")
– G_{IIC} showed improvement of 66.7% (not shown)

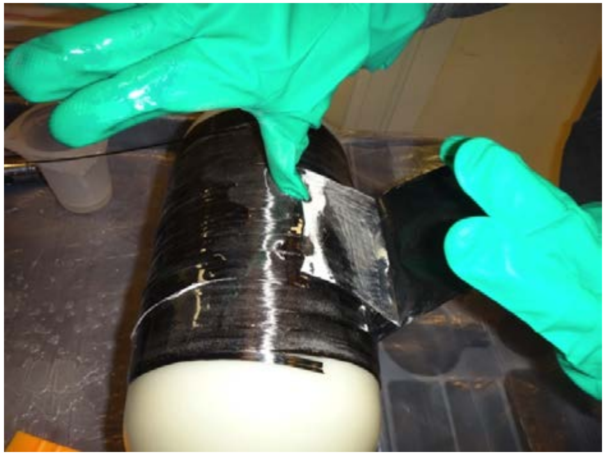
Addresses Durability/ Operability



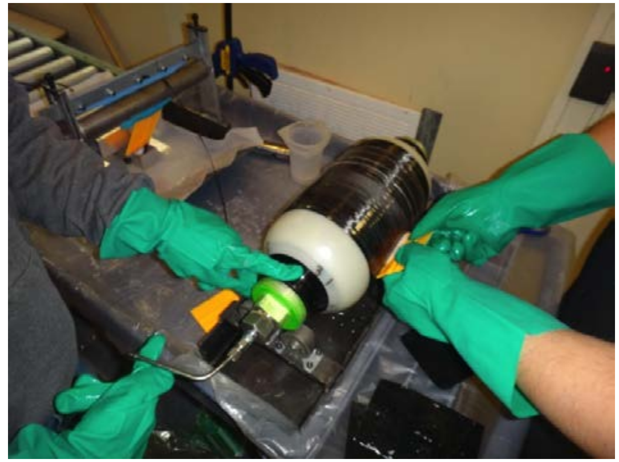
VanderVennet, J., Duenas, T., Dzenis, Y., Peterson, C., Bakis, C., Carter, D., Roberts, K., *Fracture Toughness Characterization of Nanoreinforced Carbon-Fiber Composite Materials for Damage Mitigation*. Proc. of SPIE 2011, San Diego, CA. March 6-10, 2011, 7978, 797823 (2011).

The team intends to show similar improvements as the "Prepreg" using representative hydrogen tank materials. Nanoscale improvements are highly dependent on host materials. The team sees benefit in sharing its findings and collaborate with other nanoscale approaches.

Accomplishment 1, delivery



Apply nanomat



Distribute epoxy resin

Cure part

While direct nanofiber deposition is being developed and optimized by PNT in-house, insertion of high-quality premanufactured nanofiber sheets with different (low) areal density has been evaluated in manufacturing trials at Hexagon Lincoln.

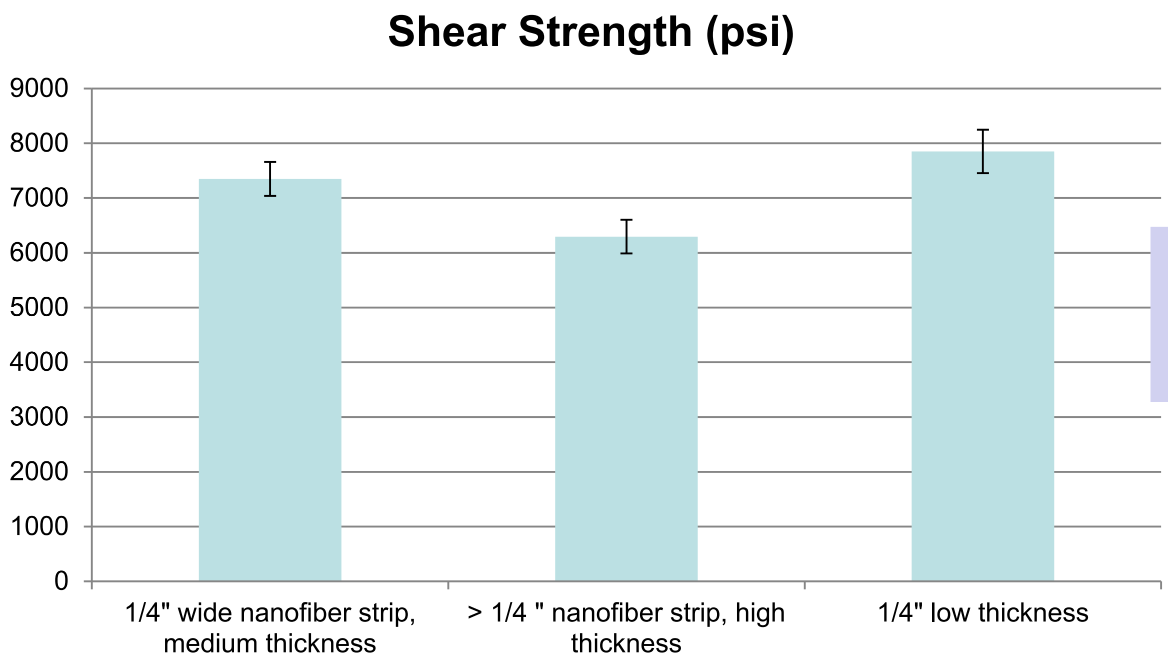
Highly-controlled nanofiber inserts were deemed advantageous for parametric materials (fracture mechanics) studies.

The trials showed the need for improved nanofiber detachment and Transfer techniques in the wet filament winding environments to avoid wrinkling and folding.

Preliminary results are provided on the next slide.

Addresses Durability/ Operability and System Cost

Accomplishment 1, trends



Addresses Durability/ Operability

Picture of Manufacturing Process at Hexagon Lincoln

- Relatively inexpensive ASTM (D2344) short beam tests were performed to characterize the effect of nanofiber quantity on results and develop manufacturing for subsequent filament winding coupons (e.g., End-Notched Flexure) and associated testing.
- The figure shows the average and standard deviation for 5 samples of each coupon type.
- In spite of the lack of optimized manufacturing, the shear strengths were on the order of the baseline and the goals of the study were achieved—i.e., to develop manufacturing and obtain results based on nanofiber quantity. Preliminary results show encouraging results that the coupons with the thinnest NF sheet have the highest shear strength.

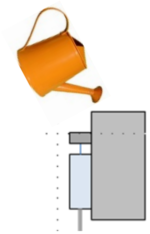
Accomplishment 2, fabrication

Nanofiber manufacturing is being optimized

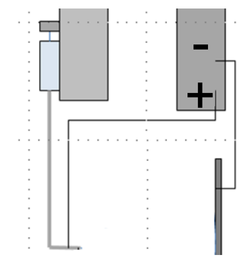
- High quality 6” wide strips were nanomanufactured with areal densities of 1, 2, 4, 6, and 10 g/m^2

Addresses Durability/Operability

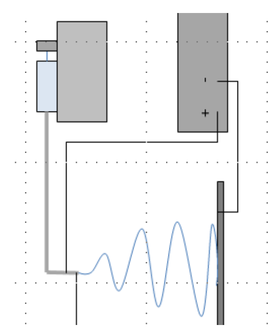
- Sheet geometry is compatible with projected needs of Double Cantilever Beam (DCB) and End Notched Flexure (ENF) specimen manufacturing



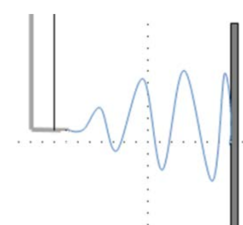
Step 1: Add PAN solution



Step 2: Set up potential difference



Step 3: Activate delivery



Step 4: Collect desired areal weight

Accomplishment 3, delivery

Nanofiber detachment and delivery is being optimized - Removing 1g/m^2 (via 7/16” dia dowel)

Addresses Durability/ Operability and System Cost

Removing the nanomats with wooden dowels is very successful as rolling the nanomats helps remove the fibers from the substrate without leaving remnant fibers behind. Also, once rolled up, the mat can be easily transferred.

Notable observations from this delivery method include:

– The thinner nanomats were more difficult to roll into dowel

– Placing the nanomats on the Hexagon Lincoln drum was considerably successful, however difficult to accomplish without nanomat wrinkling

A second detachment method is being currently explored in preparation for another manufacturing trial at Hexagon Lincoln.

Collaborations

NextGen teams with Precision Nanotechnologies (PNT) and Hexagon Lincoln (formerly Lincoln Composites) to transfer PNT's nanocomposite technology and NextGen/PNT online-process to gas storage tanks for light duty fuel cell vehicles (FCVs) including hydrogen and natural gas.

- **Subcontractors**
  - PNT, the featured nanocomposite technology is from PNT's patent 6265333, polyacrylonitrile (PAN) electrodeposition process; recent publication, ACS Nano 2013 (highlighted in Nature).
  - Hexagon Lincoln, the low-cost all-composite fuel containers will be filament wound at Hexagon Lincoln, with the innovation's design and manufacturing process improved by PNT and NextGen/PNT* technologies.
- **Collaborator:** US Army Aviation and Missile Research Development and Engineering Center (AMRDEC) - While the fiber and matrix materials are different, missile and storage tanks share common benefits from the technology featured in LINCT. NextGen's previous work in this area was funded by an Army SBIR, currently in Phase II Enhancement.

Precision Nanotechnologies

HEXAGON LINCOLN

AMRDEC

*VanderVennet et al. 2011

Proposed Future Work

Task	Description	Status
1	Establish performance requirements	100%
2	Develop nanocomposite technology • Milestone 2 (M2): G_{IC} of 10% improvement shown with CH_2 tank materials • M3: G_{IIC} of 30% improvement shown with CH_2 tank materials • M4: Nanofiber-deposition attachment ready for Hexagon Composites	50%
3	Design and analyze pressure vessels	25%
4	Verify manufacturing process	10%
5	Manufacture pressure vessels • M5: Concurrent manufacturing process verified on 240 bar tank • M6: Concurrent manufacturing process verified on 700 bar commercial winder	0%
6	Perform tests to obtain preliminary data • M7: 240 bar tanks have been tested and meet 10% improvement*	0%
7	Plan Phase II and technology transition	0%

*Short-beam shear tests using a manual filament-wound approach (slides 10 and 11) were performed ahead of all tasks to mitigate highly sensitive manufacturing dependency. Additional tests may be required to show that lack of burst-test improvement (Milestone 7) may reflect this dependency and not the benefit of PAN inclusion. At this time the team realizes the original goals are very aggressive.

Project Summary

Relevance: Improved damage-resistant and -tolerant tanks will facilitate using less fiber in manufacturing at increased pressures leading to lighter tanks, decreased volume and reduced system costs due to the reduction in tank fiber needed.

Approach: Demonstrate both improved damage resistance (e.g., improved burst strength) and tolerance (e.g., improved burst strength after impact) by developing nanofiber fabrication and delivery as well as understanding material interaction.

Technical Accomplishments and Progress:
•Demonstrated high-quality deposition of nanofiber mats
•Demonstrated trend in shear strength improvement using short beam tests

Technology Transfer/Collaborations: NextGen is collaborating with AMRDEC for similar application to missiles with like nanoreinforcement (PAN nanofiber, nylon nanofiber, and nanosilica particles), however, with different matrix and fiber materials.

Proposed Future Research:
•Manufacture, cut and test DCB (Mode I) and ENF (Mode II) coupons.
•Develop on-line concurrent process for 240 and 700 bar hydrogen storage tanks.
•Perform tests on 240 bar hydrogen tanks and perform additional tests (e.g., short shear beam) in case milestone is not achieved.
•Even with the Army collaboration, there is the risk that the program was too aggressively planned to meet all targets. As a result, NextGen is also developing risk mitigation plans.

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