NanoSonic, Inc.

2015 DOE Hydrogen and Fuel Cells Program and Vehicle Technologies Office
Annual Merit Review and Peer Evaluation Meeting

Cryogenically Flexible, Low Permeability H_2 Delivery Hose

P. I.: Dr. Jennifer Lalli, President
NanoSonic, Inc.

6/10/2015

Project ID #
PD101

Overview

Timeline

- Project Start Date: 7/28/2014
- Project End Date: 7/27/2016

Barriers

- Lack of H_2 / Carrier and Infrastructure Options
- Reliability and Costs of Gaseous H_2 Compression
- Reliability and Costs of Liquid H_2 Pumping
- Eliminate H_2 Embrittlement, Increase Durability

Budget

- FY13 DOE Funding: $150,000
- FY14 DOE Funding: $1,000,000
- Total DOE Project Value: $1,150,000

Partners

- CSA Group
- NREL
- Swagelok and Lillbacka
- New England Wire Technologies
- Shell and WEH USA
- Giles County Government

Relevance:
Develop a H_2 Hose Dispenser for Fuel Cell Vehicles

Objectives:

- Develop: Flexible dispensing hose to enable H_2 delivery < $2/gge
- Demonstrate: Reliability at -50 °C and 875 bar for H70 service
- Optimize: Ruggedness, cost, and safety, 70 fills/day, > 2 years

Impact in April 2014 – April 2015:

- Produced: Low T_g, Low H_2 Permeability, Fiber Reinforced Hose with High Pressure Fittings
- Verified: Mechanical and Solvent Durability and H_2 Dispensing Stations

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Approach:

Develop Advanced All Polymer H_2 Hose Dispenser for Fuel Cell Vehicles

- **Technical**: Low T_g Hose Matrix Resin for Cryogenic, High Pressure Flexhose Service
- **Safety**: Low H_2 Permeability, Zero VOCs, and No Residual Monomer for EGA
- **Durability**: Fiber Reinforced to Eliminate H_2 Embrittlement and Optimize Burst Strength
- **Manufacturing**: Ceramer Crimping Agent to Match CTE/Modulus of Hose and Fitting
- **Cost**: lifetime against: Spir Star, Yokohama Rubber/Iwatani IG, ContiTech, Togawa Rubber

Spir Star	Yokohama	Togawa	ContiTech
6mmHydrogen -40 °C to 65 °C Steel H70	ibar HG_{70} H70	H35	

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Approach:
Project Phases and Selected Milestones

1. **Define** FY14
critical performance metrics, hose components, and partners

2. **Evaluate** FY15 Q1-Q2
base materials, architecture, and optimize design

GO / NO GOs

- Low T_g for expected -50 °C dispensing
- Surpass 875 Bar hydrostatic strength and pressure cycle testing
- No contaminant leaching
- Competitive cost
- Validate mechanical, chemical, thermal, and environmental lifetime durability over Spir Star

3. **Test Prototype** FY15 Q2-Q3
hose/fittings with H_2 under service Pressure, temperature, and mechanical

4. **Qualify** FY15 Q4 – FY16 Q1
H70/H35 hose with OEM dispenser/nozzle for safety and environmental durability

4. **Deploy** FY16 Q2
H70/H35 hose at H_2 stations

HYD HYDROGEN

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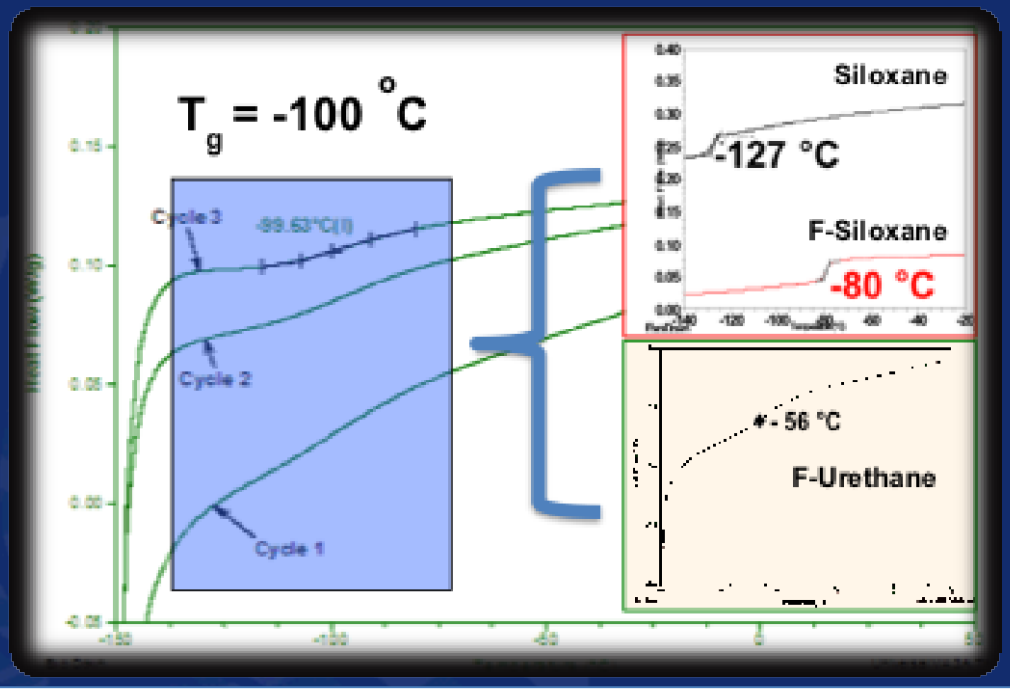
Accomplishments in Cryogenic Service

1. siloxane backbone – to meet the requisite low T_g for cryogenic flexibility
2. urethane component – amine bonding to reinforcing agents / fiber
3. fluorinated siloxane – weatherability against UV, ozone, and atomic oxygen (AO)
4. fluorinated urethane – adhesion for heat seaming,
5. tailored molecular weight (M_n) - for processability with extrusion manufacturing



Low T_g polymer matrix resin with verified low off-gassing has been engineered, tested, and down-selected for long-term use as the low temperature flexible hose material

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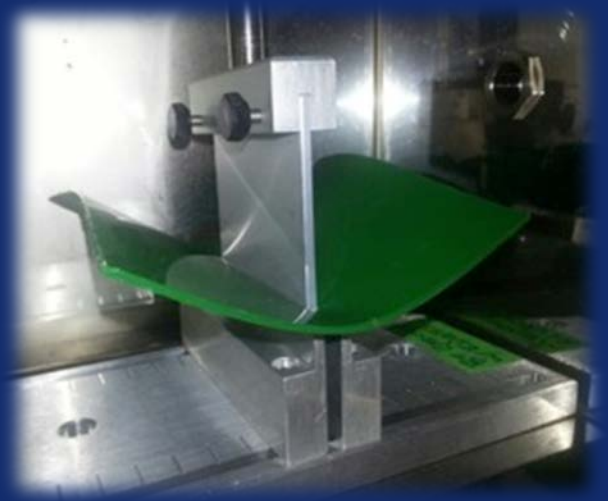
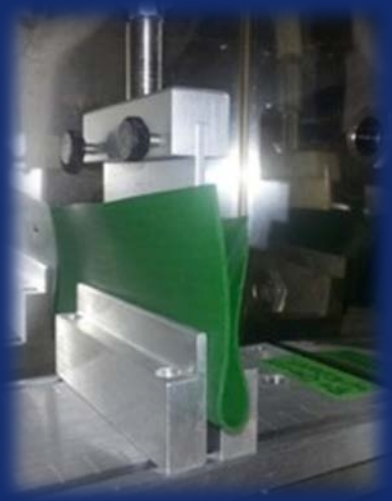
Accomplishments in Low H_2 Permeance

Sample No.	Thickness (in)	Hydrogen Permeance (cc/ 100in²·Atm·day)
Set 4 - Lot # LB199-119		
Hydrogen - 10A, 10B, 10C	0.01060	0.29 0.22 0.20 AV = 0.24 ± 0.04
Hydrogen Cold - 10A, 10B, 10C	0.01100	0.36 0.35 0.20 AV = 0.31 ± 0.09

H_2 Test Permeance, ASTM D 1434, Polyhedron Laboratories®

Triple Cold Flex Test for H_2 Permeance Specimens at -50 °C : Flat, Mid-Way, and 180 ° Fold



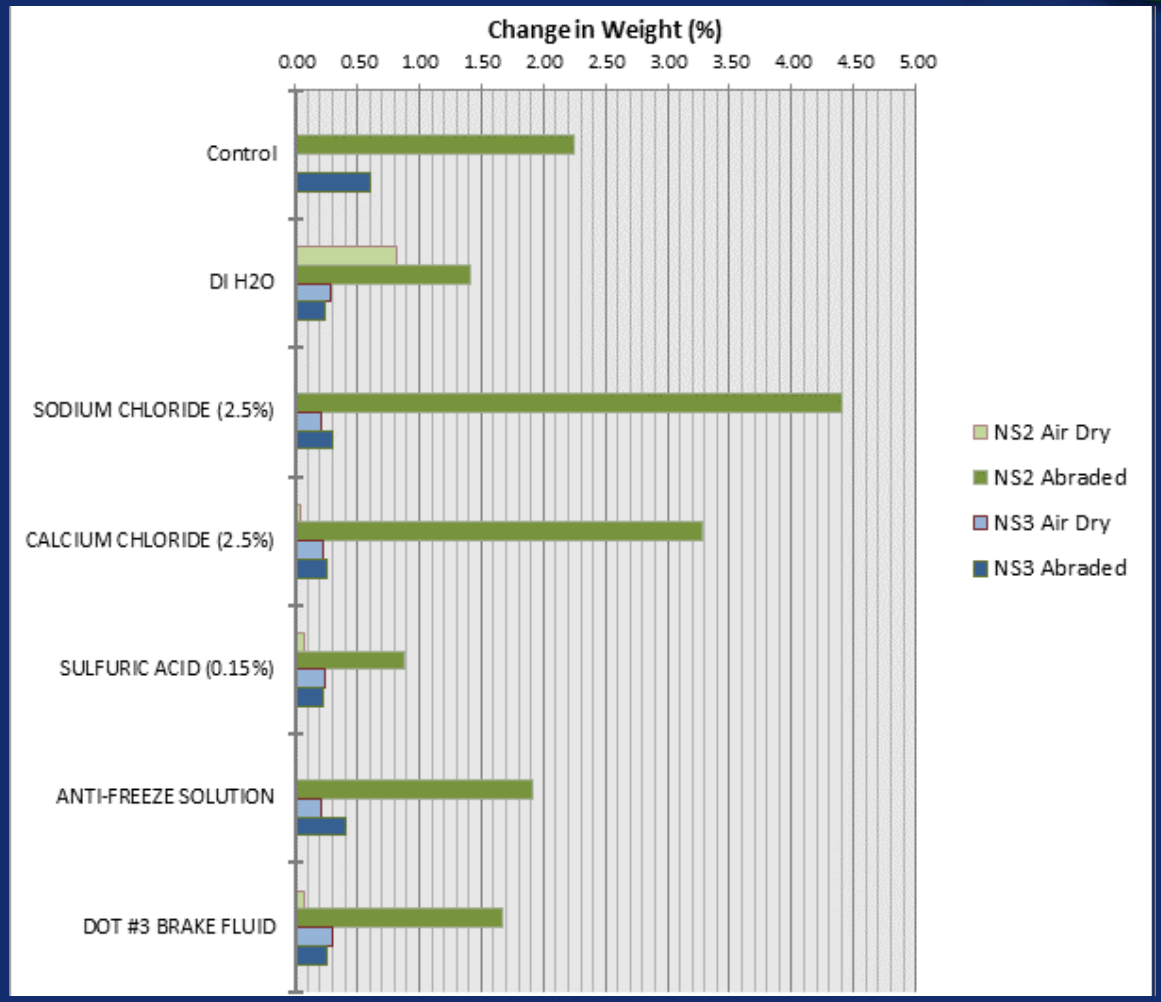


The hose material exhibits ultra low H_2 permeance before and after being subjected to the harsh 180 ° triple fold, cold flex test, conducted at -50 °C

Progress in Solvent Resistance

- 4”x4” Films
- Exposed glass wool fluid saturated pads
- 30 min
- Room Temp
- < 0.5 % uptake

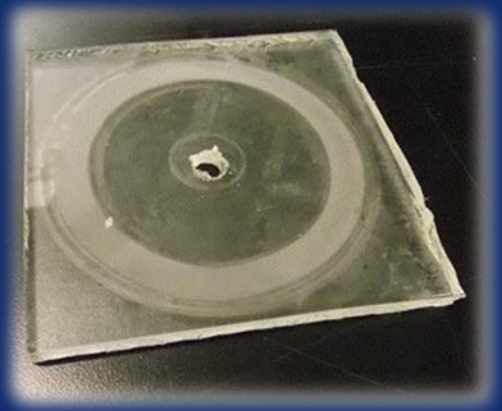
Table 2.21 in ANSI/CSA HGV



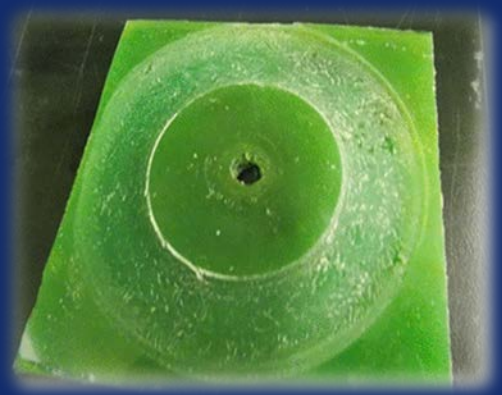
The abraded and non-abraded hose material exhibits less than 0.4% weight change upon intermittent fluid exposure with all solvents outlined in the ANSI/CSA HGV standard

Progress in Abrasion Resistance

Wear/abrasion resistance with *H-18* wheels on Hose Material



NS3
10,000 cycles
1,000 g weight



NS2
10,000 cycles
1,000 g weight

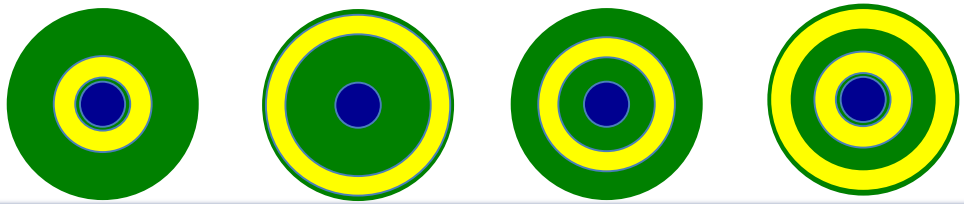
The hose material with and without pigment weathering package exhibits less than 1% after 10,000 cycles with a 1,000 g weight. Section 2.19 of ANSI/CSA HGV 4.2-2013 for the outermost portion of hose requires 500,000 cycles with a 500 g applied weight force

Accomplishments in Mechanical Durability:

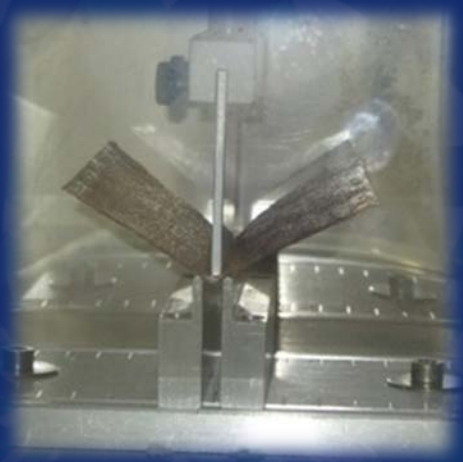
Fiber Reinforcement : $P = 2\,s\,t / (d_o\,SF) = 1705$ bar or 24,725 psi

	Polymer 1 - Kevlar	Polymer 1 - Spectra	Polymer 1	Down-Select Fiber & Design
	IB	IB	down-select fiber and design	Polymer 2
Clause 2.4	OB	OB		Polymer 3
	MB	MB		Polymer 2 + fill
	I/OB	I/OB		Polymer 3 + fill

	Down-Selected Polymer & Fiber
	IB
Clause 2.17	OB
	MB
	I/OB



A study by Savannah River National Laboratory concluded there was no mechanism for degradation and/or embrittlement of several polymers by hydrogen gas alone



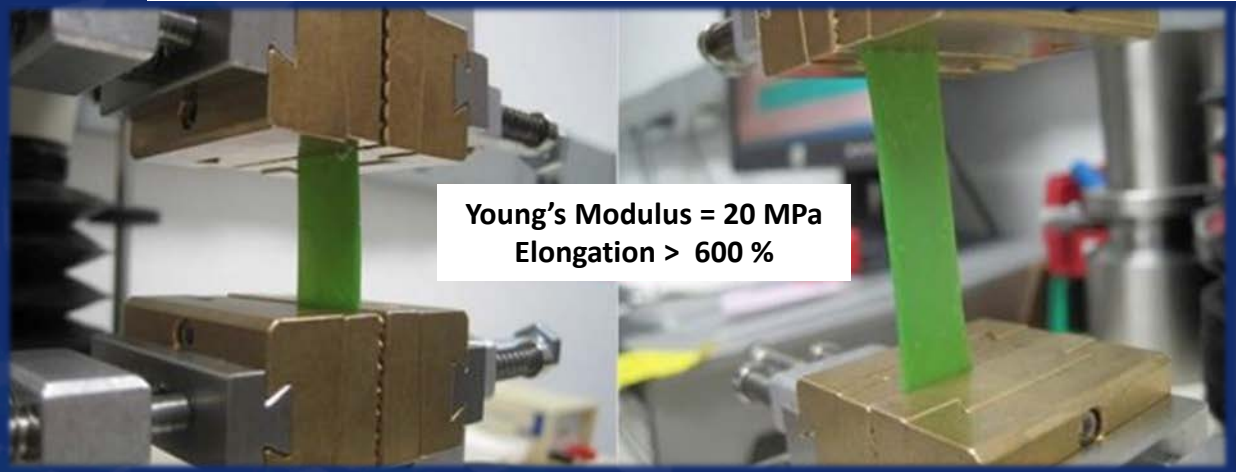
NanoSonic's all-polymer, fiber reinforced hose survives the triple cold flex test and has a predicted burst strength of 1705 bar. The design will be selected per pressure testing.

Challenges in Manufacturing

ANSI/CSA HGV 4.2-2013: Clause 2.4 Hydrostatic Strength

- NanoSonic hose Swagelok ¼-inch compression tube fitting
- Fixtured in the Hydraulic Burst Chamber
- Pressurization rate was set for 14500 psi/min
- Pressure Transducer (CSA asset Z00001141 – Viatran transmitter)
- Pressure Gauge (CSA asset PG-74 – Astragauge analog)

Sample:	Failure Pressure (PSIG):	Comments:
LB199-157-2	2,073	hose assembly pulled out of end connections
LB199-157-3	1,082	hose assembly pulled out of end connections
LB199-159-1	985	hose assembly leakage past end connections
LB199-164-2B	223	hose assembly pulled out of end connections

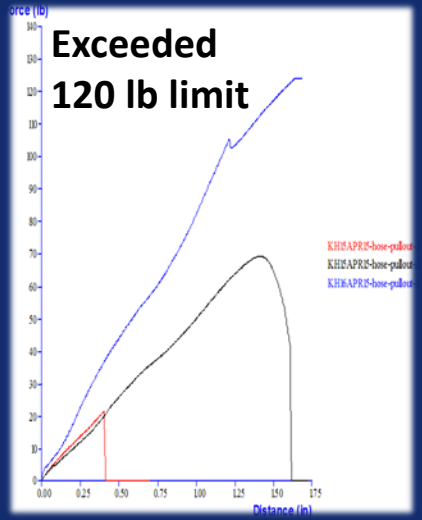


Young's Modulus = 20 MPa
Elongation > 600 %

The tough low T_g, low modulus hose posed a crimping challenge that is being addressed though chemistry, hose/fiber design, and mechanics

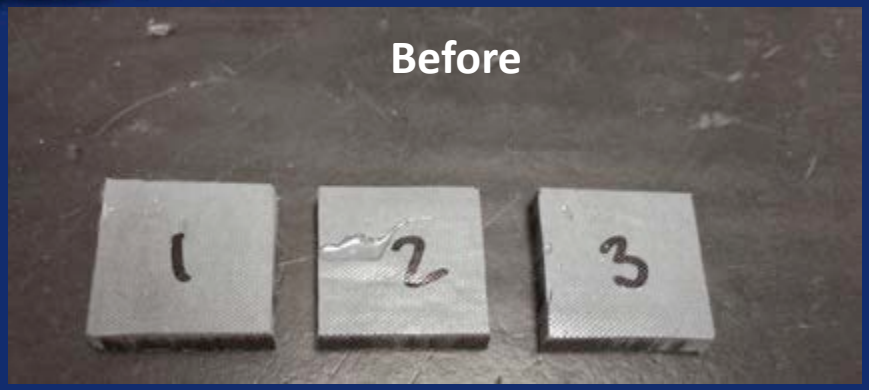
Accomplishments in Manufacturing

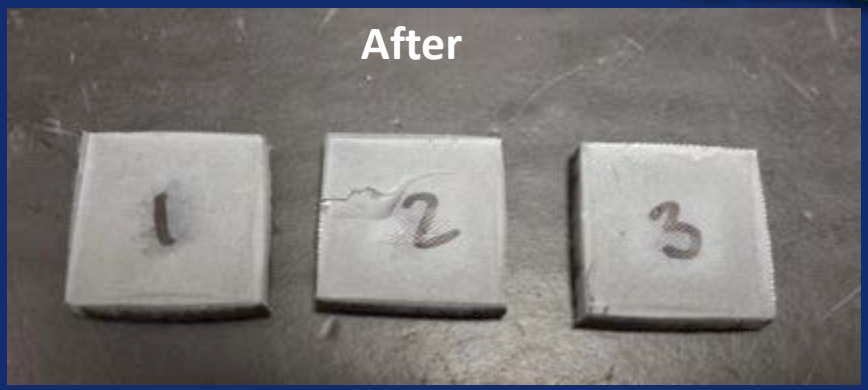
SiC ceramer adhesive



NanoSonic's SiC ceramer relieves the CTE mismatch between the hose and fitting, while bonding and crimping in-house yields a final product with complete fit and finish

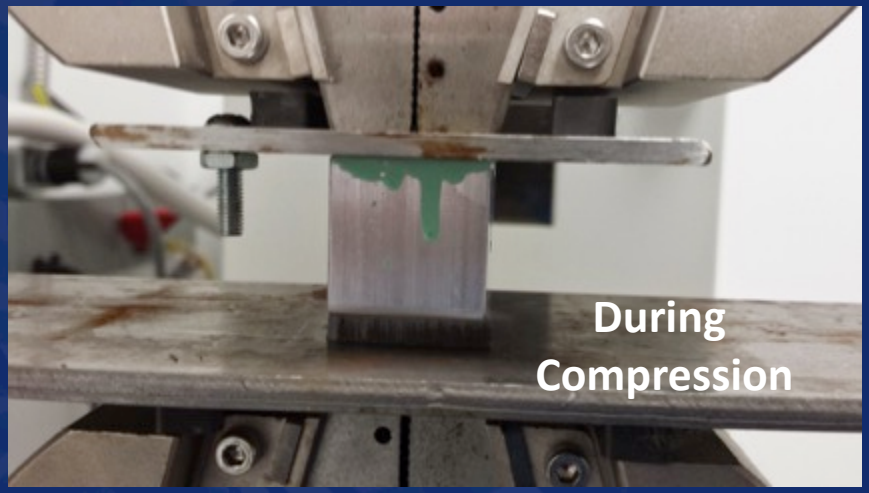
Accomplishments in Durability

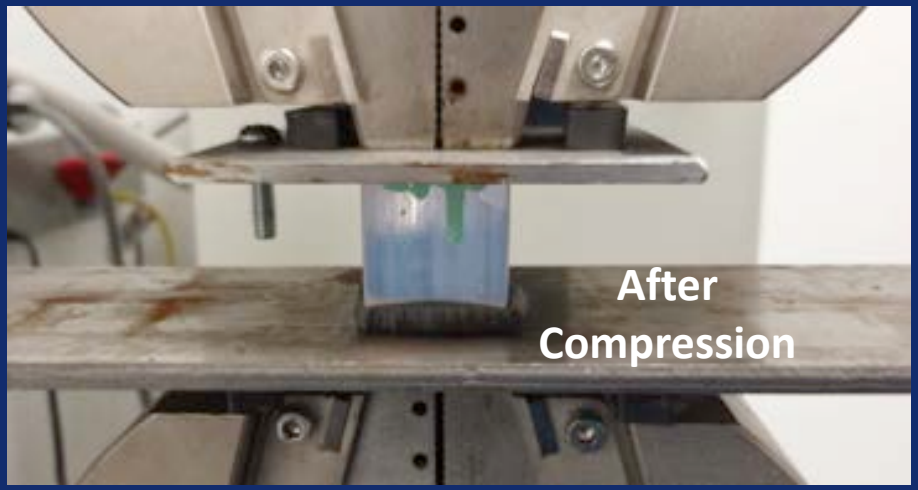




ASTM D 695: Standard Test Method for Compressive Properties of Rigid Plastics

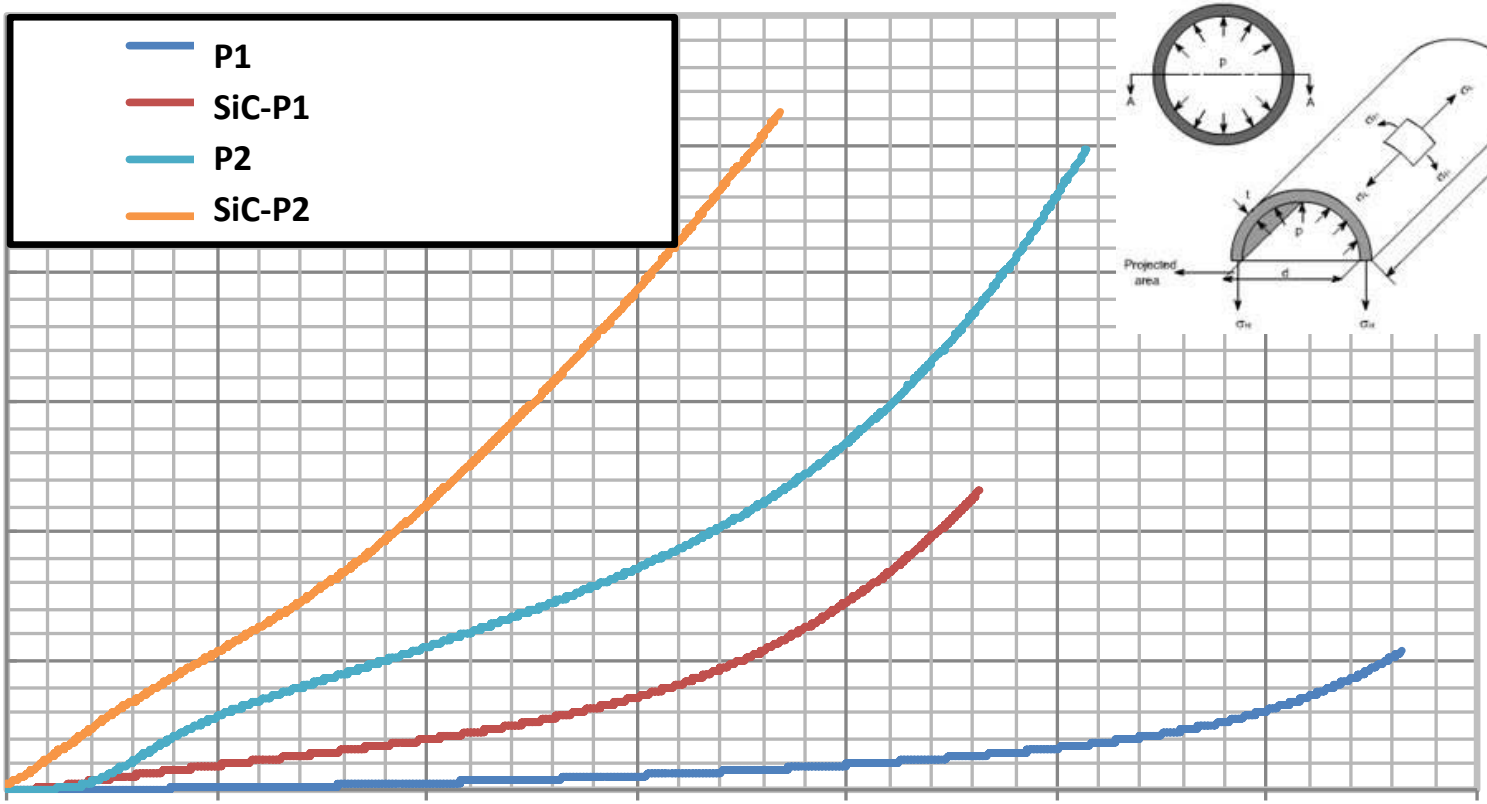
Cross-head moved at 1.3 mm/min





Compression testing simulates high service pressure (11,200 lb) within hose

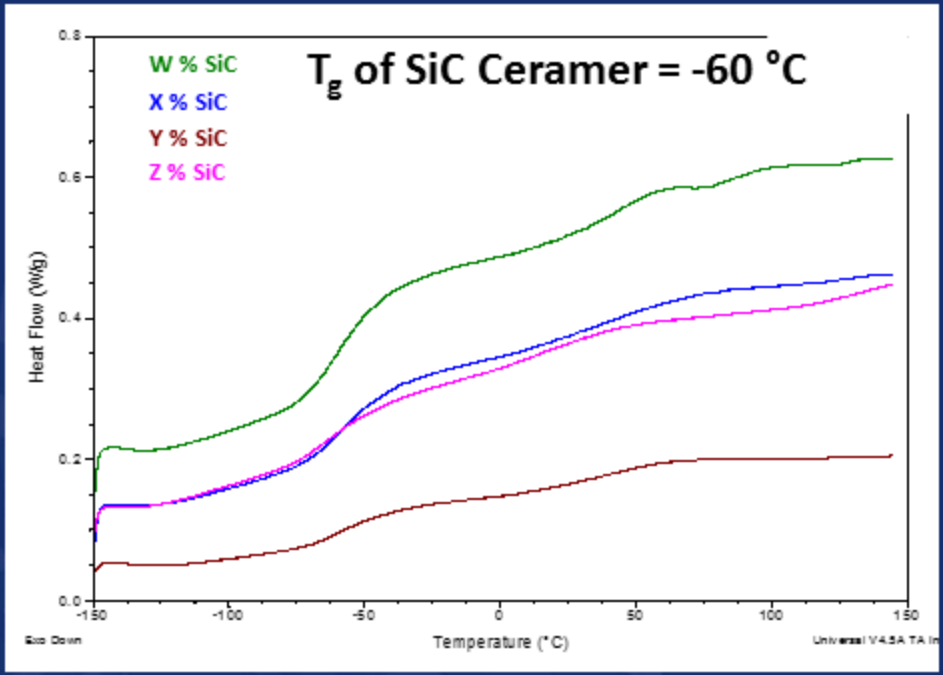
Accomplishments in Durability

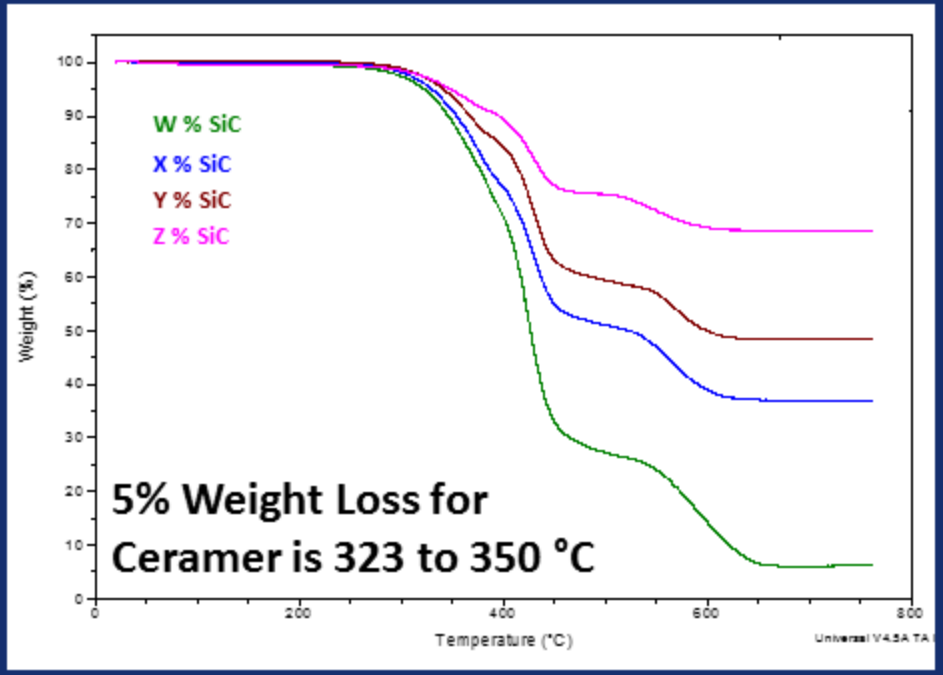


SiC ceramer technology enhances compression strength: > 50 kN (11,200 lb)

Accomplishments in Ceramer Technology

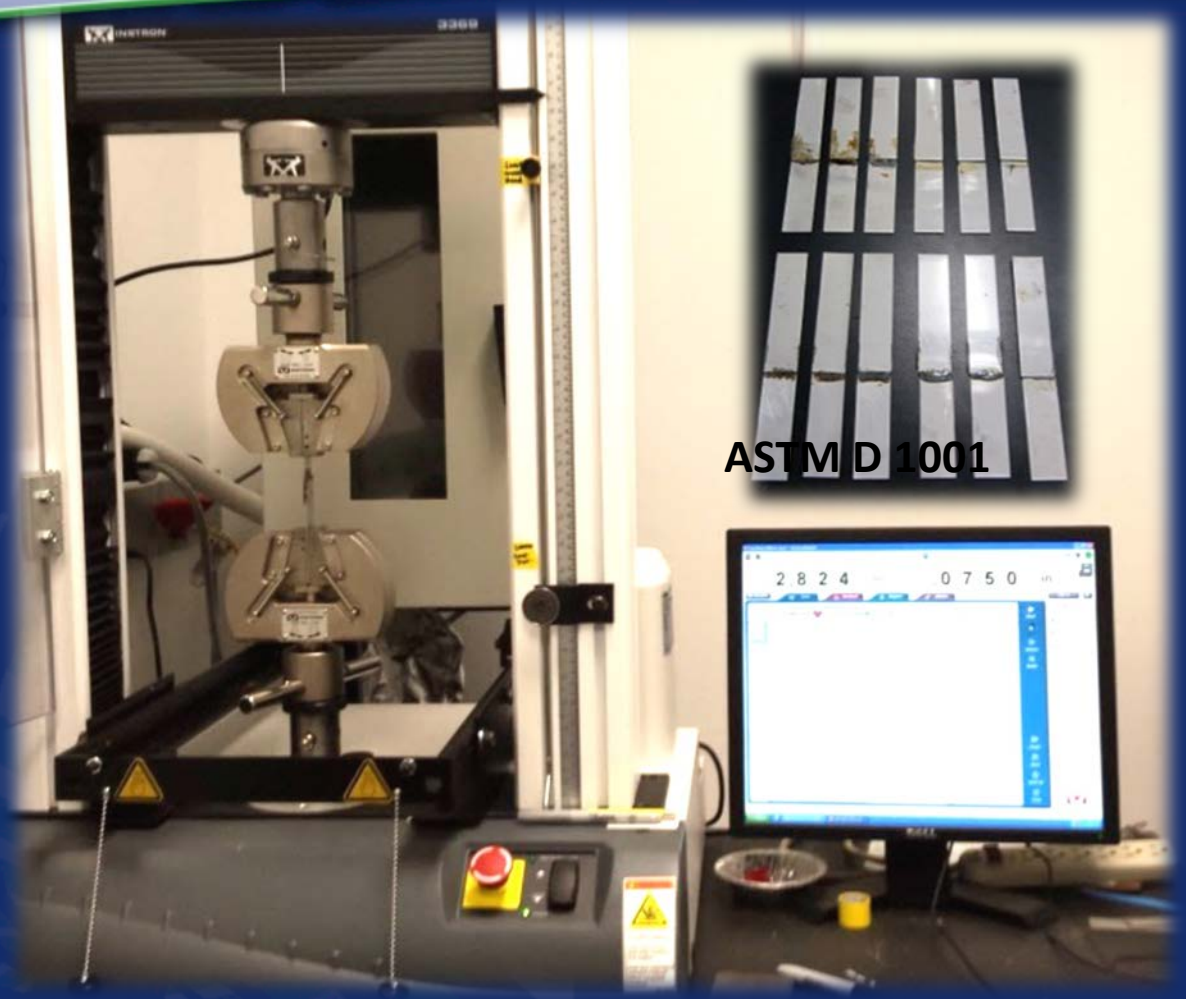
Material	Thickness (mm)	Displacement at Peak Load (mm)	Peak Load (kN)
W % SiC	5.43	-5.53	47.12
X % SiC	7.28	-6.89	52.50
Y % SiC	6.53	-5.86	51.38
Z % SiC	5.18	-3.85	52.50



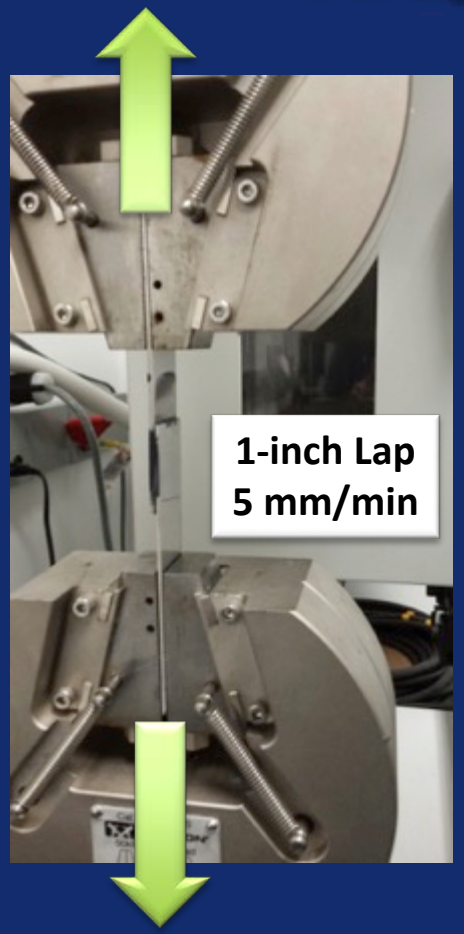


SiC ceramer technology maintains a wide service temperature range (~ -60 °C to 300 °C) upon compression testing at percentages of modification

Progress in Adhesion Testing

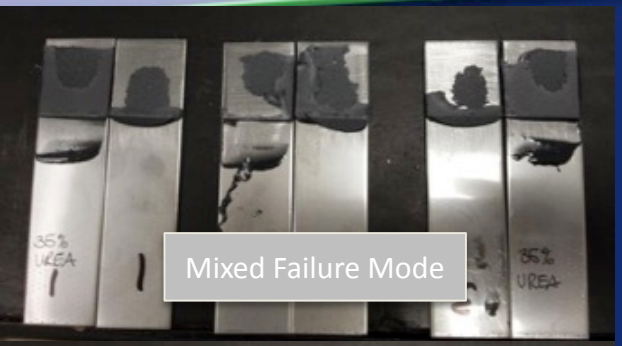


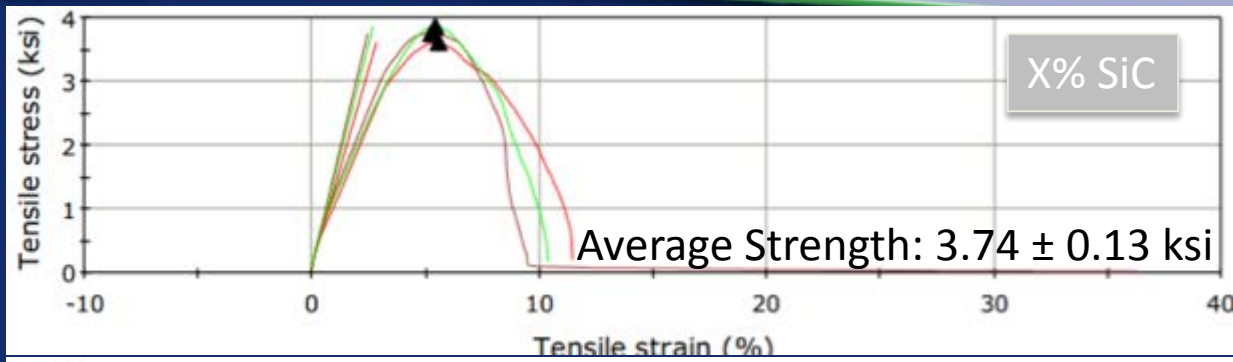
ASTM D 1001

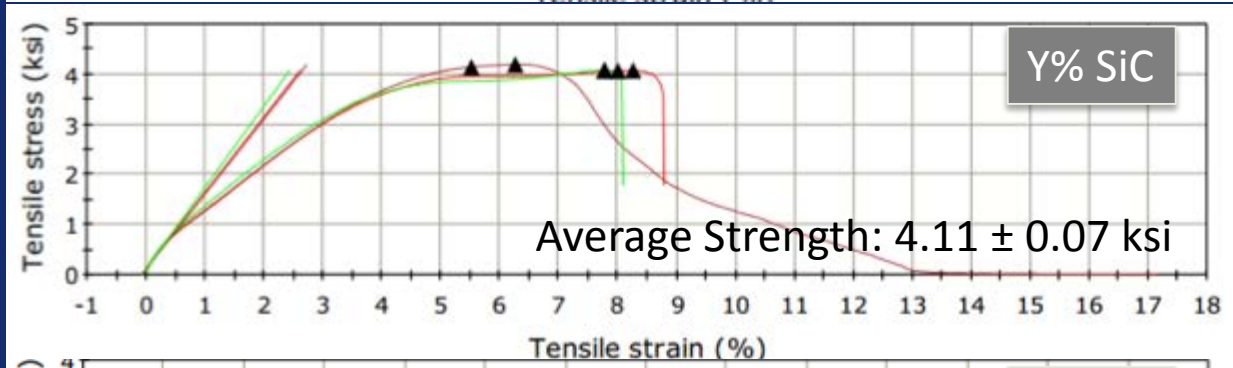


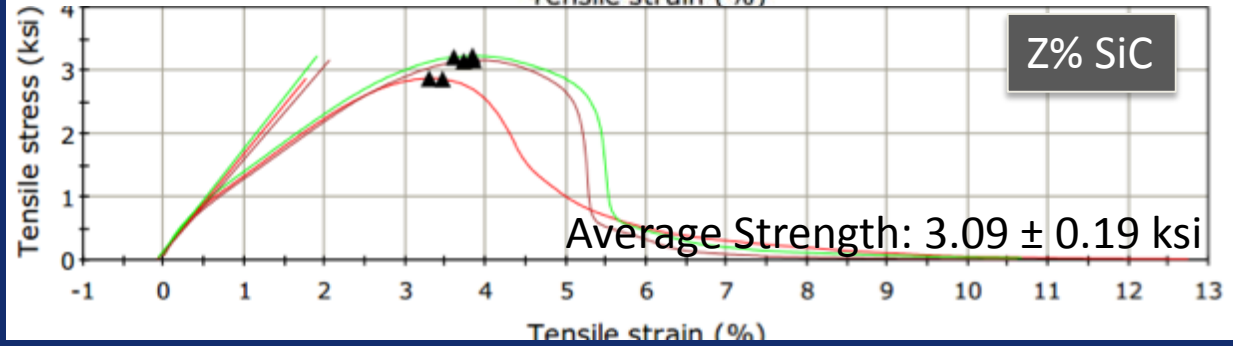
ASTD D 1001 Lap Shear Adhesion Reveals Quantitative Adhesion to Fitting Material

Accomplishments in Coupling Agent Adhesion









Optimal formulation exhibits highest lap shear adhesion strength and cohesive failure

Technical Accomplishments: Cost

Innovative Approach and In-house Manufacturing Enables Competitive and Cost Advantage at Any Scale

- Current projected cost at 300 meter with fittings is 2x less than qualified German competitor
- Cost normalized for lifetime predicts a 4x savings
- Proprietary scale-up method for hose production length may lead to an 8x savings for 600 meter

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Collaborations and Cost Sharing

1. **CSA Group**
   - Testing – briefing at CSA on 11/6/14
2. **National Renewable Energy Laboratories (NREL)**
   - Prototype evaluation – subcontract executed on 11/4/14
3. **Swagelok**
   - Fittings - ongoing consulting on fittings and high pressure hoses
4. **Lillbacka**
   - Hose crimping – purchased crimper on 1/03/15
5. **WEH USA**
   - Integration – breakaway connector and H_2 fueling nozzle
6. **New England Wire Technologies**
   - Prototype manufacturing – subcontract executed on 10/29/14
7. **Giles County Government**
   - Local large scale manufacturing support and architecture for 100ksf building

Funding Type	Source	Type	Amount	Years	Covers
Phase I SBIR	DOE	Cash	$100,000	2013	R & D, Prototype Design & Production
Phase II SBIR	DOE	Cash	$1,000,000	2014-2016	Product Engineering, Qualification
Phase III IDIQ	DOE & H2 Fueling Stations	Cash	$1,500,000	2017-2020	Purchase Order and Installation
Company Contribution	NanoSonic	Cash	$600,000	$200k annual	Commercialization and Marketing
Alliance Agreement	Lockheed Martin				Product Validation
Partner Contribution	Hose Parts Partners				Porduct Integration
County Contribution	Giles County	In-kind	$1,100,000	2010-2016	Manufacturing and Shipping
County Infrastructure	Giles County	In-kind	$7,500,000	2010	Infrastructure

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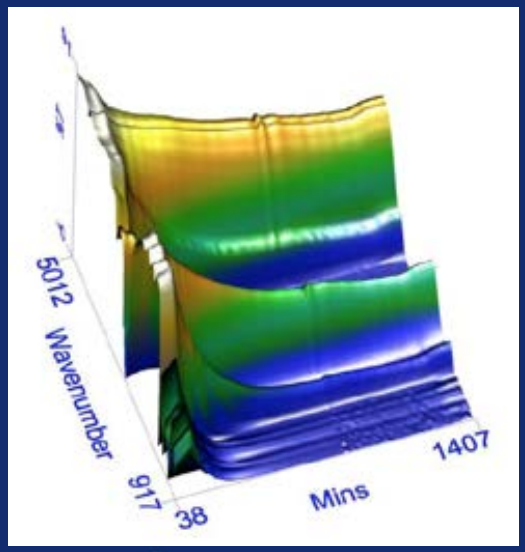
Future Work: Durability and Quality

ANSI/CSA HGV 4.2-2013: Hoses for Compressed H_2 Fuel Stations, Dispensers and Vehicle Fuel Systems
SAE J2719: H_2 Fuel Quality for Fuel Cell Vehicles

- Mechanical: Pull-Out Strength of Crimp/Hose and and pre- post- stress strain morphology at NREL
- Hydrostatic Strength 2.4: 1 min hold without burst at hydrostatic pressure of 4 times the maximum allowable working pressure (MAWP), up to 10,000 PSI MAWP
- Pressure Cycle 2.17: 50,000 cycles at MAWP at -40 °C and 50,000 cycles at 85 °C followed by compliance testing to Leakage and Electrical Conductivity
- Hydraulic Pulse: testing conducted up to 14,500 psig at 1Hz with a fluid temperature up to 150 °C
- Evolved Gas Analysis: and leak monitoring to ensure that the hose will not compromise H_2 quality per the SAE J-2719 and ISO/PDTS 14687-2 specs, where Minimum Fuel Cell Grade H_2 = 99.99%, total impurities < 100 ppmv, and total impurities < 100,000 ppb



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Future Work: Scale-up Resins in-House

NanoSonic has 50 and 200 gallon batch reactors to scale-up hose and ceramers for cost savings

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Remaining Challenges and Barriers

Dual & Single Cantilever

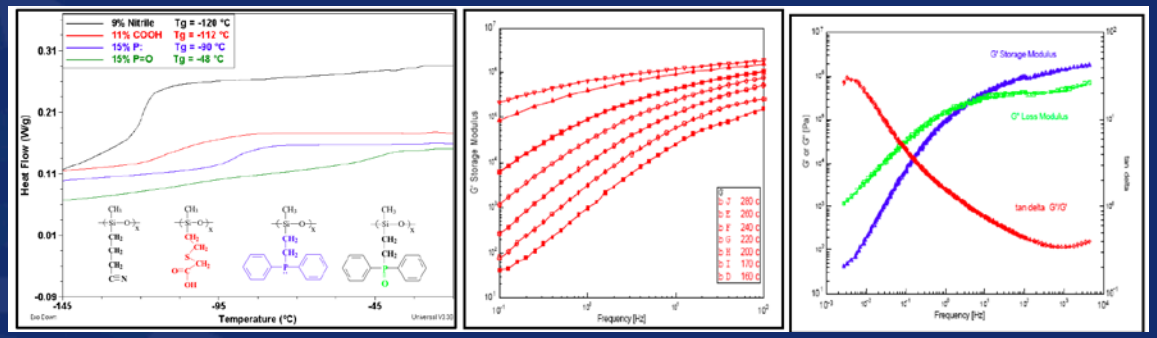
Viscoelastic properties measured dynamically over:

- Wide temperature range
- Modest frequency range

Modulus data is shifted to make master curves using:

- Arrhenius Equation
- Williams, Landel, Ferry (WLF) Equation

Film & Fiber Tension



3-point bend

Compression

NanoSonic is utilizing time-temperature superposition via DMA for lifetime prediction

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Remaining Challenges and Barriers: Hose Qualification & Deployment

- Challenge: Maintaining a planned deployment date of FY16 Q3 because of delayed pressure testing due to fittings
- Resolution: Obtained fitting crimper and developed innovative ceramer technology
- Benefit: Ceramer inclusion may surpass durability of all current or future competitors
- Future: No other milestones or deliverables are at risk
- OEMS: Meetings are in progress

Hydraulic Test Chamber


Pneumatic Test Chamber

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Project Summary

- **Relevance**: Durable and cost effective H_2 delivery hose that resists H_2 embrittlement, survives 25,550 fills/year for H70 service, cycled at pressures > than 875 bar over a range of -50 °C to 90 °C. A single qualified hose exists.

- **Approach**: NanoSonic's all polymer new class D hydrogen dispensing hose, for use on H70 station side applications, is chemically engineered to survive 51,240 fills, resist H_2 embrittlement, survive Joule-Thompson effect, and endure mechanical fatigue at the pump. Innovative SiC ceramer adhesive is under development to enhance fitting durability

- **Technical Accomplishments**:
  - Developed low T_g hose that demonstrates ultra-low hydrogen permeance after 180° bending, three times in a -50°C chamber
  - Fiber reinforced hose has a predicted burst pressure of of 1705-bar
  - Developed unique ceramer coupling agent for enhanced crimp survivability
  - Reduced cost via scale-up

- **Proposed Future Research**: Presented H_2 hose partners (dispensing stations and fittings/breakaway/fueling nozzle OEMs) with integration and cost. H70 hose compliant with SAE TIR J2601 and NIST Handbook 44, as a durable cost effective alternative to gasoline

Questions and Acknowledgements

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Phase II Integrators and Testing Facilities