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Group

Self-Healable Copolymer Composites for Extended Service of H_2 Dispensing Hoses

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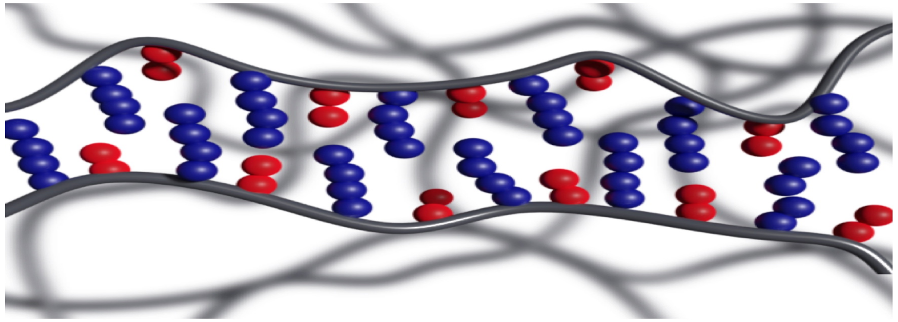
DOE Hydrogen Program
2023 Annual Merit Review and Peer Evaluation Meeting

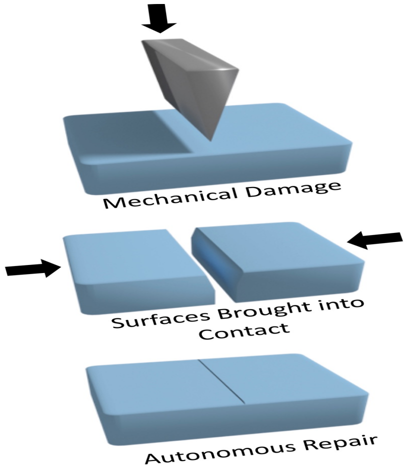
AMR Project ID: IN020

Project Goal

Develop and optimize low-cost self-healable inner layer of H_2 dispense hoses to achieve over 25,000 damage-repair cycles by integrating self-healable copolymer matrix with polypropylene (Innegra^{TM}) fibers

Develop Self-Healable
Commodity Plastics and/or Composites





Paradigm Shift in Commodity Plastics >>>> Self-Healable H_2 Fuel Dispense Hoses

Overview

Timelines

- Project Start Date: 01/01/2020
- Project End Date: 04/30/2023

Budget

- Total Project Budget: $1,250,000
- Total DOE Share: $1,000,000
- Total Cost Share: $250,000
- Total DOE Funds Spent*: $867,978
- Total Cost Share Funds Spent*: $273,946

* As of 1/1/2023

Barriers and Targets

- Key barriers addressed in this project are:
  - Fueling Site/Terminal Operations
  - Reliability and Cost of H_2 Fuel Pumping
- Target: develop inexpensive self-healable commodity copolymer fiber-reinforced composites as inner layers to extend the H_2 hose service life to over 25,000 cycles

Partners

- Clemson University (Project Lead)
- Savannah River National Lab (SRNL)
- Sandia National Lab (SNL)
- Pacific Northwest National Lab (PNNL)

Relevance and Potential Impact

DoE goals

- Introduction of hydrogen as an energy carrier
- Address delivery challenges at refueling stations
- Lower the cost of hydrogen compression
- Reduce the cost and footprint of hydrogen storage

Project goals

- Design, develop, and pre-commercialize novel, self-healable commodity copolymer fiber-reinforced composites to extend the H_2 hose service life
- Lower the cost of H_2 dispensing hose

Approach

Design, Synthesis & Characterization of Copolymers Capable of Self-Healing
self-healable copolymers w/ various compositions are synthesized using different synthetic methods; molecular, thermal and mechanical properties are determined via NMR, GPC, DSC, tensile tests

Measurement & Efficiency of Self-Healing
Efficiency of self-healing is determined both spectroscopically (NMR) and macroscopically (optical microscopy, tensile tests)

Molecular Dynamic (MD) Simulation and Molecular Level Characterization of Self-Healing
MD simulations predict van der Waals interactions between polymer chains which accounts for self-healability & provide guidance which copolymer compositons are best suited for further experimental explorations

Effects of Environmental Conditions on Self-Healing
Environmental influences (temperature, pressure, H_2O, H_2) are/will be determined both experimentally and via simulations

Technology-to-Market Transitions
T2M plan outlining roadmap and preliminary cost-performance model are established

Milestones

Budget Period	Quarter	Milestone #	Milestone	Percentage of completion (%)
1	1-4	1.1-2.4	All milestones have been met during BP1	100
		BP-1 decision point	Self-healable copolymers are able to retain properties after 1000 damage-repair cycles, w/ maintained mechanical properties > 85% of the undamaged values	100
2	5-8	2.5	At least three sets of copolymers were identified and utilized for further fabrication	100
		3.1	Design and fabrication of polypropylene-based fiber-reinforced mats	100
		3.2	Stress-strain testing and analysis of composite mats	100
		3.3	Preparation and formulation of copolymer/fiber reinforced composites	100
		3.4	Redesigning of multi-phase materials	100
		BP-2 decision point	Self-healable copolymers and composite mats are able to retain properties after 10,000 damage-repair cycles, w/ maintained mechanical properties > 85% of the undamaged values	100
	9	3.5	Optimization of copolymer/fiber composite properties	100
		3.6	Testing and analysis of composite durability upon exposure to pressures and temperature	100

Milestones

Budget Period	Quarter	Milestone #	Milestone	Percentage of completion (%)
3	10	4.1	Design of composite systems and analysis and performance	100
		4.2	Comparative testing and analysis of self-healing and non-self-healing composites	100
	11	4.3	Optimization of copolymer/fiber systems and feedback to Milestones 4.1 and 4.2	100
	12	4.4	To achieve the goal of 25,000 damage-repair cycles	90
		4.5	Detailed report on product specifications, target markets, their size, and market competition	100
		4.6	Identification of next stage partners who might be interested in pursuing business venues leading to new technology and funding opportunities	100
	13	4.7	Completion of test reports and publishing articles	80

Accomplishments & Progress

Previous period’s (BP-2) Accomplishments

- Development of prototype of inner layer composite hose composed of self-healing poly(methyl methacrylate/ n-butyl acrylate) [p(MMA/nBA)] copolymers developed in BP-1
- Stress-strain analysis, repeatability, repetitiveness, and cross-temperature analysis conducted on the inner layer composite hose prototype to achieve desired mechanical properties
- The goal of 10,000 damage-repair cycles achieved

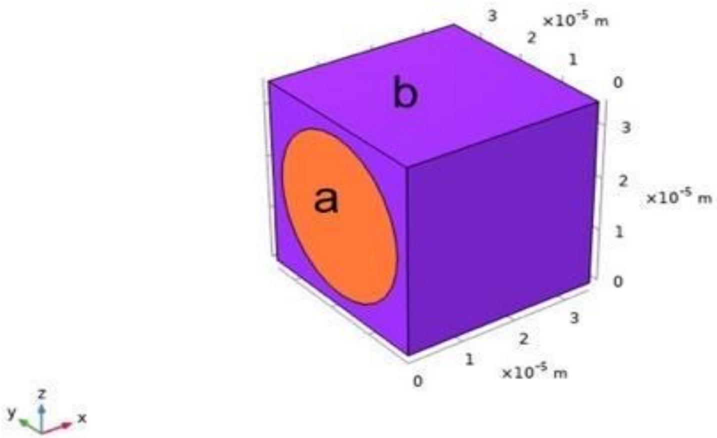
Project objectives for current period (BP_3)

- Thermomechanical testing and analysis of copolymer composite properties under working conditions using COMSOL Multiphysics® software
- Optimization of copolymer/fiber systems
- Achieve the goal of 25,000 damage-repair cycles

Design of composite inner layer hose systems

(I) Microanalysis

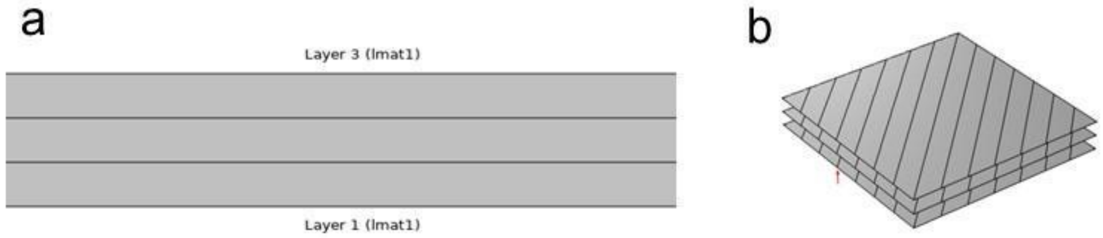
Development of micromechanical model that enables modeling of a single layer of the composite hose



An example of the unit cell used in these simulations comprising of a fiber (a) and matrix (b)

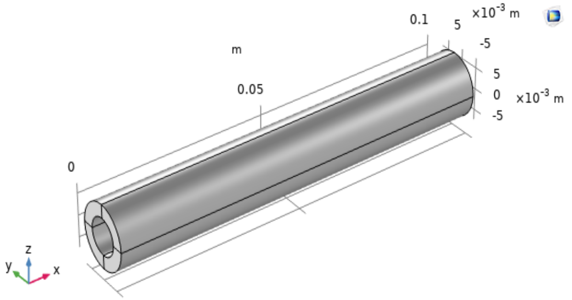
(II) Macroanalysis

Development of combined microanalysis for macroanalysis predictions that result in material properties under different loading conditions applied to the composite inner layer hose to evaluate responses

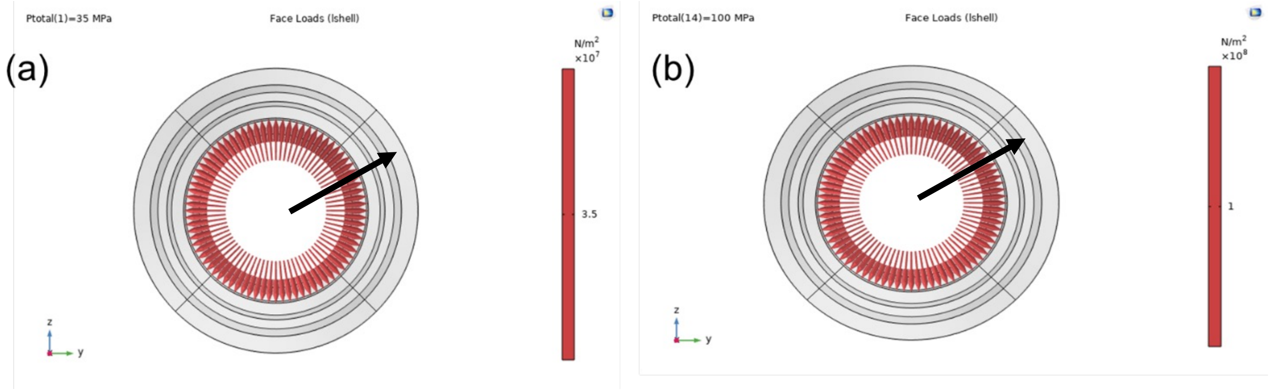


Layer cross section (a) and layer stack at 45° (b) orientation of the homogeneous composite inner layer material

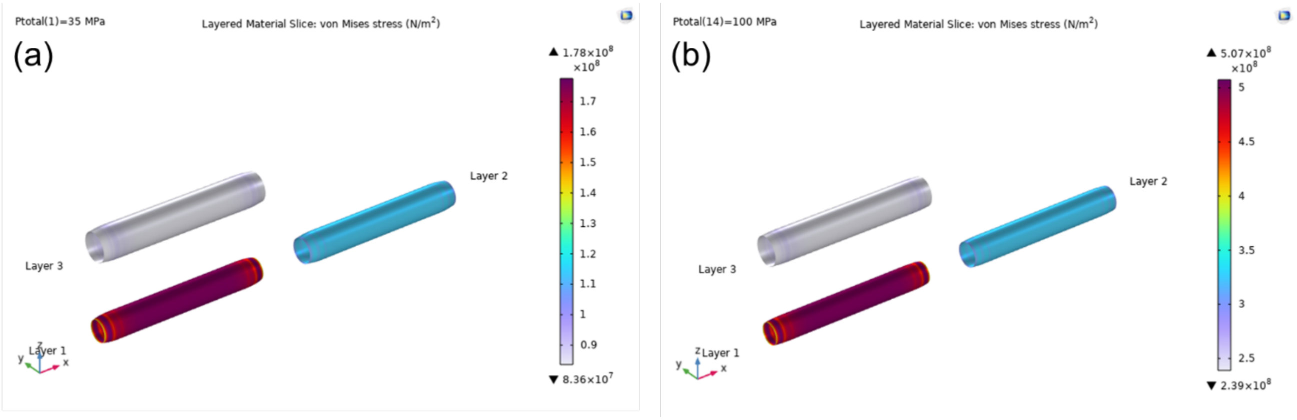
Three-layered composite inner layer hose model



Composite model under internal pressure loads (35-100-35 MPa)



Direction of internal pressure of 35 (a) and 100 (b) MPa in model of an inner layer composite hose

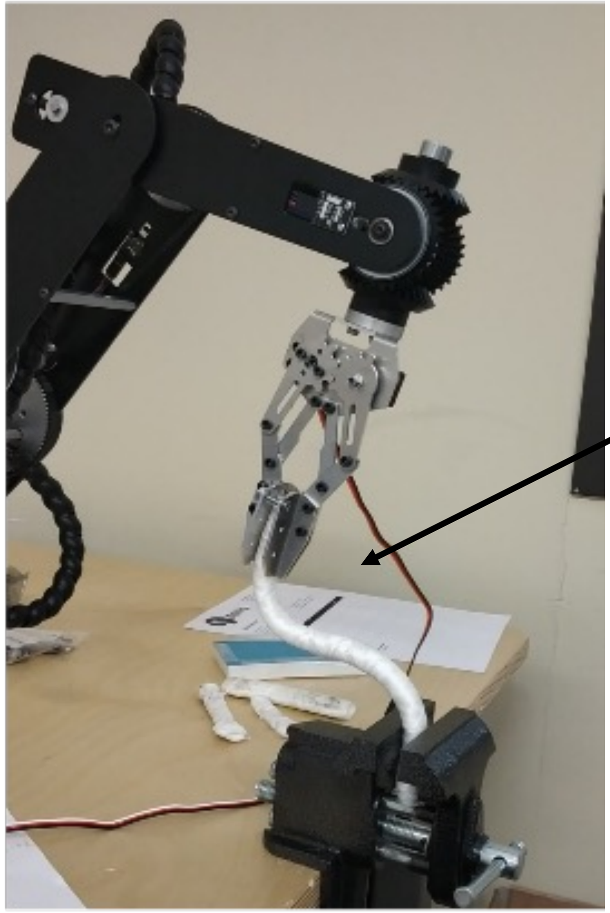


Comparison of the von Mises stress distribution of a inner layer composite hose in 35 (a) and 100 (b) MPa internal pressure loading

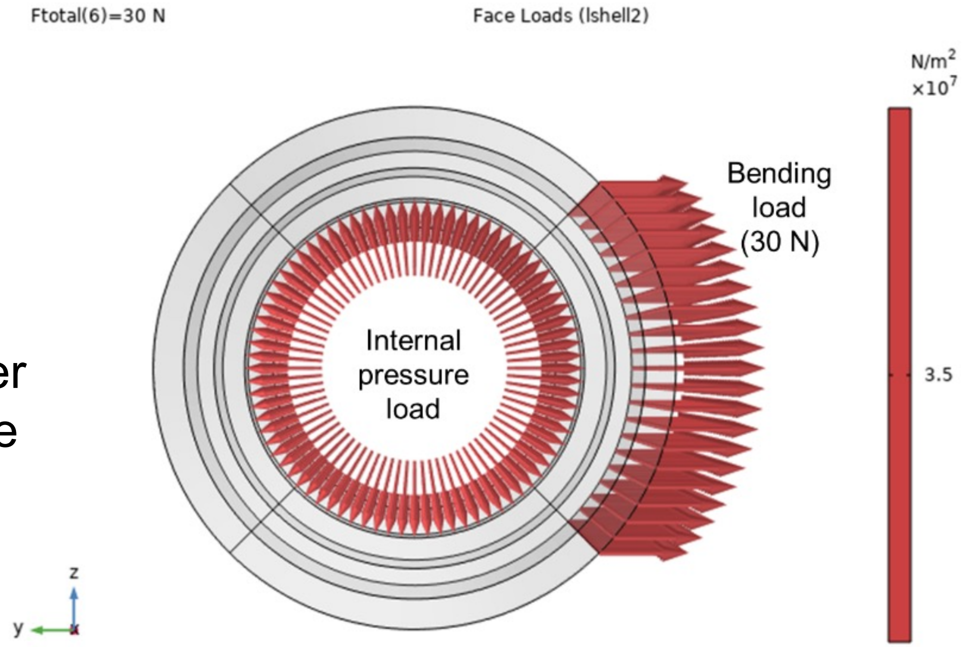
Distribution of stresses in each layer of the inner layer composite hose model for loading cases

Loading case	Stress distribution x 10^8 (N/m^2)		
	Innermost layer	Middle layer	Outermost layer
35 MPa inner pressure	1.78	0.95	0.50
100 MPa inner pressure	5.07	3.5	2.39

Determination of mechanical stresses due to pressure loads under the motion of bending of the inner layer composite model



Experimental bending of inner layer composite hose

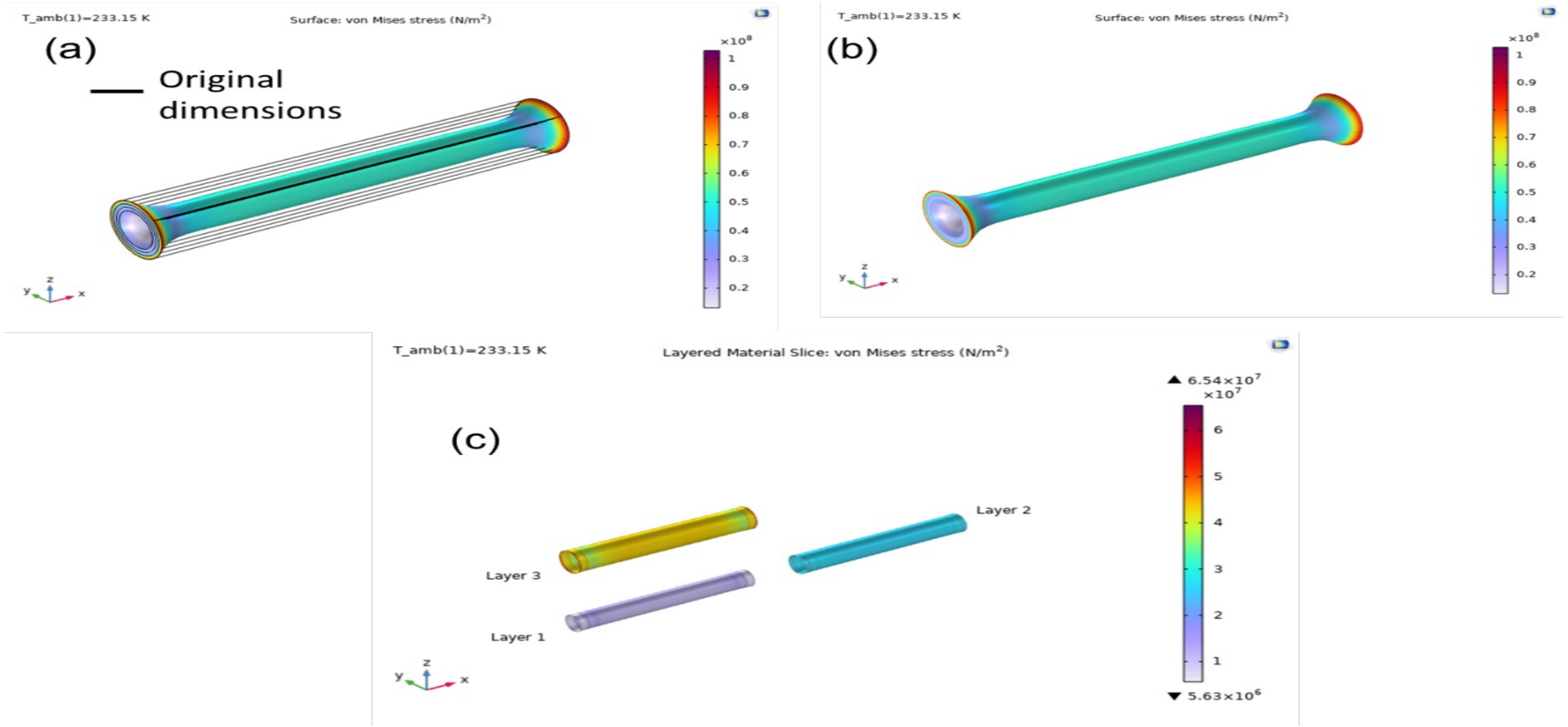


Inner layer composite hose model with a combined load of internal pressure and bending load

Determination of heat transfer mechanisms

Loading- Internal pressure: 35 MPa
Internal temperature: -40 °C
} For all model simulations in Figs. I to IV
Outside temperature values: -40 °C (Fig. I), 0 °C (Fig. II), 25 °C (Fig. III), and 80 °C (Fig. IV)

(I)



Inner layer composite hose with internal pressure and temperature of 35 MPa and -40 °C, respectively (a) before applying external temperature loading (b) at -40 °C ambient temperature and (c) stress slices of an inner layer composite hose at -40 °C ambient temperature

Determination of heat transfer mechanisms

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Loading- Internal pressure: 35 MPa
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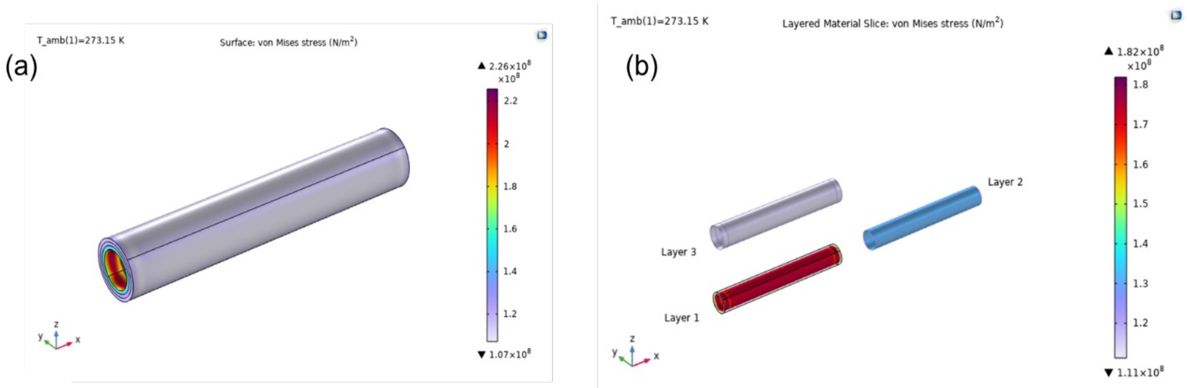
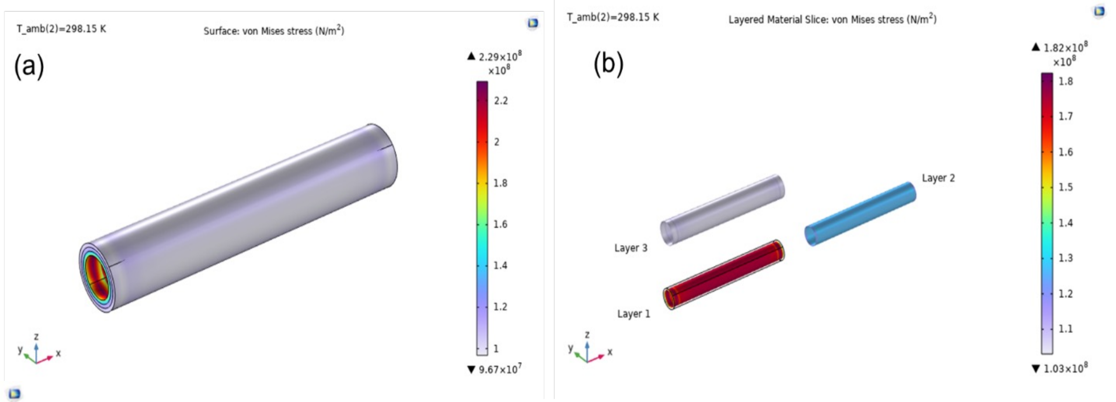
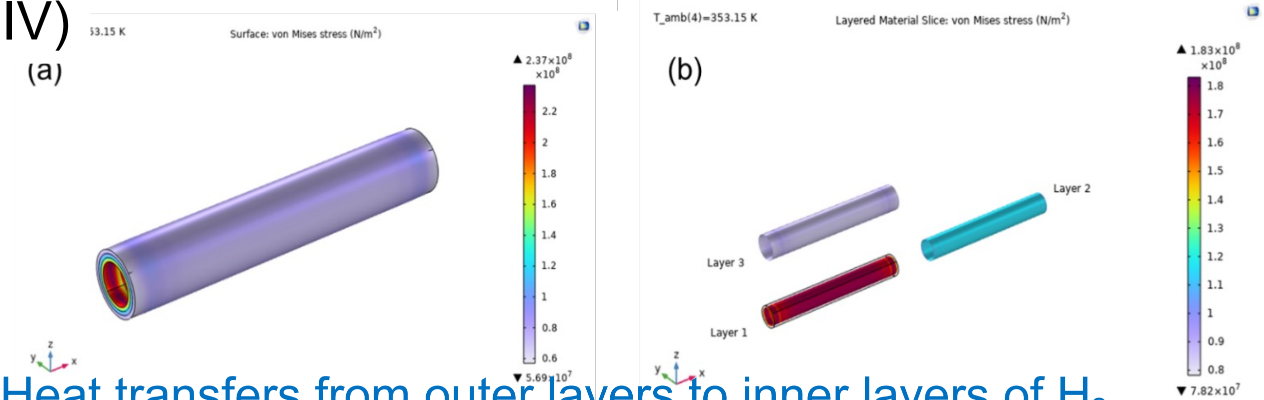
(II)



(III)



(IV)



Loading case: External temperature conditions	Stress distribution x 10^7 (N/m²)		
	Innermost layer	Middle layer	Outermost layer
-40 °C	1.2	2.5	4.5
0 °C	18	13	11
25 °C	18	14	11
80 °C	18	12	8

Distribution of stresses in each layer of the inner layer composite hose model

Heat transfers from outer layers to inner layers of H_2 carrying hose as the ambient temperature is increased from 0 to 80 °C

Model of an inner layer composite hose with outer aluminum layer to simulate a commercial hose

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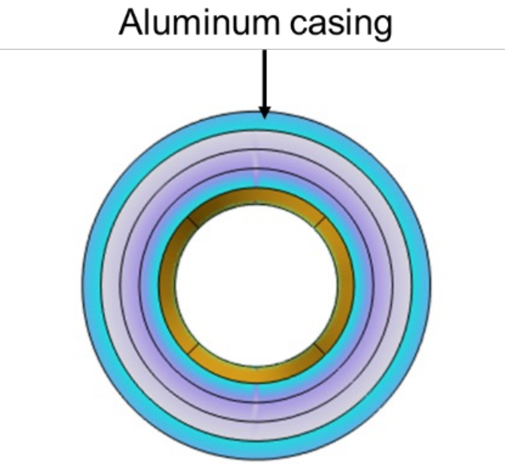
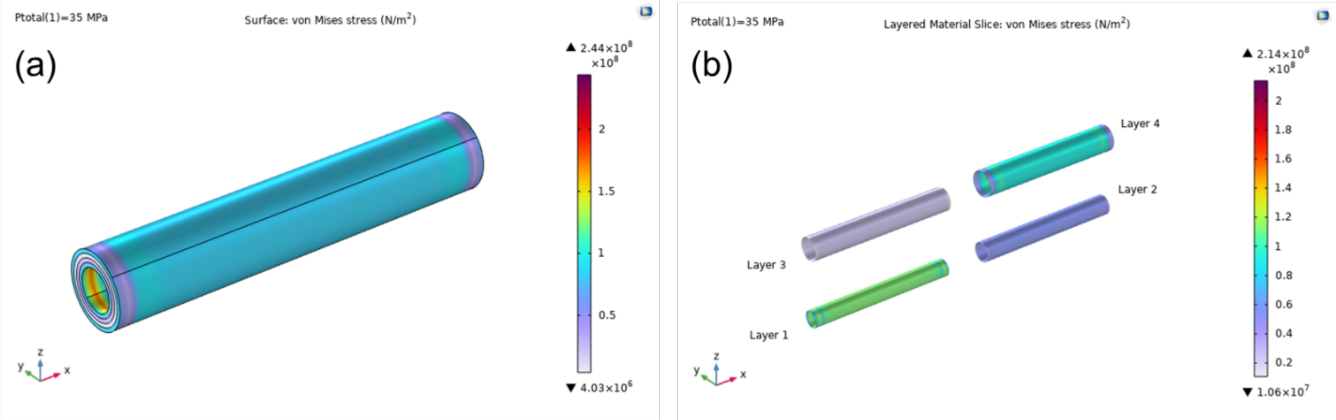
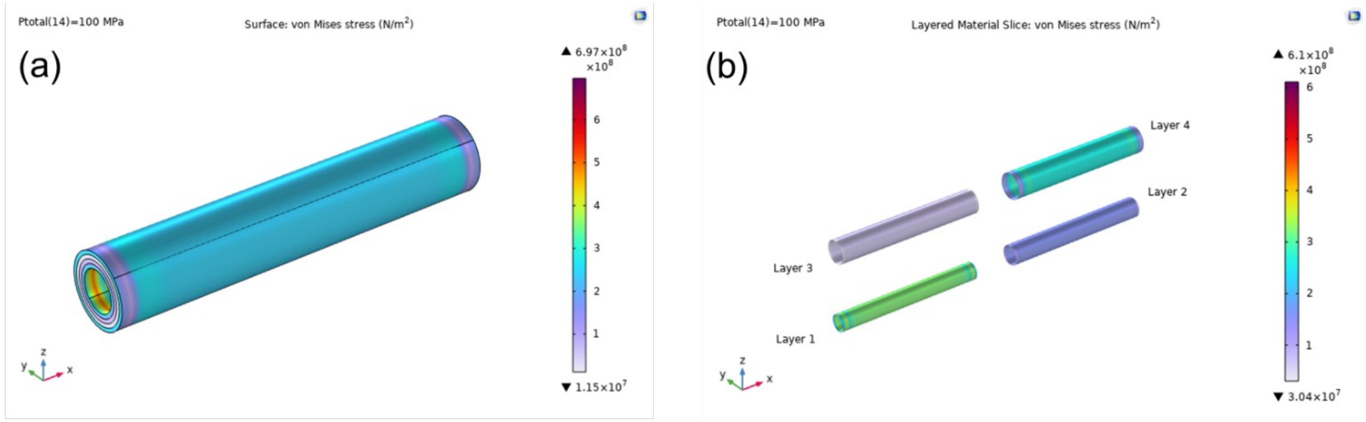


Loading case: Internal pressure	Stress distribution x 10^7 (N/m²)			
	Innermost layer	Middle layer	Outermost layer	Al casing
35 MPa	12	5	3	10
100 MPa	31	18	10	31



Inner layer composite hose with internal pressure load of 35 MPa (a) and its stress slices (b)



Inner layer composite hose with internal pressure load of 100 MPa (a) and its stress slices (b)

Outer layers surrounding the inner layer composite hose material will lower the stresses on inner layers

Technology-to-Market (T2M) and commercialization plan and Identification of next stage partners and funding agencies

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The global market for hydrogen storage materials/technologies by region and applications

Region	2020	2021	2026	CAGR% 2021-2026
APAC	1,780.0	1,900.0	2,798.6	8.1
North America	1,310.0	1,375.0	1,962.8	7.4
Europe	1,043.6	1,100.8	1,528.8	6.8
MEA	202.0	216.0	312.2	7.6
South America	120.0	130.0	197.9	8.8
Total	4,455.6	4,721.8	6,800.3	7.6

Application	2020	2021	2026	CAGR% 2021-2026
Stationary power	3,213.3	3,418.9	4,914.7	7.5
Portable power	838.9	886.5	1,256.8	7.2
Transportation	403.4	416.4	628.8	8.6
Total	4,455.6	4,721.8	6,800.3	7.6

- The USA is the largest hydrogen storage materials and technologies market in North America and is the second largest market globally after China
- Asia-Pacific (APAC) at 39.9%-accounted for the largest share of the market in 2020. APAC was followed by North America (with a market share of 29.4%) and Europe (with a market share of 23.4%)

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Technology-to-Market (T2M) and commercialization plan and Identification of next stage partners and funding agencies

Commercially Available Market Competition

US Manufacturers: Parker, Lifeguard Technologies

Company	**Commercially available**	**Core Material**	**Core process**	**Reinforc-ement**	**Inner Diameter**	**Working Pressure**	**Temperature Range**	**Bending Radius**	**Links**
Parker	yes	Polymer	extrusion	braided steel	.25"	875 bar	-40 °C – 85 °C	150mm	Parker Hydrogen Hose 2440P-04V32_UK.pdf
Lifeguard	yes	ETFE	extrusion	braided steel	.22"	413 bar	-100 °C – 450 °C	68mm	https://lifeguard-tech.com/wp-content/uploads/2018/09/hydrogen-hoses.pdf

Intl. Manufacturers: Polyfluor, SpirStar, Aflex Hose

Company	**Commercially available**	**Core Material**	**Core process**	**Reinforcem-ent**	**Inner Diameter**	**Working Pressure**	**Temperature Range**	**Bending Radius**	**Links**
Polyflour	yes	ETFE or Zytel (Nylon)	extrusion	braided steel	0.24"	300 bar	-270 °C – 600 °C	25mm	https://www.polyfluor.nl/en/products/high-pressure-hoses/high-pressure-hose-for-hydrogen-helium/
Spirstar	yes	Polyoxylmethelene (Delrin)	extrusion	braided steel	0.25"	3500 bar	-40 °C – 85 °C	180mm	https://www.spirstar.de/ProductConfigurator/pdf/Hose_type_16mm_hydrogen_EN.pdf
Aflex Hose	yes	PTFE	extrusion	braided steel	0.59"	41 bar	up to 150 °C	no data	https://www.aflex-hose.com/

Technology-to-Market (T2M) and commercialization plan and Identification of next stage partners and funding agencies

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Opportunities for partnership

- **Toyota** (https://global.toyota/en/newsroom/corporate/37405994.html) –
    - ➢ Toyota has developed a working prototype of portable hydrogen cartridge.
    - ➢ This cartridge design will facilitate the everyday transport and supply of hydrogen energy to power a broad range of daily life applications in and outside of the home.
    - ➢ Aim is to use hydrogen as an energy source in our homes and daily life and achieve 0% CO_2 emission.
- **Universal Hydrogen** (https://hydrogen.aero/) –
    - ➢ California based startup working on hydrogen infrastructure for making hydrogen-powered commercial flight.
    - ➢ Has developed a conversion kit for existing regional aircraft, ATR72 and the De Havilland Canada Dash-8, to fly on hydrogen.
    - ➢ Aiming for 0 emission by 2025 by providing conversion kits for regional passenger aircrafts.
- **Toray** (https://www.cf-composites.toray/markets/energy/fuelcell/pressure.html) –
    - ➢ Manufacturer of H_2 gas pressure vessels for fuel cell vehicles (FCVs).
    - ➢ Uses filament winding technique for fabricating carbon fiber-based vessels.
- **Huntsman** (https://www.huntsman-transportation.com/news/2022-11-JEC-Composites-Sustainability-Report-2022-Huntsman-Advanced-Materials-stands-out-by-responding-to-the-emerging-challenge-of-hydrogen-storage.html) -
    - ➢ Design and production of composite pressure vessels for hydrogen storage and transportation.
- **Danfoss** (https://assets.danfoss.com/documents/207658/AM426057295580en-000101.pdf) –
    - ➢ Hydraulic hose manufacturer; petrochemical transport hose.
    - ➢ Operating temperatures of -40 to 80 °C.

Technology-to-Market (T2M) and commercialization plan and Identification of next stage partners and funding agencies

Opportunities for partnership

- World Hydrogen Summit 2023 – The Global Platform Where Hydrogen Deals Get Done (world-hydrogen-summit.com)
  - Will bring together governments and leading companies within the Hydrogen domain to establish partnerships and set key priorities to scale up hydrogen deployment.
- Home - HydrogenOne Capital Growth plc
  - This company deliver an attractive level of capital growth by investing in a diversified portfolio of hydrogen and complementary hydrogen focused assets.
- Sustainable Energy Fund (SEF) - We Help Fund Green Projects (thesef.org)
  - They provide financing for renewable energy projects, energy efficiency projects, and energy companies.
- Southeast Hydrogen Energy Alliance | E4Carolinas
  - They help in commercialization of hydrogen and related technologies in the Southeastern United States by serving as the regional connector for companies and organizations surrounding hydrogen energy opportunities while being a resource to inform regional stakeholders on the benefits and opportunities of hydrogen technologies through seminars, workshops and events.
- Clean Transportation Funding Areas (ca.gov)
  - This program invests up to $100 million annually in projects that support adoption of cleaner transportation powered by alternative and renewable fuels.

Response to reviewers' comments

Comment: The omission of an overall scheme for how this polymer will be integrated into a full hose assembly makes it difficult to know whether the results can be translated into a deployable product.

Response: It has been shown at AMR 2022 meeting that these copolymers are integrated into a hose by fabricating fiber-reinforced composite inner layer prototypes.

Comment: Ultimately, the project team would benefit by defining several key metrics that can be used to direct the project moving forward. These metrics should explain concepts such as the following: (1) what self-healing is, (2) whether self-healing includes restoration of strength and ductility or just hydrogen permeability/ ability to seal hydrogen, (3) what the success level of self-healing is, (4) whether a scratch at 50% through thickness would be expected to self-heal more so than a completely severed membrane, and (5) how the properties and functionalities recovered through self-healing are defined (i.e., quantifying factors such as a membrane's ability to seal hydrogen, a specific measure of strength, or the elongation-to-failure measure). Each should be defined, and each metric should be quantified.

Response: (1) The ability of copolymers to restore their physical and/or chemical functions is referred to as self-healing, (2) self-healing results in the restoration of strength and ductility, (3) for this specific application, the success level of self-healing after 25,000 damage-repair cycles, (4) the scratch at 50% depth will self-heal faster than completely severed membranes, (5) Recovery of > 85% of the mechanical properties such as strength, viscoelastic properties (storage and loss moduli), and permeation to H_2.

Response to reviewers' comments

Comment: One of the slides shows that CED decreases with an increasing number of hydrogen molecules. It is unclear whether that means that the “healing action” will occur only when hydrogen is not being dispensed.

Response: When the MMA/nBA to H_2 ratio in p(MMA/nBA) is 1:1, self-healing is most effective. For example, a 1,000,000 Da copolymer of p(MMA/nBA) would have ~4,386 repeating units, and ~4,386 H_2 molecules will enhance the self-healing efficiency of these materials.

Comment: An industrial partner could also provide insight into the integrated design of a hose using these self-healing polymers and into additional materials testing that might be required to ensure the developed materials meet the required technical specifications of a polymer that could easily be utilized in such a design.

Response: We look forward to working with industrial partnerships, and these opportunities are being explored.

Comment: The project assumes that it is the inner lining that is the limiting feature of a dispensing hose. It would be useful to know whether prior DOE funded work on dispensing hose damage can validate this assumption. This work seems to address the matrix material but assumes that there will be no loss due to fiber damage.

Response: All experiments were performed on a composite hose fabricated using p(MMA/nBA) copolymer matrix and Innegra^{TM} fibers as a reinforcement. Matrix is the weakest component of a composite, and we are focusing on improving its lifetime by introducing self-healing.

Collaboration and Coordination

Partners	Contact Person	Project Roles
Savannah River National Lab SRNL	Dr. Charles (Will) James Dr. Dale Hitchcock	H_2 gas permeability tests
Sandia National Lab SNL	Dr. Nalini Menon	H_2 pressure resistance tests
Pacific Northwest National Lab PNNL	Dr. Kevin Simmons	Comparative electron microscopy analysis

Future Work (beyond the DoE project)

Note: Any proposed future work is subject to change based on funding levels

- Identification of future commercial partners and funding opportunities are being explored.
- Preparation of manuscripts for publications.

Summary

During BP-3 (Q9-Q13) all milestones were met:

1. Macroanalysis predictions using COMSOL Multiphysics® software that result in material properties under different loading conditions applied to the composite hose to evaluate responses was developed.

2. Comparison of stress distribution under internal pressure load of 35 MPa and 100 MPa was performed.

3. A model for self-healing and non-self-healing inner layer composite hose was developed and comparison was made for stress distribution under internal pressure load on 100 MPa.

4. Stress distribution was also performed to simulate the actual bending cycle during H_2 fuel refueling by applying an internal pressure load and bending load on the inner layer composite hose model.

5. Heat transfer mechanisms were determined by applying a constant load of internal pressure of 35 Mpa and a temperature of -40 °C and a variable external loads of -40 °C, 0 °C, 25 °C, and 80 °C.

6. A model of an inner layer composite hose with an outer aluminum layer to simulate a commercial hose was developed to evaluate the stress distribution upon application of a pressure load of 35 MPa and 100 MPa.

7. Copolymer/fiber composite systems were optimized.

8. Detailed studies on product specifications, target markets, their sizes, and market competition were conducted.

9. Next stage potential partners and funding sources were identified.

10. Test reports were completed.