Self-healable Copolymer Composites for Extended Service H_2 Dispensing Hoses

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Project ID #IN020

Overview

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Timeline and Budget

- Project Start Date: 01/2020
- Project End Date: 12/2022
- FY2020: $540,853
- Total Project Budget: $1,250,000
  - Total Recipient Share: $250,000
  - Total Federal Share: $1,000,000
  - Total DOE Funds Spent*: $91,140

* As of 05/30/2020: $91,140

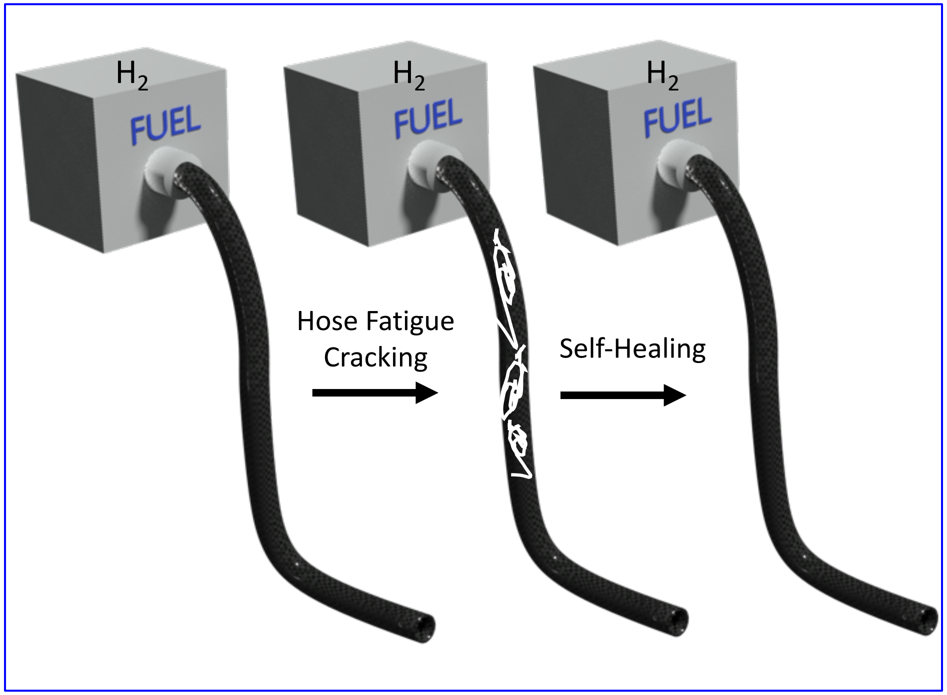
Barriers

- Barriers addressed
  - developing a H_2 delivery green house infrastructure
  - developing innovative process technologies that will reduce H_2 fueling costs
  - Determine applicability and cost effectiveness of commodity self-healable copolymer composites in H_2 delivery systems
  - Reduced cost of production by minimizing rates of H_2 leaking
  - Develop materials-based system strategies to meet and exceed target refill cycles in H_2 dispensing hoses

Partners

- Savanah River National Labs
- Project leads: Dr. Charles (Will) James; Dr. Dale Hitchcock

Relevance



When micro-cracks develop around 1000 fill cycles, self-healing will occur in an inner layer of a dispense hose.

The objective is to demonstrate that over 25,000 cycles can be obtained thus increasing sustainability of H_2 dispense hoses.

Relevance

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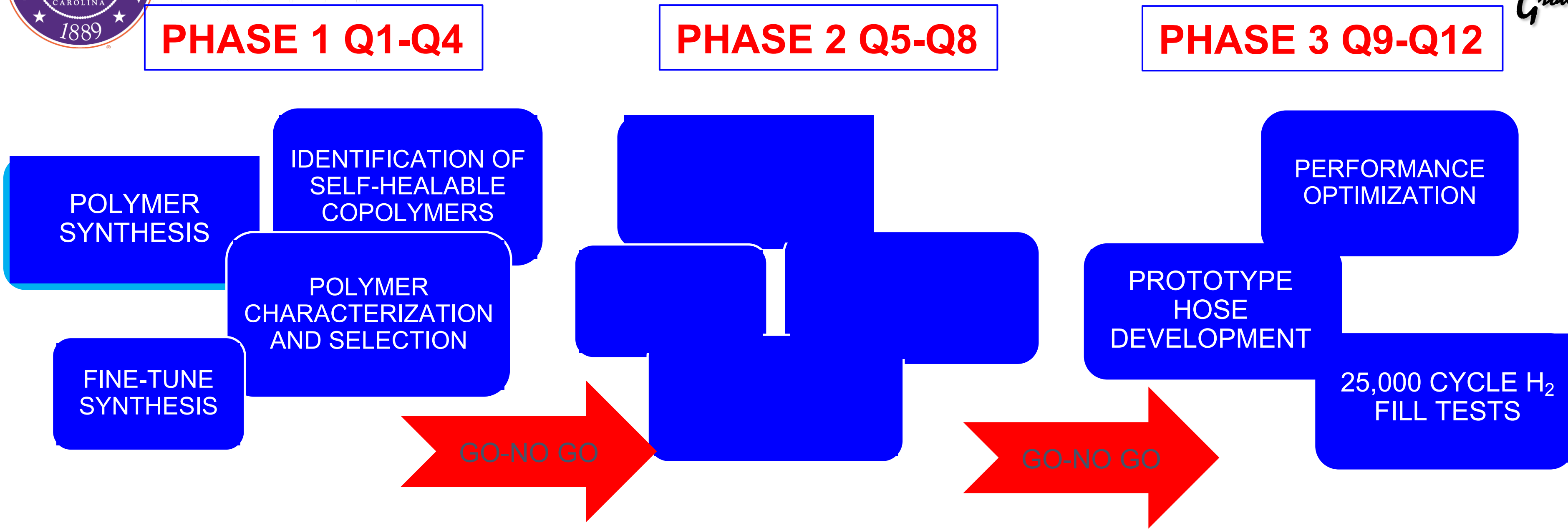
Objectives

- Design, development, and testing of a new generation of commodity self-healable copolymers and composites for the inner core of a H_2 dispensing hose to extend the hose service life
- Development of new knowledge and experimental methods that will impact other energy-related technologies

Key Milestones & Deliverables

- Year 1: Develop commodity copolymers with self-healing properties that undergo damage-repair cycle
- Year 2: Develop commodity composites with self-healing properties that undergo damage-repair cycle
- Year 3: Develop and optimize self-healing composite hoses to extend the H_2 hose service life beyond the current target of 1000 fills.

Project Phases



Approach/Milestone Q1

Date	Milestone/Deliverables	Complete
01/30/20	Development of Project Management Plan	100%
02/15/20	Development of Collaborative Path with SRNL	100%
03/31/20	Copolymerization of Copolymers	100 %
03/31/20	Characterization of Copolymers	100%
03/31/20	Copolymer Characteristics and Self-healing Properties	100%
03/31/20	Copolymer requirements and specifications	100%

Approach

- Copolymerize commodity p(A/B) copolymers that exhibit self-healing attributes
- Develop and test self-healing properties of fiber-reinforced p(A/B) copolymers by Innegra^{TM} fibers
- Conduct molecular dynamic simulations to optimize copolymerization to achieve desirable self-healable structural features.
- Develop and test prototypes of an inner layer hose to achieve > 25,000 refill cycles

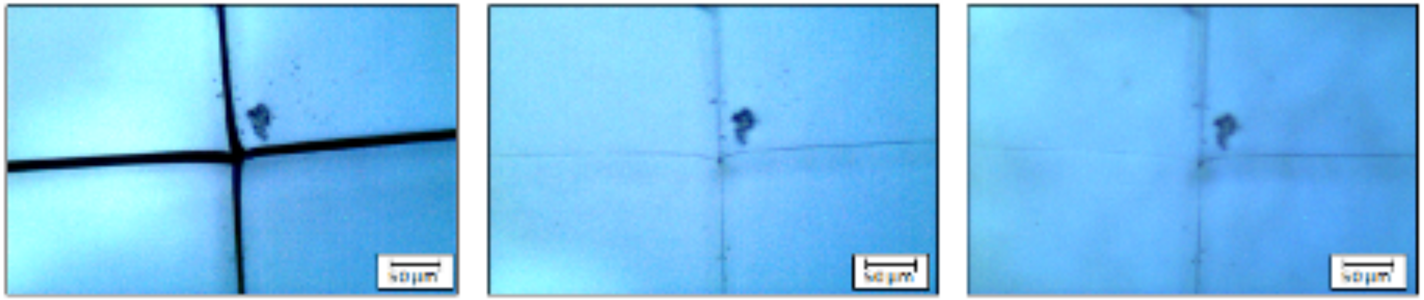
Accomplishments and Progress

The following self-healable copolymers were developed using three polymerization methods: atom transfer radical polymerization (ATRP), colloidal, and statistical copolymerization.

Monomer	Copolymer	Copolymerization Method	Molar Feed Ratio (f)	Actual Molar Ratio (F)	M_n (Da)	M_w (Da)	Đ	T_g (K)	Self Healing
A	p(A/B)	ATRP	50/50	51/49	19359	23395	1.21	278	+
A	p(A/B)	ATRP	45/55	44/56	27532	36908	1.34	269	+
A	p(A/B)	Colloidal	50/50	*	159000	774000	---	268	+
B	p(A/B)	Colloidal	45/55	*	>1000000	ultrahigh	---	253	+
B	p(A/B)	Statistical	50/50	53/47	44603	86518	1.94	283	+
B	p(A/B)	Statistical	45/55	46/54	68962	163493	2.37	272	+

Summary of f, F, M_n, M_w, Đ, and T_g values for self-healable compositions of p(A/B) copolymers within 45/55 to 55/45 molar A/B monomer ratios prepared by atom transfer radical polymerization (ATRP), colloidal, and statistical copolymerization. "*", "---" due to ultra-high molecular F values could not be determined. "+" denotes self-healability

Accomplishments and Progress



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Optical images of self-healing of p(A/B) copolymer films. Optical images of damaged p(A/B) copolymers with the A/B molar ratio of ~50/50. Copolymers were allowed to repair under ambient conditions.

Summary of requirements and specifications for p(A/B) copolymers to be used in the development of H_2 dispense hoses: f, F, M_n, M_w, Đ, T_g, and self-healing efficiency. Yellow shaded fields indicate work in progress. The values for E (MPa), ε_{max} (%), ε_{max} (14hrs) (%), σ_{break} (MPa), and σ_{break} (14 hrs) (MPa) will be reported in subsequent quarterly reports.

Monomer	Copolymer	Molar Feed Ratio (f)	Actual Molar Ratio (F)	M_n (Da)	M_w (Da)	Đ	T_g (K)	Self Healing	Mechanical Properties				
									E (MPa)	ε_{max} (%)	ε_{max} (14hrs) (%)	σ_{break} (MPa)	σ_{break} (14 hrs) (MPa)
A	p(A/B)	40/60	37/63	32607	75966	2.33	248	-					
		45/55	46/54	68962	163493	2.37	272	+					
B		50/50	53/47	44603	86518	1.94	283	+					
		55/45	57/47	45801	120029	2.62	300	-					

Accomplishments and Progress

We copolymerized and identified p(A/B) copolymer compositions that exhibit self-healable properties. The following properties were determined: f, F, M_n, M_w, (Đ), and T_g.

Optical image analysis showed that the optimum monomer A/B molar ratios are 45/55 to achieve self-healing properties.

p(A/B) copolymers are in the process of being characterized and the following mechanical properties will be determined: E (MPa), ε_{max} (%), ε_{max} (14hrs) (%), σ_{break} (MPa) and σ_{break} (14 hrs) (MPa).

Spectroscopic analysis is being performed (FTIR, NMR) to be used for structural fine tuning abnd input to simulations.

Accomplishments and Progress: Responses to Previous Year Reviewers' Comments

- This project was initiated in FY20 and was not reviewed last year.

Collaboration and Coordination

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The proposed project aims to develop self-healable commodity copolymer composites for an inner core of a H_2 dispensing hose to extend the hose service life cycles.

These materials are being developed by the Clemson Team H_2 testing is performed at Savanah River National Labs (SRNL). The results of SRNL tests will be fed back to the Clemson Team for fine tuning of self-healing properties.

During this period two sets of p(A/B) copolymer films were sent to Savanah River National Labs for initial H_2 permeability studies.

SRNL Project Leads:
Dr. Charles (Will) James
Dr. Dale Hitchcock

Remaining Challenges and Barriers

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- Critical GO/No GO challenge in this project was accomplished: self-healable p(A/B) copolymers were developed.

- Current and Future Challenges:

  Personnel:
  - Difficulty hiring new personnel due to COVIT-19 (hiring freeze).

  Technical:
  - Shorten self-healing times in ultra-high molecular weight copolymers.
  - Control of the degree of alternating/random copolymer structural content.
  - Control self-healing of fiber-reinforced p(A/B) copolymer composites.
  - Fatigue and durability analysis of composites.
  - Mechanical and spectroscopic analysis of fiber-reinforced copolymer composites containing F-copolymers.
  - Cost-performance analysis.
  - Demonstrate and test prototypes of an inner layer H_2 hose achieving > 25,000 refill cycles.
  - Identify private sector which would commercialize these technologies.

Proposed Future Work

- Polymerization of ultra-high high molecular weight copolymer compositions capable of self-healing for the use in H_2 services. This is critical in achieving desirable mechanical properties.
- Control of copolymer compositions will be essential to achieve repetitive self-healing of p(A/B) copolymers, fiber-reinforced copolymers, and F-containing p(A/B) copolymers.

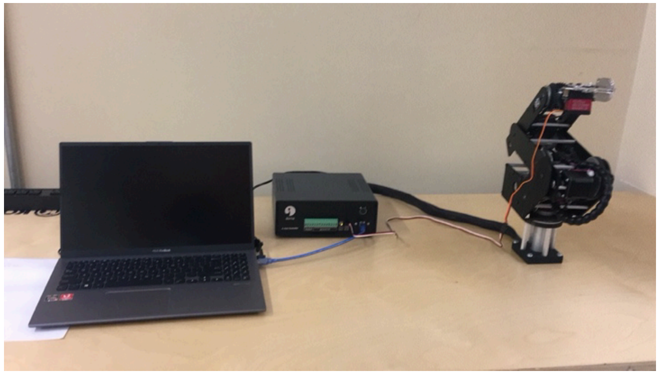
UPCOMING MILESTONES

- Preliminary cost-performance model will be developed which will include all key cost drivers. Draft T2M will be developed.
- Each copolymer will be characterized using spectroscopic and mechanical testing methods.
- Copolymers will be characterized and identified for composite development.

Proposed Future Work

- MD simulations will be conducted and used for fine tuning of copolymer compositions and H_2 and H_2O permeability. The latter will be used to predict the role of these molecules on self-healing properties in H_2 dispense hose actual working environments.
- Cost-performance studies will be conducted with assistance of Clemson University Research Foundation (CURF).
- Fatigue analysis will be conducted as a function of copolymer compositions in fiber-reinforced and F-containing p(A/B) copolymers.

Robotic device will be used to mimic fatigue of interior section of H_2 dispensing hoses



Technology Transfer Activities

Technology Impact

- A new generation of commodity self-healable copolymers and composites will be developed using commodity starting materials
- Low cost self-healing materials for many energy-related applications will lead to new technological opportunities in the US.

T2M Plans

- Initiated work with the Clemson University Research Foundation (CURF) to develop the commercialization plan.
- CURF will assist the team in disclosure and reporting of IP, evaluations of commercial opportunities (PatSnap software), protect through patenting, and find opportunities for further development through sponsored research and/or licensing.
- Plans are being developed for future commercialization as well as marketing strategies.

Summary

- Commodity copolymers p(A/B) with self-healable properties were identified, developed, and tested.
- Target copolymer compositions were identified and developed using three copolymerization methods.
- Most suitable monomer ratios were identified and copolymers with alternating/random distribution of monomers exhibit self-healing properties.
- Collaborative efforts with SRNL have been established.
- Commercialization plans between the Clemson Team and CURF are progressing.