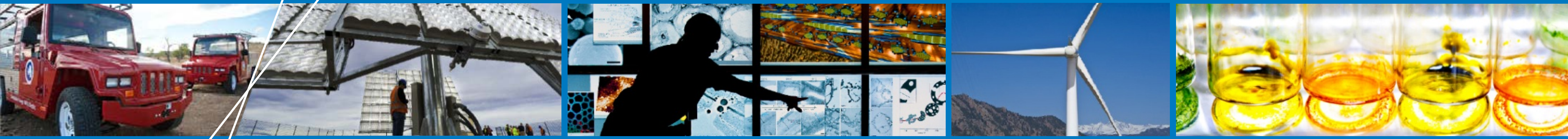
700 bar Hydrogen Dispenser Hose Reliability Improvement



Kevin Harrison, Owen Smith, Huyen Dinh, Mike Peters, Clay Macomber, Svitlana Pylypenko, Krista Isham

National Renewable Energy Laboratory

2015 Annual Merit Review
June 9, 2015

PD100

Overview

Timeline

Project start date: June 2013

Project end date: October 2016

Barriers

- **Reliability**
- **Safety**
- **Cost**

Budget

Total Funding Spent: $375k

Total DOE Project Value: $775k

Internal NREL Funding

- **$1.1M – 700 bar Fueling Station**
- **$55k – Compression & storage**

Partners

- **Spir Star**
- **NanoSonic**
- **Sandia National Laboratory**
- **NREL**
  - Hydrogen Sensor Group
  - Chemists
- **Colorado School of Mines**

Relevance & Impact

To characterize and improve upon 700 bar refueling hose reliability under mature market conditions

- **By working closely with the original equipment manufacturer, Spir Star and other stakeholders, NREL's hose reliability R&D project aims to improve the reliability and reduce the cost of 700 bar hydrogen refueling hose assemblies.**
- **NREL has designed a test system that unifies the four stresses to which the hose is subjected (P, T, t and Mechanical)**
- **The high-cycling autonomous test apparatus is designed to reveal the compounding impacts of high volume 700 bar fuel cell electric vehicle refueling that has yet to be experienced in today's low-volume market.**

Approach - Summary

- Conduct long-duration accelerated life testing with hydrogen autonomously to simultaneously stress the hose assembly with realistic fueling protocol and back-to-back cycle conditions
  - The mechanical stress is applied to the hose assembly during the process of bending, twisting, connecting and disconnecting the hose to the vehicle during the fueling event.
- The work includes performing physical and chemical analysis on hose material before (PRE) and after (POST) testing to understand the relative changes in its bulk properties and degradation mechanism of the inner hose polymer.

Approach – DMA

Dynamic Mechanical Analysis [DMA]

- Measure of viscoelasticity
- Variables include Force, Temperature, Frequency… Stress/Strain
- Calculate and compare material modulus [storage, Young's or other]
- Small amount of material required

Typical DMA setup

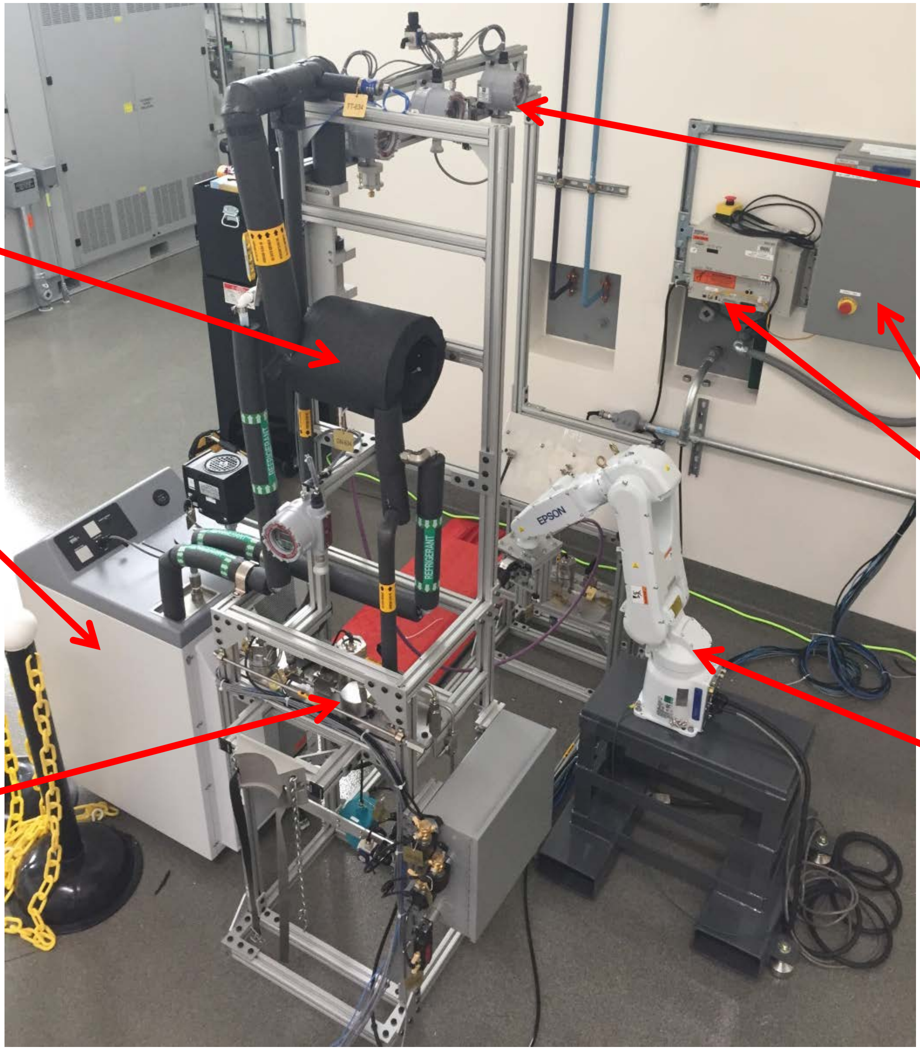
Common method of determining differences in physical properties of polymers.

Approach – Technical Description

- **Pressure profile and holds will closely follow SAE J2601**
  - $P_{tank, Initial}$ = 2 – 4 Mpa
  - A-70 Type fills, APRR 25 – 30 MPa/min - using flow control
  - T_{fuel} -33°C to -40°C – measured prior to hose
  - 'Tankless' filling (< 85°C will be maintained on the vehicle side)
- **3 – 5 minute H_2 fills using < 100g / cycle**
  - Hydrogen not recycled
- **Cycle time**
  - Short delay between cycles to maintain low temperature components
  - 70 cycles back-to-back, long delay to simulate overnight warm up
- **6-axis robotic arm to provide mechanical stress of routine consumer refueling**
  - Automated activation of the refueling nozzle, valves, etc…
- **H_2 leak monitoring of fittings, connections and interfaces**

Progress & Accomplishments

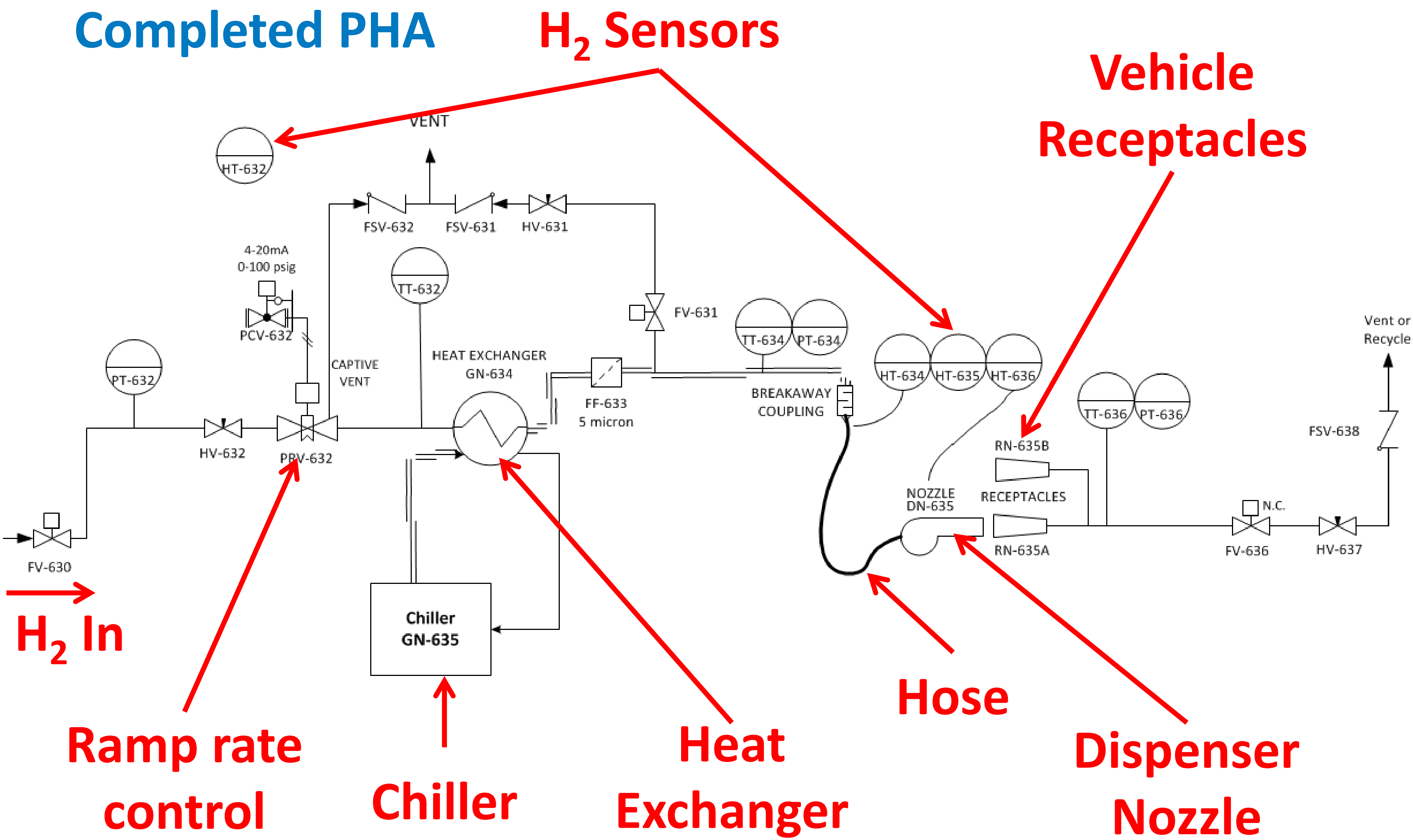
Hose Test Apparatus – Design/Build



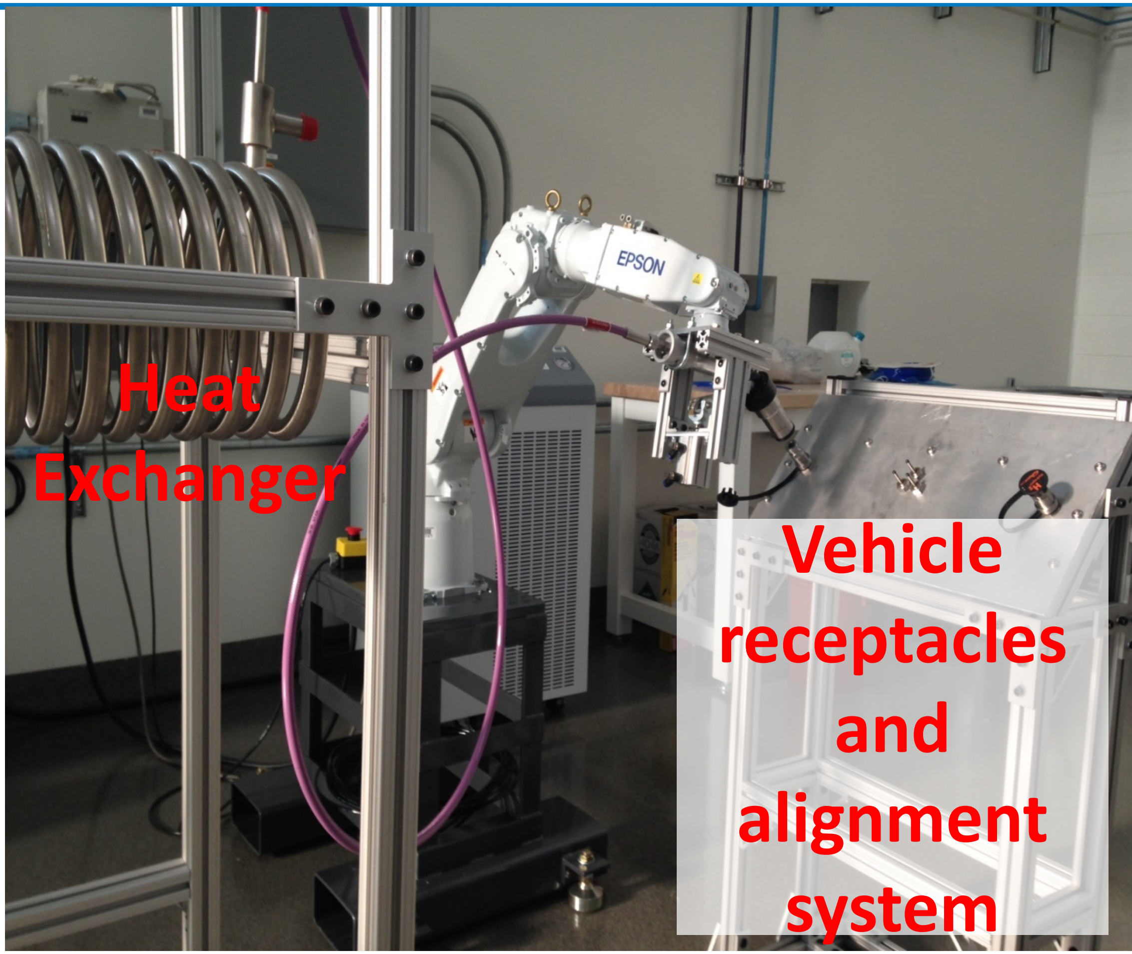
Progress & Accomplishments

Final PID – 'Dispenser' and 'Vehicle' sides

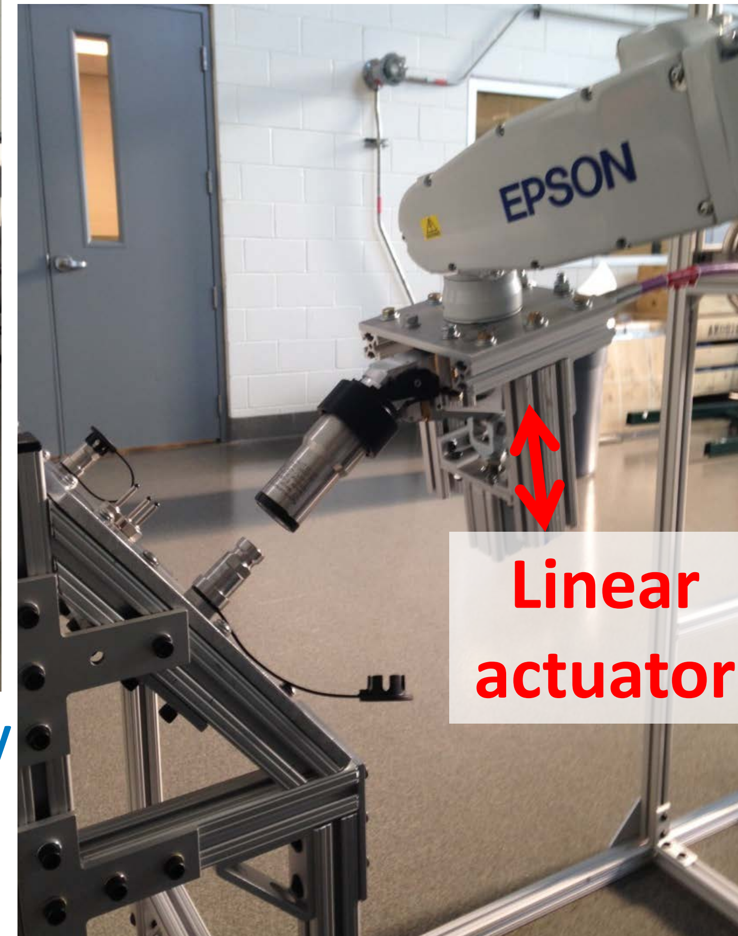
Completed PHA



Progress & Accomplishments



System Components



Alignment system will periodically confirm nozzle-to-receptacle parallelism using linear variable differential transformer (*LVDT*)

Progress & Accomplishments

Safety Systems

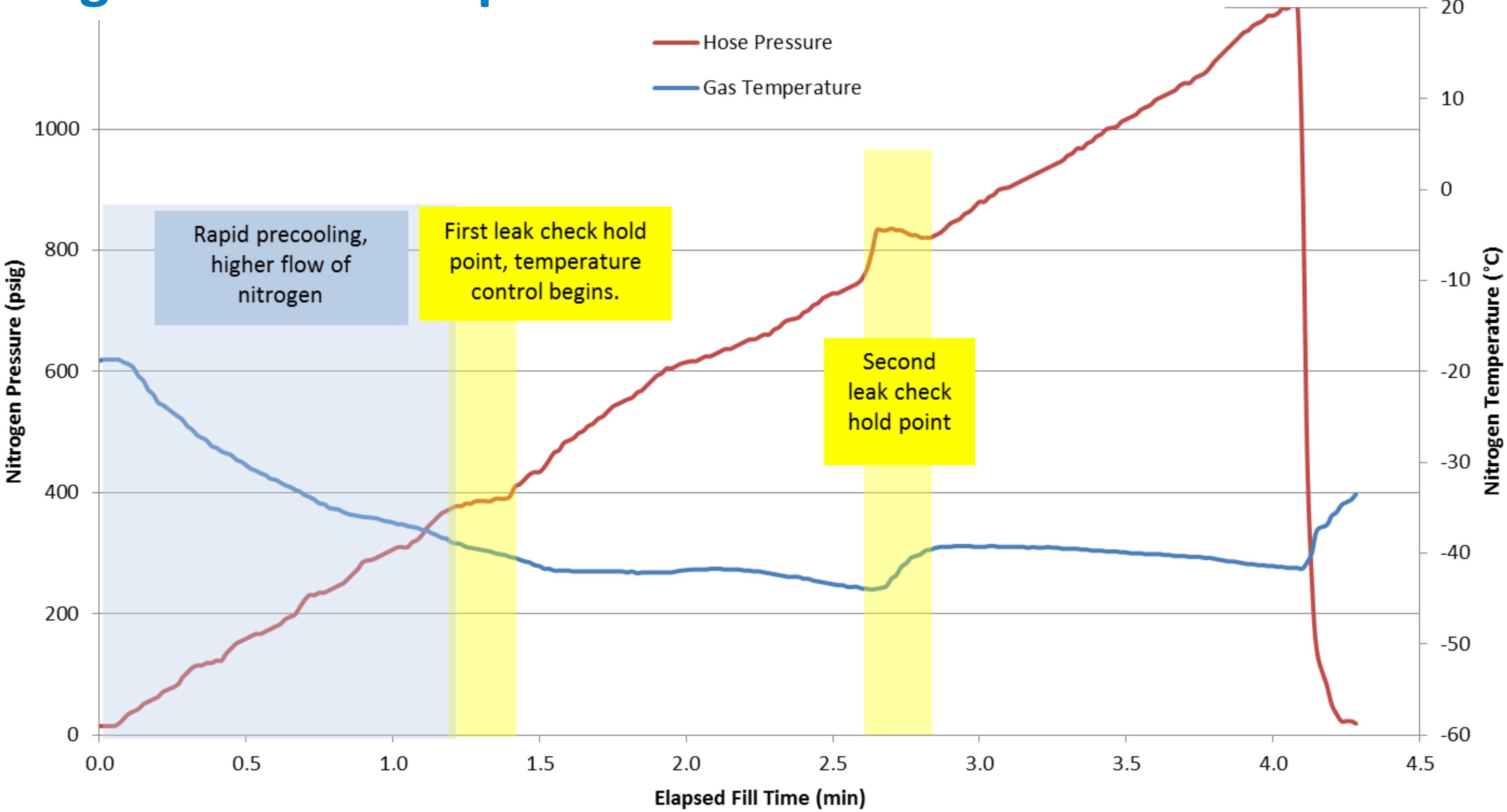
- **Three dedicated RKI hydrogen detectors monitor critical fittings, connections and interfaces**
    - (Sensors tested and calibrated by NREL Sensor Test Group)
- **Video camera feedbacks back to Control Room**
- **Robot torque controls shuts down robot in case of collision**
- **Standard 700 bar refueling equipment, including break away**
- **Proximity sensors and LVDT's used for nozzle to receptacle parallelism and position guidance**
- **Pre-Start Conditions**

Imposed by NREL AHJs

- Additional H_2 detection over valves
- Room ventilation monitoring
- Additional isolation valve on high pressure H_2 in to room

Progress & Accomplishments

Hose pressure and temperature control algorithm development



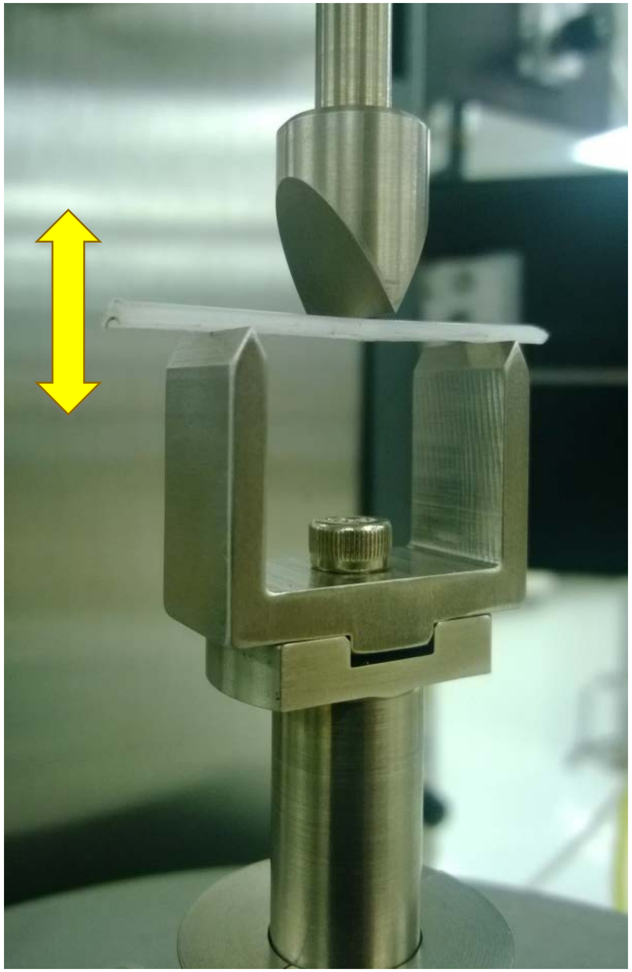
Methodology – TTS

Time-Temperature Superpositioning (DMA)

Sample Preparation

Polyoxymethylene [POM]

- Narrow sections of the polyoxymethylene hose were cut to be tested on the RSA G2 3 Point Bending clamp.
- Length: 25 mm
- Thickness: 1.09 mm
- Width:
  - 3.45 mm
  - 5.45 mm
  - 4.38 mm
    - The sample width was minimized to reduce the effects of curvature.



Methodology – TTS

Method Parameters

Polyoxymethylene [POM]

Instrumentation

- TA Instruments RSA G2
- Forced Convection Oven (FCO) with nitrogen purge gas
- 3 Point Bend clamp
- Force Rebalance Transducer (FRT)

Axial Force Control

- Force Tracking, Axial Force > Dynamic Force by 20%

Temperature Program

- 30˚ – 100˚ C, increments of 5˚
- 3 minute soak time at each temperature step to equilibrate sample.

Frequency Sweep: 0.001 to 10 Hz, log scale, 3 points per decade (13 frequencies)

Total test time: approximately 20 hours

Progress & Accomplishments

TTS Summary

The POM experimental material does not appear to be appropriate for TTS

This may be due to the semi-crystalline nature of the material – crystallinity is likely to increase at elevated temperatures.

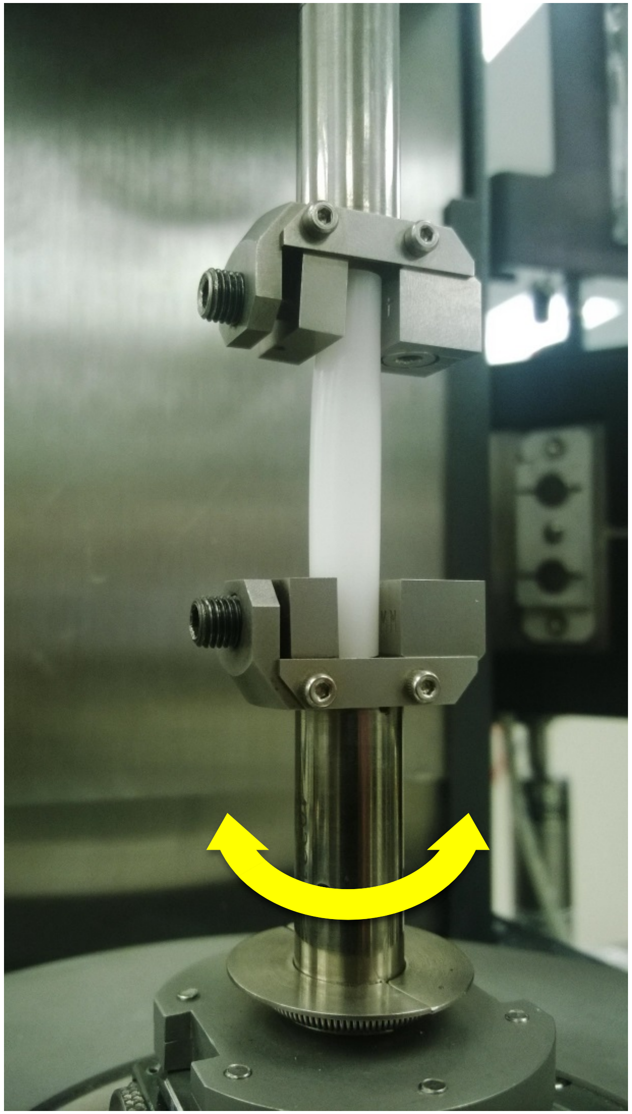
Polyoxymethylene [POM] TTS analysis may be possible at very low temperatures. However, low temperature TTS can only be used to predict shorter time scales or high frequencies.

To generate TTS Master Curves for longer time scales or low frequencies, elevated temperatures are needed. The POM hose material does not show a usable time-temperature relationship at elevated temperatures.

TTS will not be used for future PRE/POST analysis

Methodology – Torsion

Sample Arrangement
Polyoxymethylene [POM]



Sample Dimensions

- Inner Diameter: 6.30 mm
- Outer Diameter: 8.47 mm
- Cross-sectional Area: 25.17 mm^2
- Clamped Length at -75˚ C: 26.589 mm
- Clamped Length at 60˚ C : 27.410 mm (due to sample's thermal expansion)

Sample Stiffness

- 20.89 N.m/rad at -75˚ C,
- 5.79 N.m/rad at 50˚ C
- Transducer Stiffness: 770 N.m/radian
- Sample Stiffness << Transducer Stiffness. Measurement is not compromised by instrument compliance.

Clamping Torque: **10 cN.m**

Methodology – Torsion

Torsion Method Parameters - Polyoxymethylene (POM)

Instrumentation

- TA Instruments ARES G2
- Forced Convection Oven (FCO) with nitrogen purge gas
- Standard Torsion Clamp
- Normal Force Transducer: Spring Mode
- Torque Transducer: Force Rebalance Transducer (FRT) Mode

Axial Force Control

- Approximately 1 N of tension force maintained throughout test

Temperature Program

- -75˚ – 50˚C, at 1˚C per minute

Strain Amplitude: 0.0001%

Frequency: 1 Hz

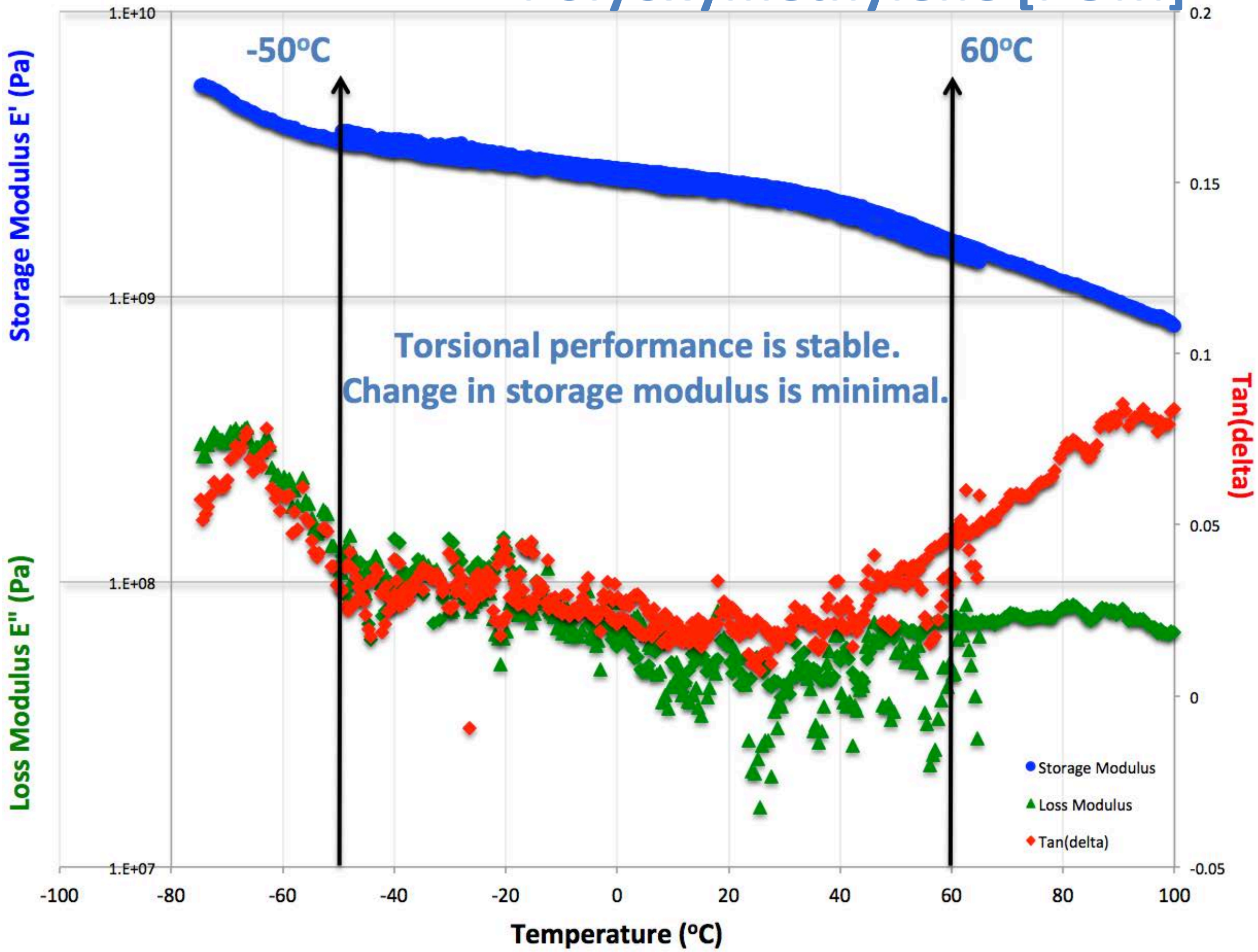
Total test time: Approximately 2 ½ hours

Progress & Accomplishments

PRE – Torsion performance characterization

Temperature ramp applied to 2 different experimental samples

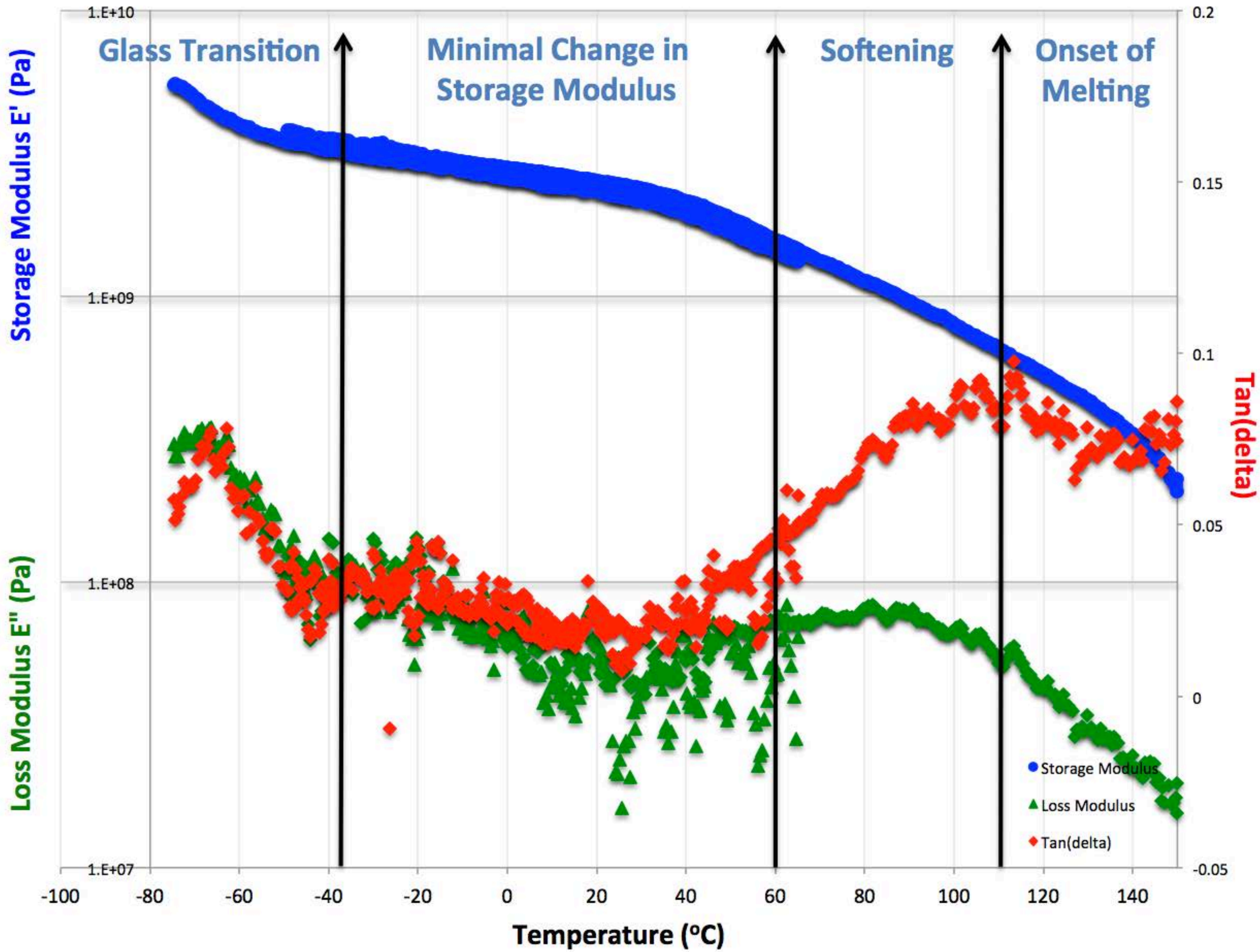
Polyoxymethylene [POM]



Samples overlay very well. Sample dimensions are well defined. Accurate modulus can be calculated.

Progress & Accomplishments

PRE



Torsional Performance Characterization (DMA)

Torsion Summary – PRE

Material torsion testing under simulated environmental conditions provides meaningful data in Polyoxymethylene [POM] performance characterization.

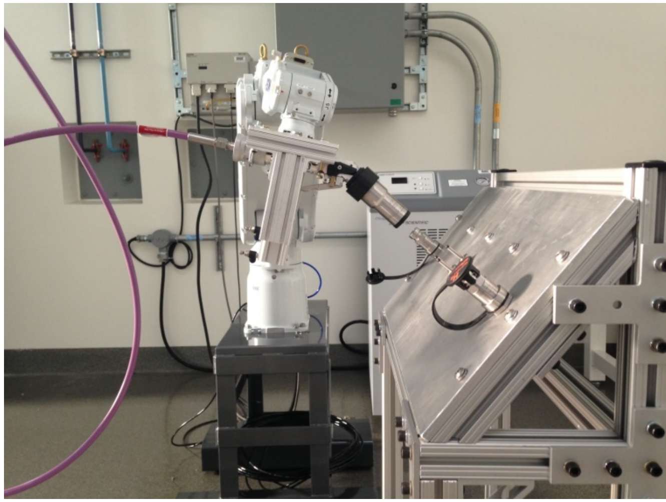
The storage modulus data measures transitions in material rigidity/response and mechanical strength under applied stress.

Minimal sample preparation is required. The Polyoxymethylene [POM] experimental hose material can be tested in it's functional form, simulating real-world stress applications.

The Polyoxymethylene [POM] experimental hose material maintains structural integrity under torsional stress from temperatures -50^{o}C up to 60^{o}C.

Collaborations

- **Spir Star**
  - Has provided hose material and hose assemblies
- **WG22 -** ISO19880-5
  - Requested results for the standardization of ISO/TC197 WG22
- **NanoSonic**
  - SBIR Phase II, "*Cryogenically Flexible, Low Permeability Thoraeus Rubber™ Hydrogen Dispenser Hose*"
- **NREL Chemists & Hydrogen Sensor Group**
  - Chemical analysis, Detector calibrations
- **Colorado School of Mines**
  - SEM-EDX, XPS
- **Sandia National Laboratory**
  - Burst testing
- **Hydrogen Delivery Technical Team – 8/14**



Proposed Future Work

- Complete multiple hose tests to 25,000 cycles or until failure and pre/post chemical and physical analysis of inner POM material
- Work closely with NanoSonic to test their hose material from the SBIR Phase II project

Summary

Relevance & Impact: To characterize and improve upon 700 bar refueling hose reliability under mature market conditions. Project is expected to reveal the compounding impacts of high volume 700 bar fuel cell electric vehicle refueling that has yet to be experienced in today's low-volume market.

Approach: By working closely with Spir Star and industry stakeholders, NREL has designed a test system that unifies the four stresses (Pressure, Temperature, Mechanical and Time) in one high-cycling autonomous test apparatus. The work includes performing physical and chemical analysis on hose material before and after cycling to understand the relative changes in its bulk and surface properties and material degradation mechanisms.

Progress & Accomplishments

- The POM experimental material does not appear to be appropriate for TTS
- The Polyoxymethylene [POM] experimental hose material maintains structural integrity under torsional stress from temperatures -50^{o}C up to 60^{o}C.
- Lessons learned from development system (FY14) integrated in to final test apparatus cycling with Nitrogen. Moving in to high pressure test bay in June 2015 to cycle with hydrogen.

Technical Back-Up Slides

DMA Viscoelastic Parameters

<u>The Modulus:</u> Measure of materials overall resistance to deformation.

$$E^{*} = (Stress^{*} / Strain)$$

<u>The Elastic (Storage) Modulus:</u>
Measure of elasticity of material. The ability of the material to store energy.

$$E' = (Stress^{*} / Strain)\cos\delta$$

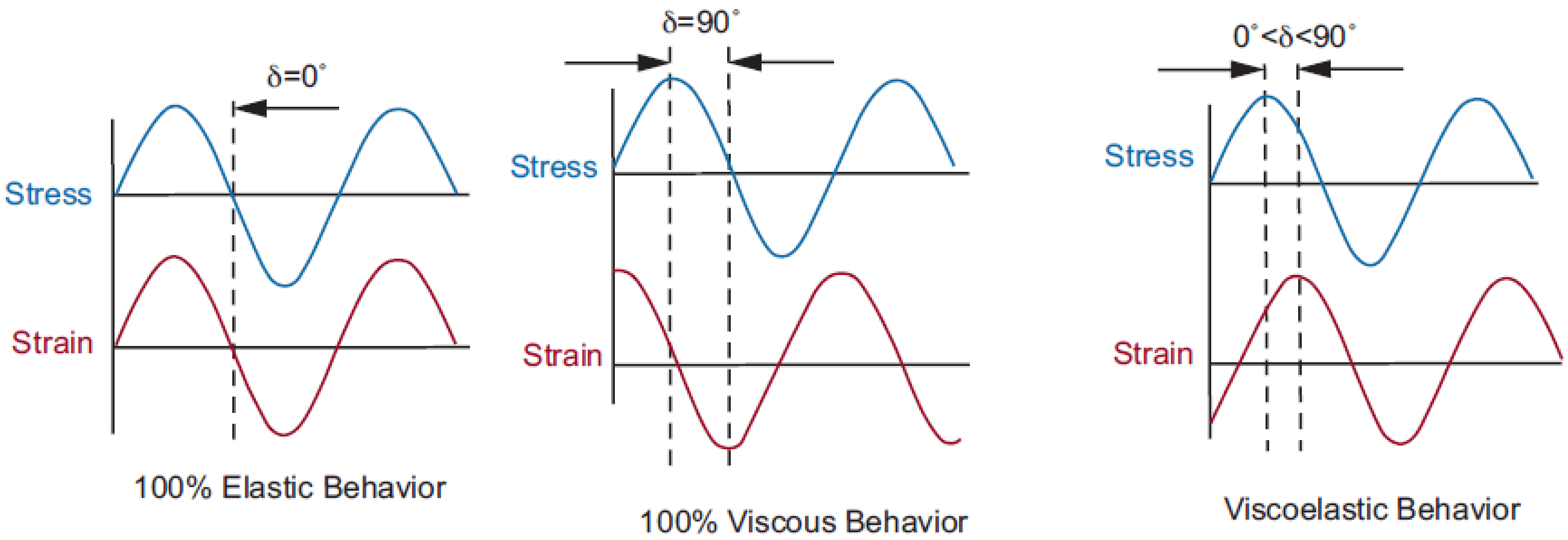
<u>The Viscous (loss) Modulus:</u>
The ability of the material to dissipate energy. Energy lost as heat.

$$E'' = (Stress^{*} / Strain)\sin\delta$$

<u>Tan Delta:</u>
Measure of material damping - such as vibration or sound damping.

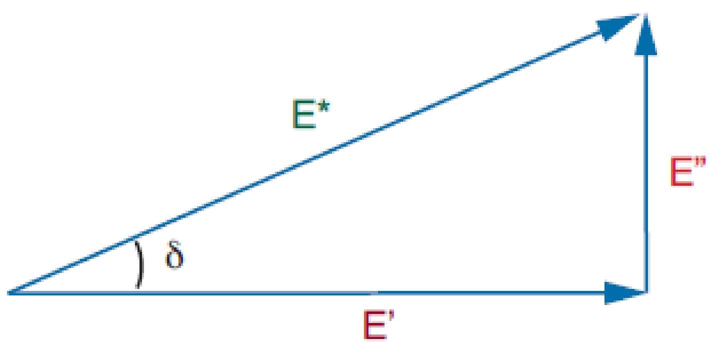
$$\tan\delta = (E'' / E')$$

Dynamic Mechanical Analysis



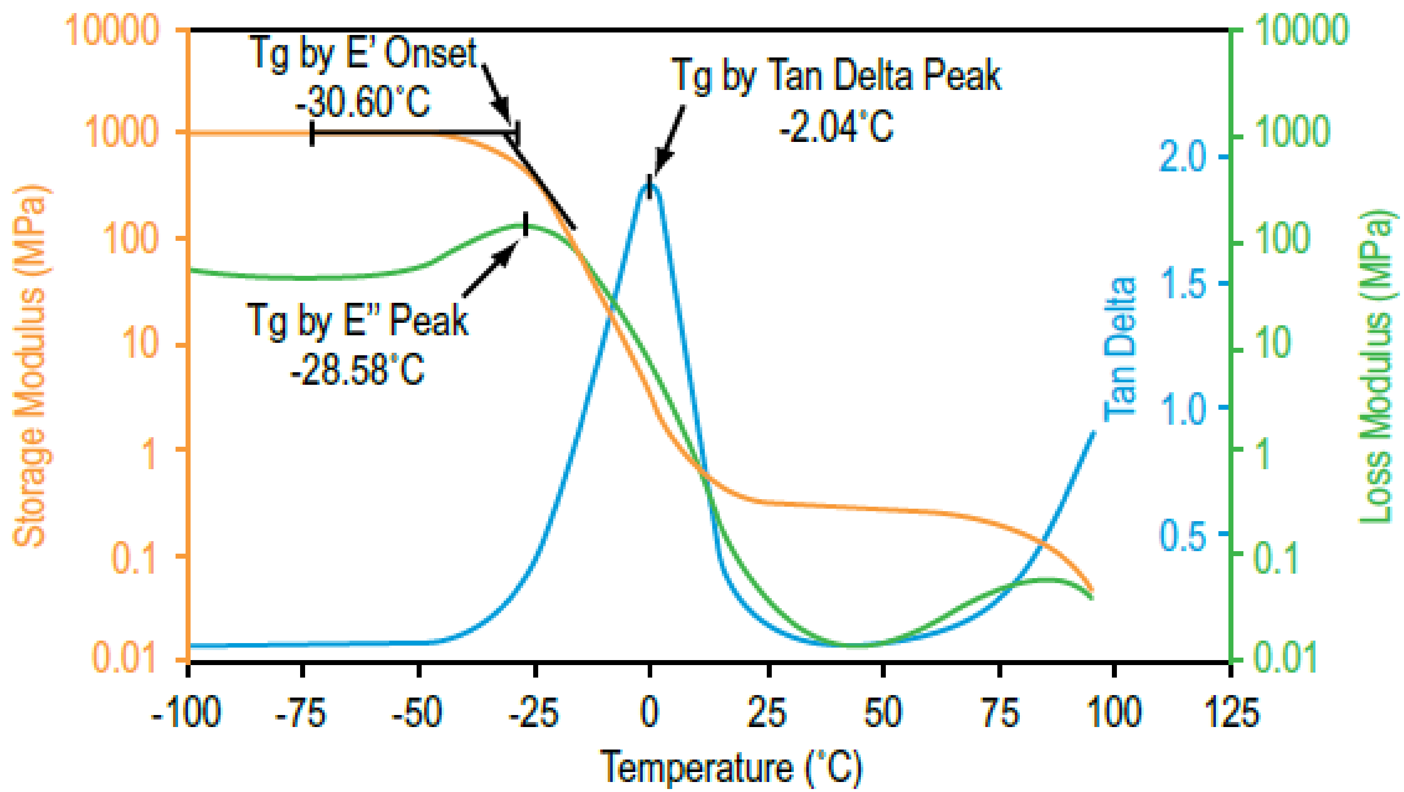
Rheological Parameters

- $E^* = Stress^*/Strain$
- $E^* = E^*/\cos\delta$
- $E^* = E^*/\sin\delta$
- $\tan\delta = E''/E'$



DMA Testing – Glass Transition

Example: Modulus Transitions of Viscoelastic Polymers



DMA Deformation Modes

Young's Modulus: E', E", E*

Bending

Tension

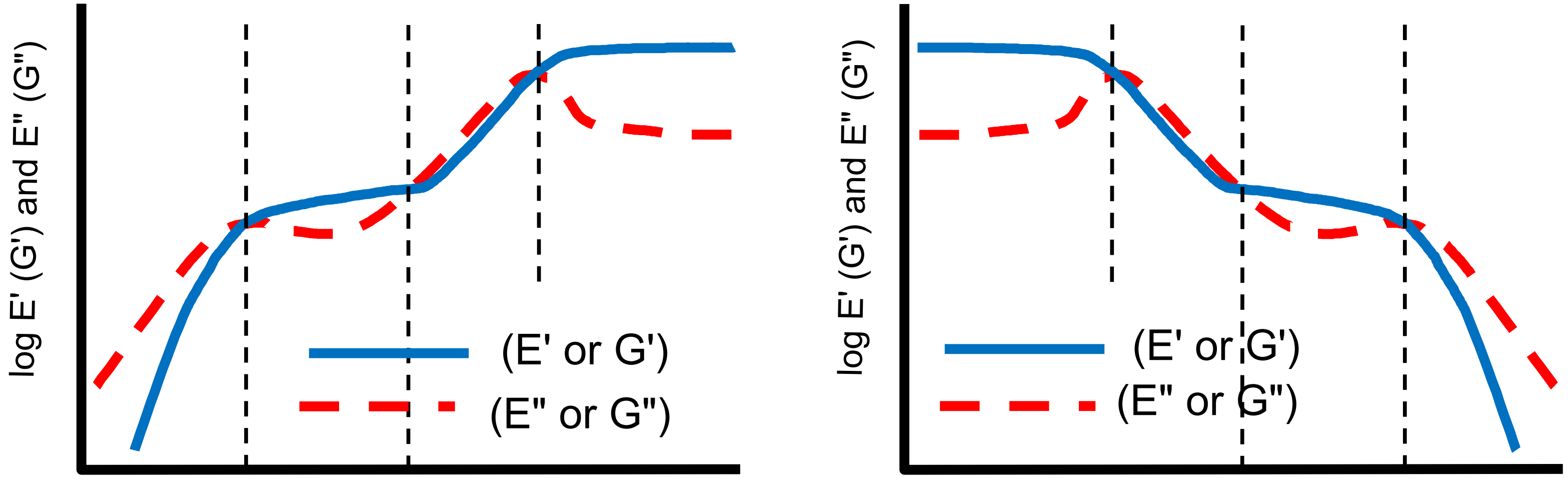
Shear Modulus: G', G", G*

Torsion

$E = 2G(1+\nu)$

ν = Poisson's Ratio

Time-Temperature Superpositioning (DMA)



- Linear viscoelastic properties are both time-dependent and temperature-dependent
- Some materials show a time dependence that is proportional to the temperature dependence
- Decreasing temperature has the same effect on viscoelastic properties as increasing frequency
- For such materials, changes in temperature can be used to “re-scale” time, and predict behavior over time scales not easily measured

Time-Temperature Superpositioning (DMA)

Why TTS?

- TTS can be used to extend the frequency beyond the instrument’s range
- Creep TTS or Stress Relaxation TTS can predict behavior over longer times than can be practically measured
- Can be applied to amorphous, non modified polymers
- Material must be thermo-rheological simple
  - One in which all relaxations times shift with the same shift factor a_T

Time-Temperature Superpositioning (DMA)

When Not to Use TTS…

- If crystallinity is present, especially if any melting occurs in the temperature range of interest
- The structure changes with temperature
    - Cross linking, decomposition, etc.
    - Material is a block copolymer
    - TTS may work within a limited temperature range
    - Material is a composite of different polymers
- Viscoelastic mechanisms other than configuration changes of the polymer backbone
    - e.g. side-group motions, especially near the Tg
- Dilute polymer solutions
- Dispersions (wide frequency range)
- Sol-gel transition