Load-Sharing Polymeric Liner for Hydrogen Storage Composite Tanks

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Overview

Timeline

- **Project start date: 10/2014**
- **Project end date: 06/2014**
- **Percent complete:** ***85%***

Budget

- Total project funding
  - DOE share: $ 200K
  - Contractor share: $ 0K
- Funding received in FY14: $ 200K
- Total funding planned for FY14: $ 250K

Barriers

- **Barriers addressed**
  - **B. System Cost**
  - **E. Charging/Discharging Rates**
  - **G. Materials of Construction**
  - **J. Thermal Management**

Partners

- Virginia Polytechnic Institute and State University (VT)
  - Prof. Don Baird's Group

Relevance

Overall Objectives:

- Reduce cost of compressed H_2 storage tanks
  - Develop basis for using load-sharing liner to displace expensive CF
  - Enhance mechanical properties of polymer
- Reduce off-board impact of fast-fill refueling
  - Increase thermal conductivity of polymer to allow better heat transfer

Objectives in this reporting period:

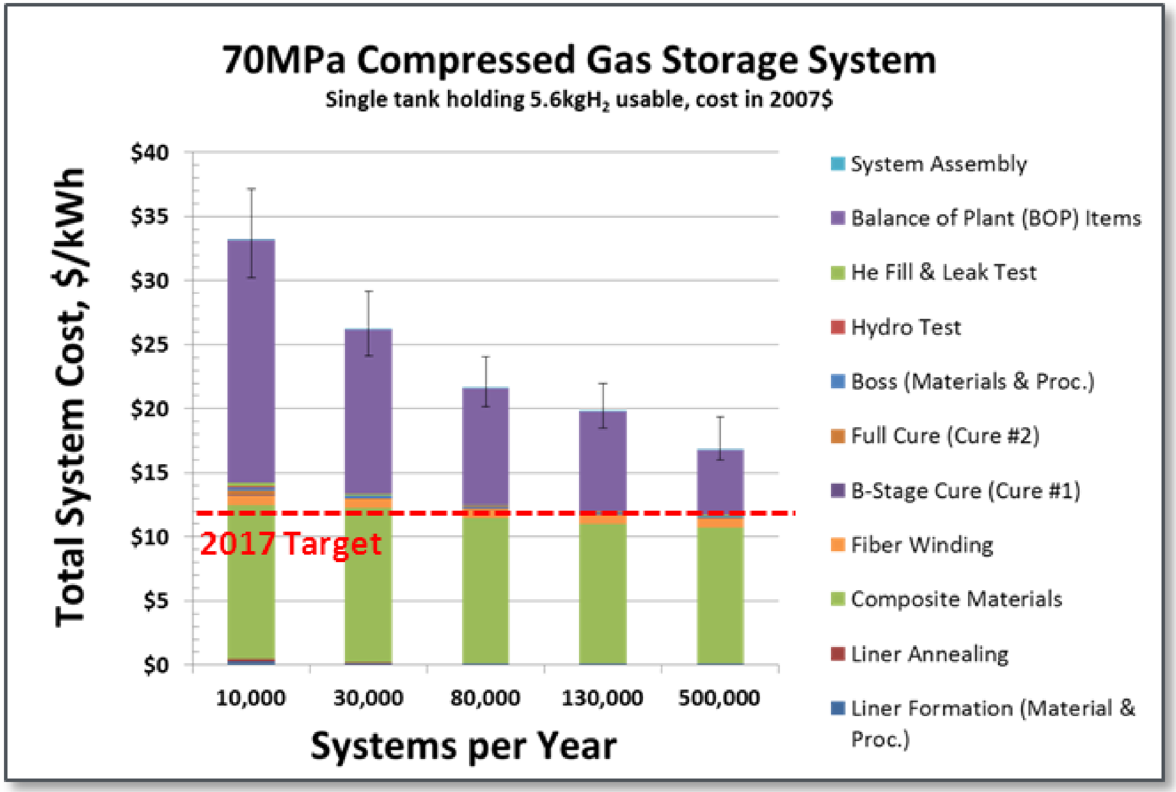
- Determine optimum properties for injection and blow molding TLCP composites while maximizing tensile modulus, strength and thermal properties
- Measure mechanical and thermal properties of polymer samples

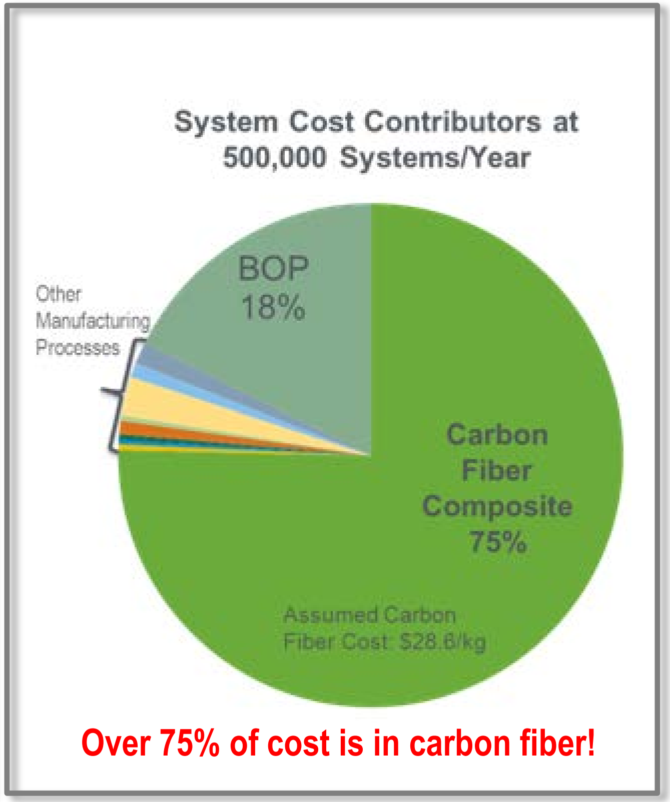
Addresses Key H_2 Storage LDV Targets and Requirements:

Target /Requirement	
Not exceed 85°C for a fill time of 3 – 5 minutes	Allows compressed tanks for LDVs to more easily meet J2601 requirements
Cost of Compressed Gas Storage	Could offset CF; lowering cost of tank
Loss of Useable H_2	Permeation is 4-5X lower than HDPE

Relevance – Offsetting CF

Load-sharing reinforced polymeric liners could potentially displace Carbon Fiber



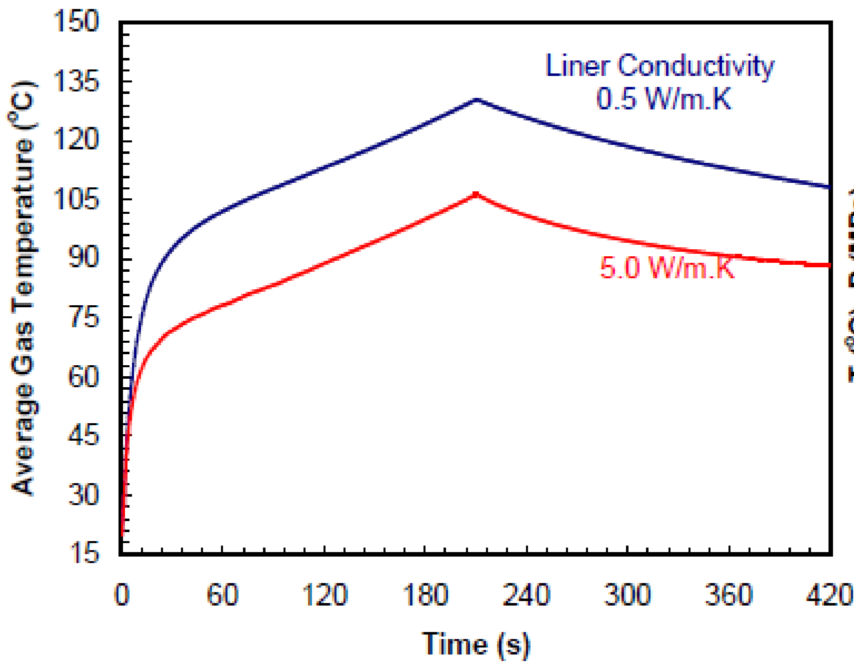


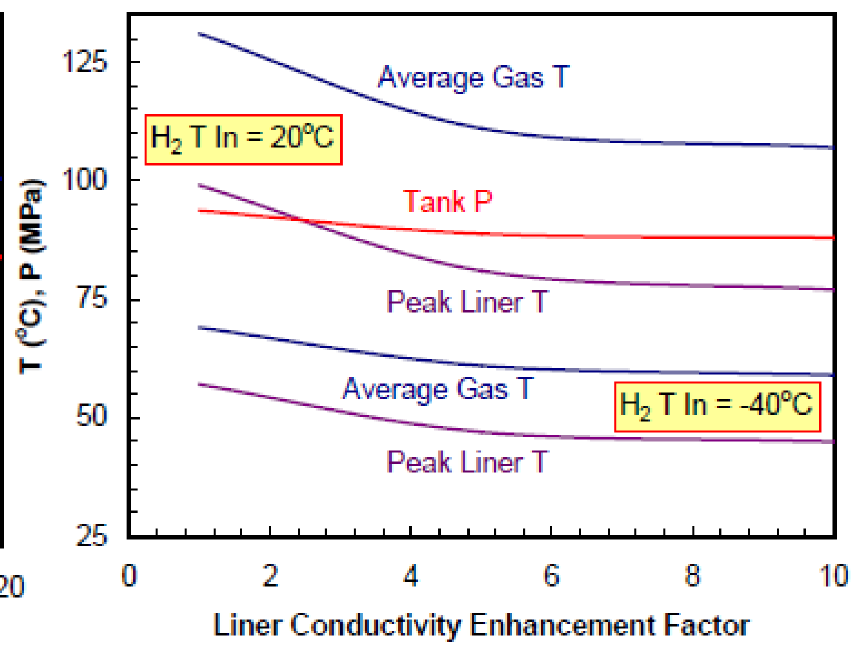
Over 75% of cost is in carbon fiber!

Initial FEA modeling using strength and modulus of 200 MPa and 10 GPa predicts that 7% of the current carbon fiber mass could be offset. Overall, replacing the current HDPE liner and offsetting CF would reduce mass of vessel by 20%.

Relevance – Fast Fill impact

Analysis by ANL shows that Liner Thermal Conductivity can have a significant impact on gas temperature





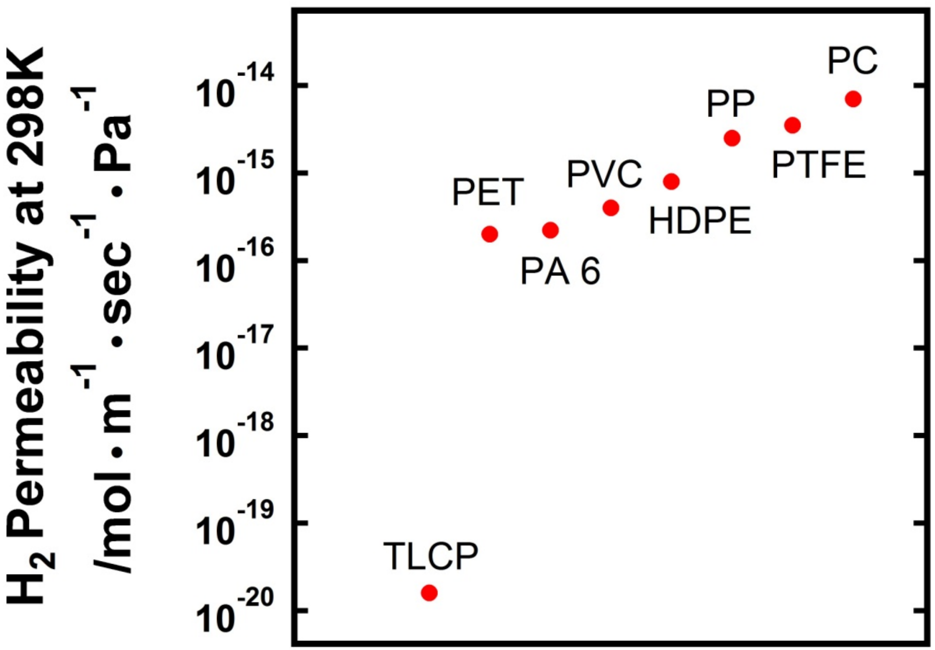
Thermal Conductivities of Base Polymers

HDPE	W/m-K	0.45-0.50
TLCP	W/m-K	0.19-0.22

5X – 10X increase in current liner thermal conductivity could decrease liner temperature by 20°C

Relevance – Permeation

H_2 permeability of several polymer materials[a]



Material	H_2 permeability mol/(m.sec.Pa)[b]
TLCP	$1.6X10^{-20}$
PET	$2.0X10^{-16}$
PA 6	$2.2X10^{-16}$
PVC	$4.0X10^{-16}$
HDPE	$8.0X10^{-16}$
PP	$2.5X10^{-15}$
PTFE	$3.5X10^{-15}$
PC	$7.0X10^{-15}$

a. H_2 permeability data was summarized by Schultheiss in his Ph.D dissertation. Schultheiss, D. PhD dissertation, "Permeation barrier for lightweight liquid hydrogen tanks." University of Augsburg.

b. H_2 permeabilities were measured at the temperature of 298K. The TLCP reported in reference 1 has similar structure as Vectra A950.

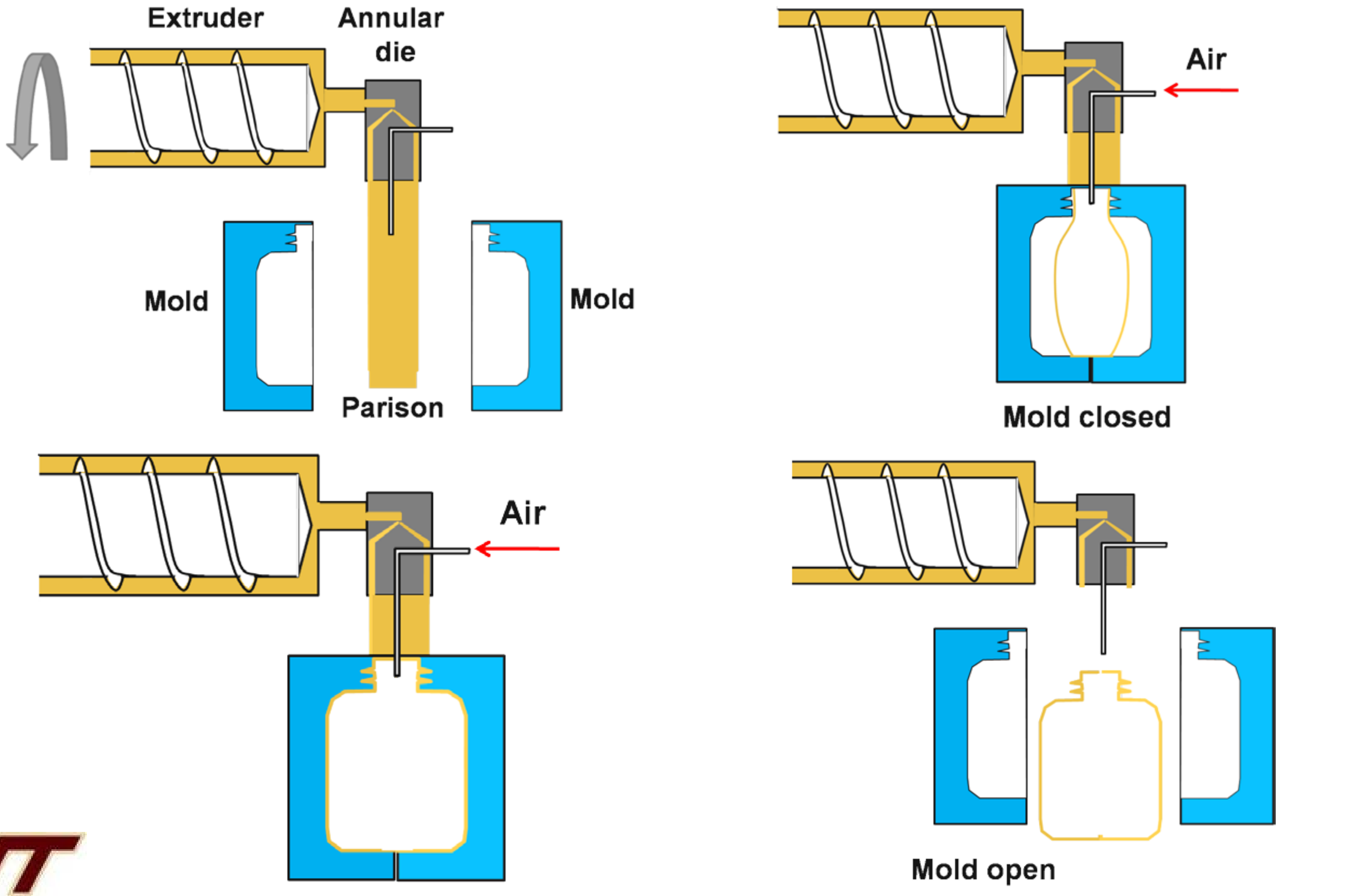
1. Chiou, J. S. *et al. Journal of Polymer Science Part B: Polymer Physics* **1987**, *25*, 1699.
2. Humpenoider, J. *Cryogenics* **1998**, *38*, 143.

Approach

	Milestones, Deliverables, or Go/No-Go Decision	Progress Notes	% Complete
Processing	Virginia Tech will process TLCPs through a range of process variables including nanofiller concentration, extrusion temperatures, % stretch.	• Over 20 TLCP extrusion/injection molded samples prepared using a range of TLCP chemistries (HX-8000, Vectra A950[Vectra A130 & A230]), nanofiller concentrations (Nanocyl CNT 0%, 1%, 3%, 5% & glass fiber), extrusion temperatures with samples along both machine (flow) and transverse directions has been completed • Over 15 TLCP stretch blow molded bottles were prepared and shipped to SRNL for analysis • Preparation of TLCP plaques with nanofiller loading of up to 15% is in process	90% (April 2014)
Material Characterization	SRNL completes mechanical testing (yield strength, ultimate tensile strength) and thermal conductivity of TLCP material samples manufactured by Virginia Tech and both SRNL and Virgina Tech evaluate the test results to determine the potential use of TLCP as a load-sharing liner for a composite hydrogen tank.	• Mechanical analysis of injection molded plaques completed; blow molded bottle samples currently being analyzed • Thermal Diffusivity measurements were initiated	80% (April 2014)

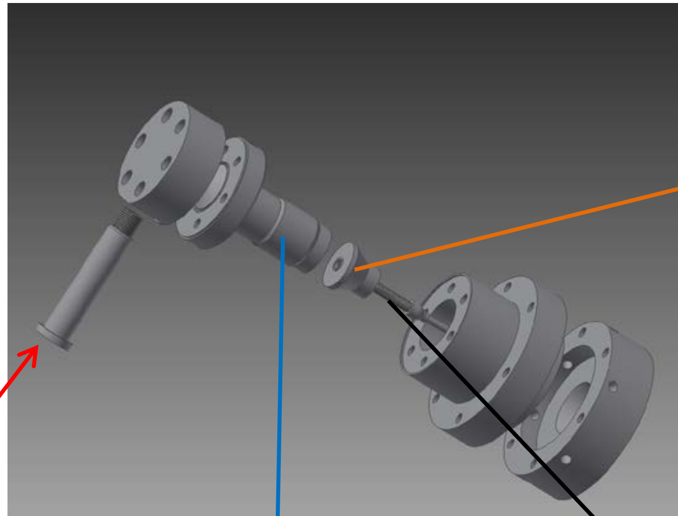
Approach

Extrusion Blow Molding Process



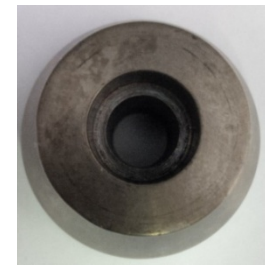
Approach

Controlling Article Properties - Annular Die Assembly



Polymer melt inlet

Mandrel tip



TLCP melt converges. Bottle thickness can be controlled by selecting different mandrel tips.

Mandrel

Air inlet

TLCP melt diverges radically from mandrel top, and splits at four spider support legs (circled with red).

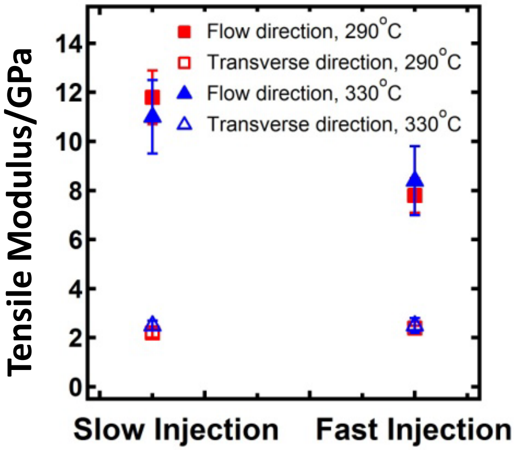
Air needle

Air flows in from the air inlet on the mandrel, escaping from the air needle, inflating parison into the hollow mold.

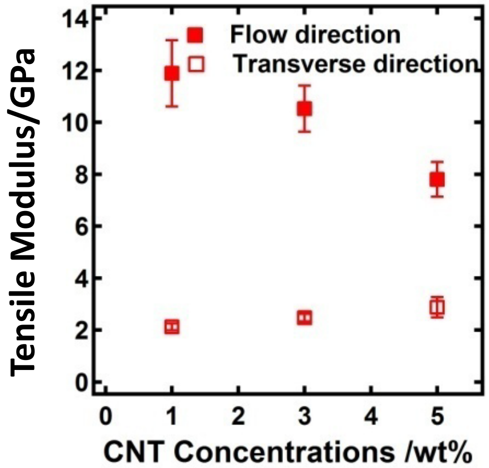
Technical Progress

Nanofiller modification exhibits increased modulus in injection molded TLCP plaques

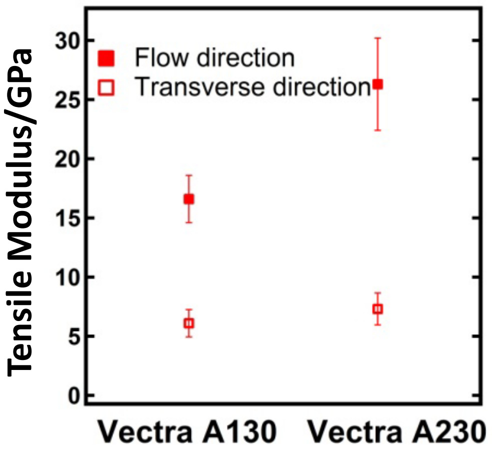
Effect of Nanofillers on Tensile Modulus



unfilled HX-8000



directly blended Nanocyl CNT/HX-8000;
slow injection molded at ~300°C



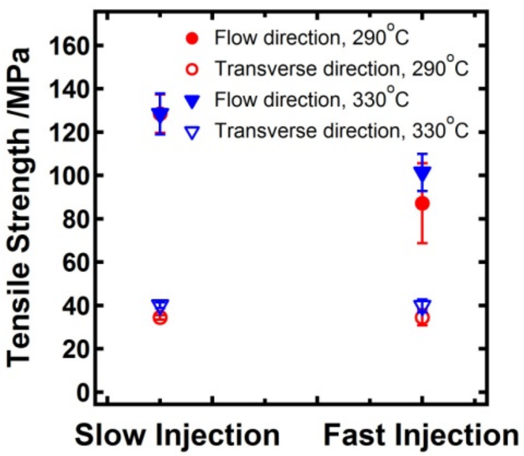
30 wt% glass fiber reinforced Vectra A950

Bubble formation because of trapped gas during pellet melting or nanofiller incorporation causing voids. Could be resolved by purging or agitation.

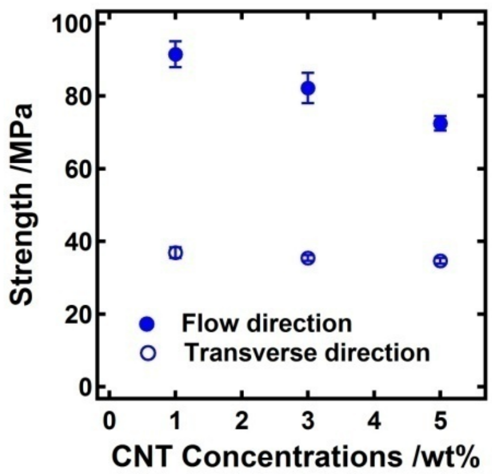
Technical Progress

Void formation during extrusion limits tensile strength of injection molded plaques

Effect of Nanofillers on Tensile Strength



unfilled HX-8000



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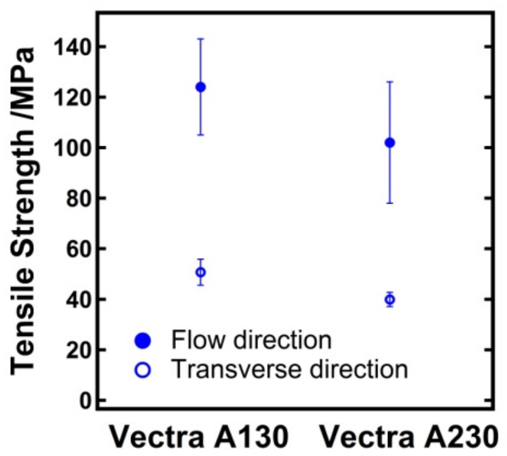
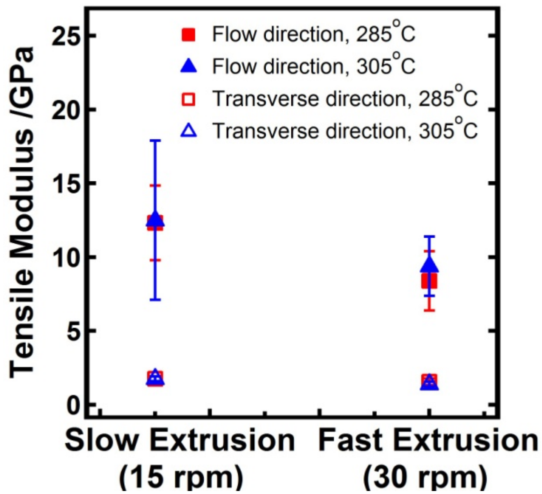


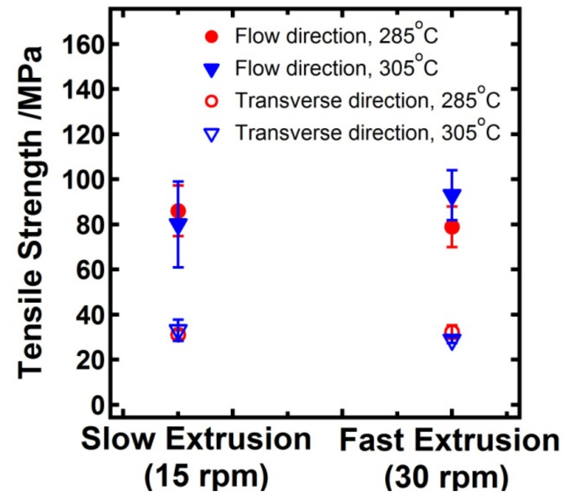
30 wt% glass fiber reinforced Vectra A950

Technical Progress

Stretch Blow Molded TLCPs demonstrate reasonable tensile properties

Effect of Nanofillers on Tensile Properties of bottles



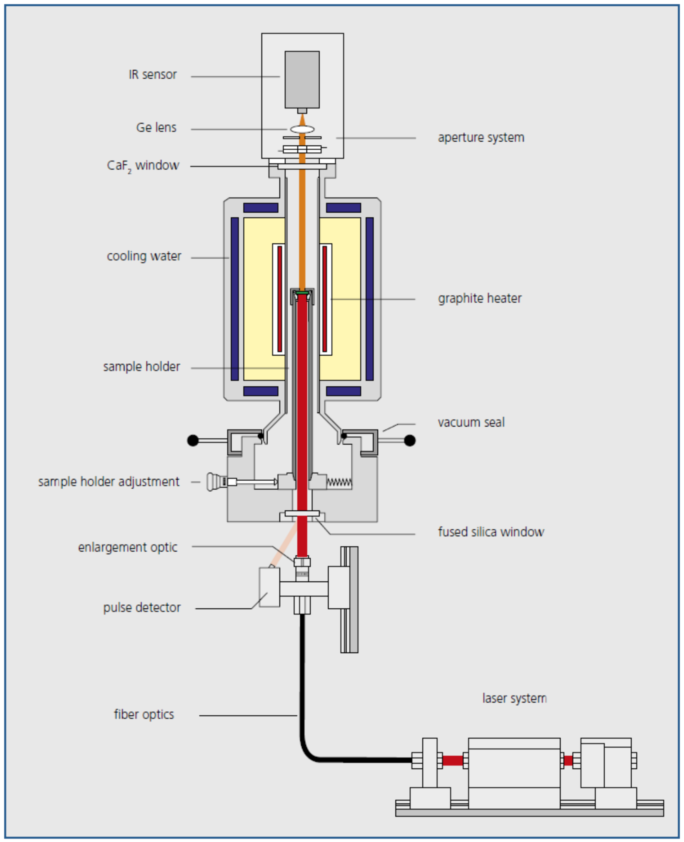


Mechanical properties are limited by stretch and blow up ratios of current equipment. Tests are underway with a smaller mandrel tip to increase blow up ratio and device to increase stretch during extrusion. However, minimal voids were observed in base TLCP bottles.

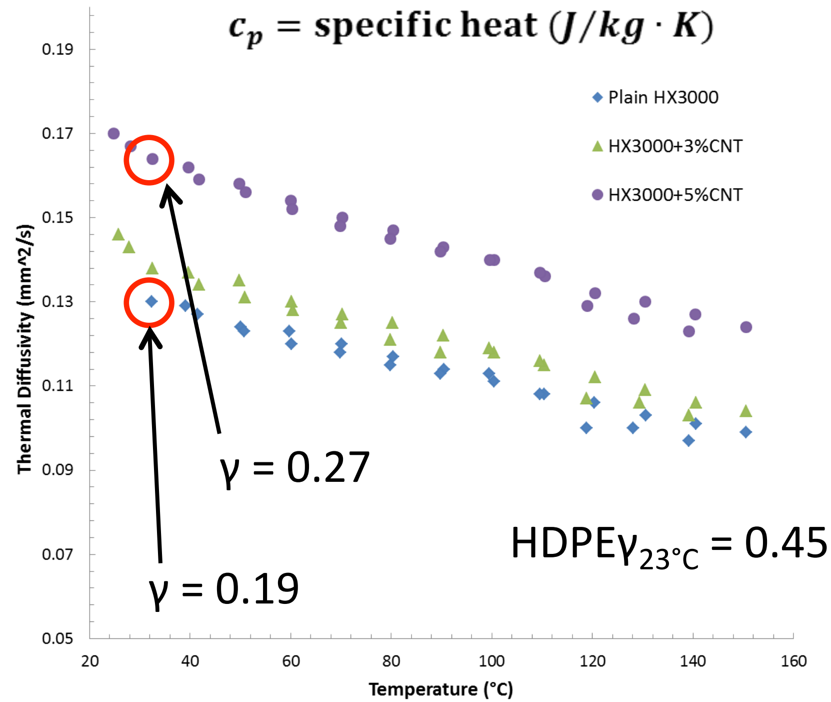
Technical Progress

Nanofiller modification indicates route to increased thermal conductivity

Laser Flash Thermal Diffusivity measurements of Nanofiller Modified TLCPs



$$\gamma(\tau) = \alpha(\tau) \cdot \rho(\tau) \cdot c_p(\tau)$$
$$\gamma = \text{thermal conductivity } (W/m \cdot K)$$
$$\alpha = \text{thermal diffusivity } (m^2/s)$$
$$\rho = \text{density } (kg/m^3)$$
$$c_p = \text{specific heat } (J/kg \cdot K)$$



R.A. Hauser, 2008 Dissertation, MTU, demonstrated increases of 20X in TLCPs

Collaborations

- **Savannah River National Laboratory**
  - Project Management
  - Mechanical and Thermal Property Measurements
- **Virginia Tech**
  - Subcontract to SRNL
  - Prof. Don Baird
  - Polymer Processing, Mechanical and Rheological Measurements
- **Celanese Corporation**
  - Providing support through donation of materials

Remaining Challenges and Barriers

- Resolve void formation while incorporating nanofillers that will allow increased tensile, thermal and processing properties
- Incorporation of higher amounts (~15wt%) of nanofillers to significantly enhance thermal properties
- Designing device to hold and stretch parison during extrusion that will give enhanced mechanical properties through alignment of nanofillers and polymer fibrils

Proposed Future Work

- Injection mold TLCP plaques with up to 15 wt% CNT for further thermal diffusivity screening
- Demonstrate processing parameters to stretch blow mold nanofiller modified TLCP bottles with minimum voids
- Continue measuring tensile and thermal properties of nanofiller modified stretch blow molded TLCP bottles
- Document findings in final report

Summary

During the past 6 months the SRNL/VT has:

- Demonstrated injection molding parameters for initial nanofiller modified TLCP plaques that show increases in mechanical and thermal properties; however, voids limit properties;
- Demonstrated stretch blow molding parameters to produce almost void free bottles from base TLCPs that show reasonable tensile properties; and
- Initiated thermal diffusivity measurements to characterize the through-plane thermal conductivity of the nanofiller enhanced TLCPs and established a route to increase the thermal conductivity of the TLCPs.