IV.F.5 Load-Sharing Polymeric Liner for Hydrogen Storage Composite Tanks

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Overall and Fiscal Year (FY) 2014 Objectives

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

Technical Barriers

This project addresses the following technical barriers from the Hydrogen Storage section of the Fuel Cell Technologies Office Multi-Year Research, Development, and Demonstration Plan:

(B) System Cost

(E) Charging/Discharging Rates

(G) Materials of Construction

(J) Thermal Management

Technical Targets

This project is addressing the needs of compressed gas storage through fundamental material development that shows potential to meet the targets. The goal of the project was to investigate the idea of using nanofilled thermotropic liquid crystalline polymers (TLCPs) for advanced liners and collect data to demonstrate concept feasibility and not to explicitly address specific targets. However, insights gained from these studies will be applied toward the design and synthesis of advanced polymeric liner materials that meet the following DOE 2017 hydrogen storage targets:

- Storage System Cost — \$12 kWh_{net}
- Min/Max Delivery Temp — -40/85°C
- System fill time (5 kg) — 3.3 min
- Loss of Usable H_2 — 0.05 $(g/H_2)/kg\ H_2$ stored

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INTRODUCTION

Currently, Type IV hydrogen storage tanks, are designed for operational pressures between 350 and 700 bar of compressed gas service that utilize a composite overwrap for reinforcement that is fabricated using expensive aerospace-grade carbon fiber, such as Toray T700S, around a no-load bearing polymeric liner, commonly high density polyethylene (HDPE). While the use of carbon fiber composite overwraps coupled with lightweight, inexpensive no-load bearing liners can significantly lower the weight of high-pressure cylinders compared to all-metallic, analyses have shown that the cost of the carbon fiber composite layer [1] and the limited heat transfer of the liner [2] can add significant cost and complexity to the tank and off-board refueling processes. Furthermore, hydrogen exhibits a reverse Joule-Thomson effect during 700-bar refueling from high-pressure stationary tanks causing heating of the gas, especially during fast-fill protocols that require 5.6-kg of hydrogen be transferred in 3.3 min where the gas temperature inside the tank can rise over 50ºC; adversely affecting the liner and composite integrity when starting at ambient conditions [3]. To compensate for the increase in gas temperature, the gas must be precooled to -40ºC and the tank overpressurized to ensure a complete fill once equilibrium is reached which adds costs from additional energy for refrigeration and compression of more than 20% of the nominal work of compression. Analysis by the Argonne National Laboratory [2] has demonstrated the effect of liner thermal conductivity on gas temperature during a 700-bar fast-fill scenario and projected that a five- to ten-fold increase in the HDPE liner thermal conductivity would have the potential to reduce the liner and gas temperatures by up to 20ºC.

The focus of this project is to demonstrate a viable method to producing a low-cost, high-strength, polymeric load-sharing liner that will allow displacement of expensive aerospace-grade carbon fiber, reducing the cost and mass of the tank, as well as increasing the thermal conductivity of the liner material compared to that of HDPE, thus reducing the impact of precooling and overpressurizing hydrogen during fast-fill refueling to 700-bar.

APPROACH

TLCP liner plaques and bottles (material samples) were injection stretch blow molded by Virginia Tech under various conditions. Zenite is a class of TLCPs originally developed by DuPont™, then bought by Ticona/Celanese. Zenite molecules contain various amounts of 4-hydroxy benzoic acid, terephthalic acid and hydroquinone, but the detailed monomer contents belong to the proprietor. Three grades of Zenite series were used in this project: HX-8000 has a melting temperature of 280°C, HX-3000 and HX-6000 are high melting grades, with melting points around 330°C. Fiber-reinforced Vectra materials were kindly supplied by Ticona/Celanese. Both Vectra A130 and Vectra A230 are based on the same matrix, Vectra A950. Vectra A130 contains 30 wt% short glass fibers, while Vectra A230 is reinforced by 30 wt% short carbon fibers. The composite matrix, Vectra A950, is probably the most extensively discussed commercial TLCP in the literature, which is a copolyester composed of 73 mol% 4-hydroxy benzoic acid and 27 mol% 2-hydroxy-6-naphthoic acid. Due to the lack of a nondisclosure agreement with Celanese in this project, Vectra A950 was not available.

For the samples, three rates of fill (chosen by Virginia Tech) were selected to demonstrate the influence on the initial orientation of the TLCPs. A subsection of samples were heated and subjected to moderate and substantial degrees of stretch in both the axial (machine) direction and the transverse (hoop) direction to generate samples with varying strength as a function of orientation. Samples were also fabricated with varying concentrations of carbon nano-tube and glass fillers to provide initial data on the effect of nanofillers on the mechanical strength of injection molded TLCPs while simultaneously increasing the thermal conductivity. The mechanical and thermal properties of the plaques were measured by Virginia Tech and SRNL using dynamic mechanical analysis, tensile testing and thermal diffusivity, to assess the effect of the processing variables described above.

FY 2014 ACCOMPLISHMENTS

To understand the influence of processing histories on the mechanical properties of unfilled and fiber-reinforced TLCP materials, three materials were injection molded: HX-8000, Vectra A130 and Vectra A230 and mechanical data are shown in Figure 1a-f. Significant tensile property anisotropy can be observed from the mechanical measurements, which could be problematic in hydrogen fuel storage. It seems the longitudinal properties decrease as extrusion speed is increased (Figures 1a and 1d). The injection molded plaques were found to consist of three main sublayers: two skin layers

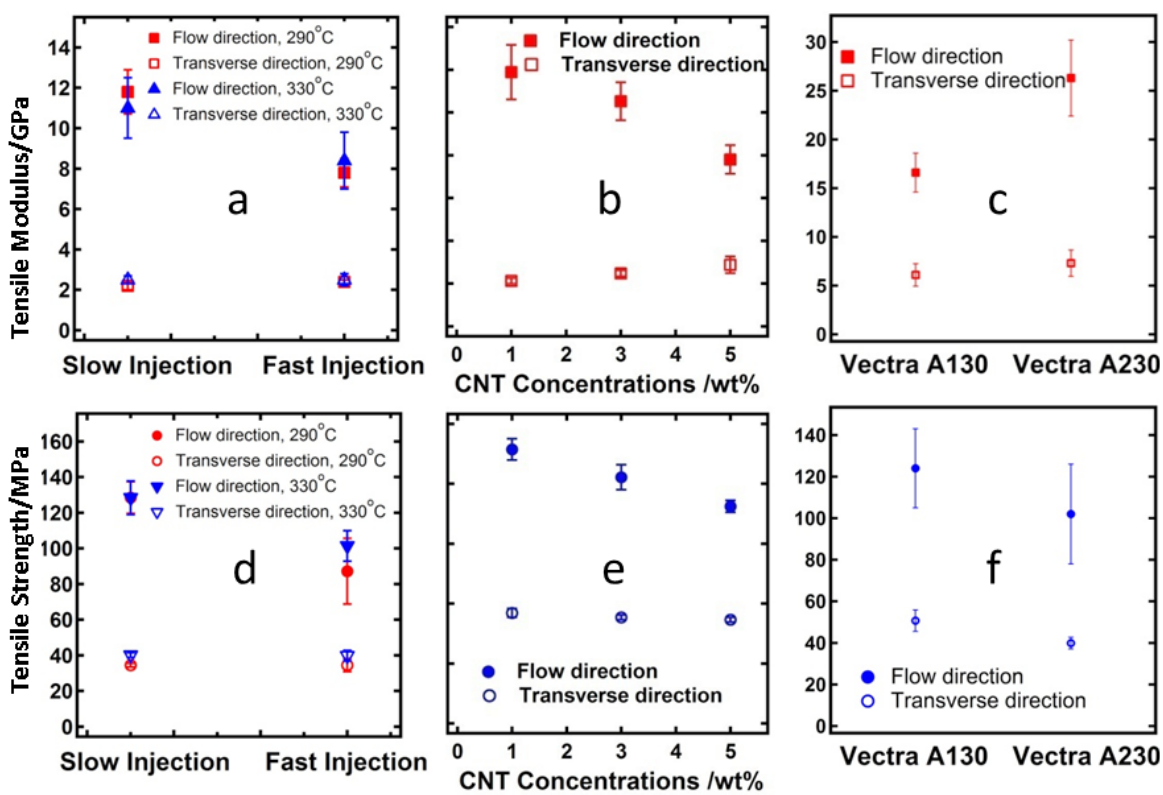

FIGURE 1. Tensile properties of initial blending and extrusion of TLCPs; (a/d) effect of injection speed on unfilled HX-8000, (b/e) effect of nanofiller addition to HX-8000 and (c/f) glass-filled Vectra A130 and A230.

with more oriented molecules and a more isotropic core layer in between, each layer accounted for approximately one-third of the total thickness. High shear stress near the mold wall and the elongation flow field at the flow front ("fountain" flow) are responsible for the formation of the highly oriented skin layers. On the other hand, the core region possesses an overall in-plane random orientation. The tensile modulus in the machine direction shows an increasing trend with slower injection speed and lower barrel temperature (closer to nominal melting point) (Figure 1a). Intuitively, higher injection speeds lead to a higher degree of orientation. However, it is worth noting that the higher injection speeds require a longer time to cool the melt, which leaves the nematic melt more time for orientation relaxation. The relaxed orientation leads to reduced mechanical properties at higher injection speeds as observed in Figure 1a/d.

To determine effect of nanofillers, the maximum carbon nanotube (CNT) concentration is mainly limited by the CNT induced viscosity increment and the CNT concentration gradient in the hopper (low CNT bulk density). For TLCP nanocomposites, the low viscosity of the matrix benefits the extrusion. However, in the hopper the low-density CNTs float above the polymer pellets bed, making extrusion at high CNT concentrations rather challenging so that 5 wt% is the highest possible concentration for $scCO_2$-treated Nanocyl CNT. Shown in Figures 1b/e, as CNT concentrations increase, the modulus and strength in the flow direction exhibits a decreasing trend. The only improvement is observed in the transverse modulus. Lack of surface interaction between the CNT and the polymer matrix is speculated to be the cause for the worse mechanical properties. Thus surface modification of CNTs might be necessary.

Although the lack of unfilled Vectra A130/230 makes the fiber induced property increments difficult to calculate, our objective was to choose materials with superior properties and use them for extrusion blow molding. Thus it is still fair to take the properties of HX-8000 as reference. As clearly indicated in Figure 1c/f, fiber reinforced grades exhibit much better modulus in the flow direction than HX-8000, especially for the carbon fiber composite. Moreover, the transverse moduli are much higher for Vectra A130/230 as well. For overall strength, the fiber reinforced grades are only slightly better. However, the higher melt strength of these materials could be advantageous over the unfilled grades.

Determining the most appropriate die temperature serves as a key to the success of blow molding. The die temperature has to be lower than the melting temperatures of the TLCPs, thus the parisons are in their supercooled state to obtain enough melt strength. On the other hand, if the die temperature is too low, the parisons start to solidify, which makes completion of inflation impossible. The HX-8000 bottles were successfully blow molded and are pictured in Figure 3. With the mold that is currently used, the blow up ratio (bottle diameter to parison diameter) is 1.75.

Thermal conductivity in polymers is predominantly transferred by lattice vibrations with electron transport also occurring slightly. The factors that affect the thermal conductivity in a polymer composite are the filler size, shape, concentration, dispersion (degree of mixing), orientation, bonding between the filler and polymer matrix, thermal conductivity of the constituents (filler and matrix) and the crystallinity of the polymer (increasing crystallinity improves thermal conductivity). Studies were initiated in FY 2014 to determine the thermal conductivity of the unfilled and filled

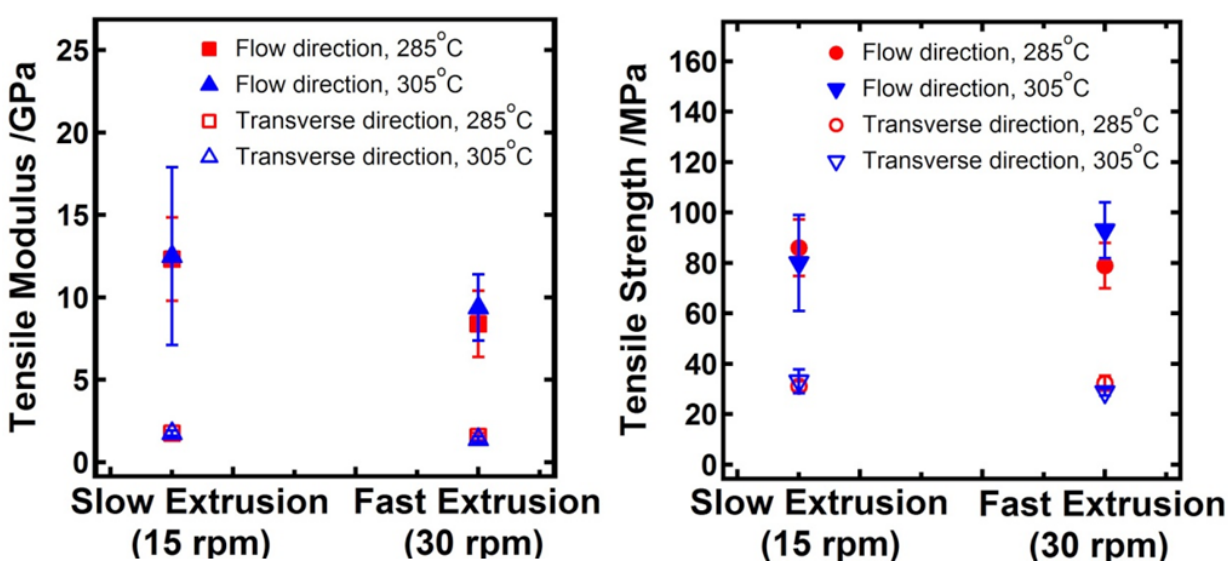

FIGURE 2. Tensile properties, (a) modulus and (b) strength, of blow-molded HX-8000 bottles as a function of extrusion barrel temperatures and extrusion speed.

FIGURE 3. Images of a stretch blow-molded HX-8000 bottle showing the weld lines at mold interfaces. Blow-up ratio (bottle diameter to parison diameter) of 1.75.

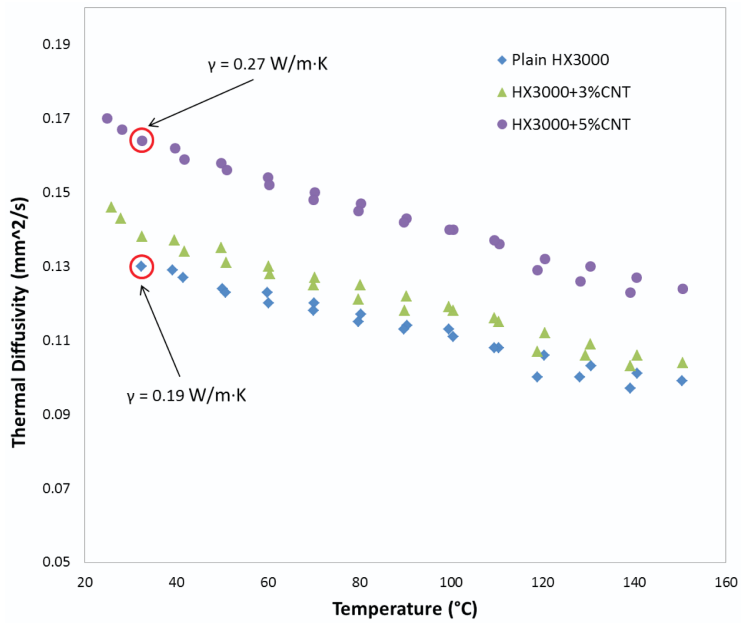

FIGURE 4. Thermal diffusivity of unfilled and CNT-filled HX-3000 between room temperature and 140°C, measured using laser flash diffusivity.

TLCP plaques created for mechanical property improvement and develop a path to increasing the thermal conductivity of the materials. In this case, laser flash thermal diffusivity was used to measure the conductance of heat through 10-mm rounds of TLCP (HX-3000 polymer was chosen due to availability) samples with the data shown in Figure 4. The samples demonstrated a significant increase in the thermal diffusivity which could be indicative of the orientational alignment due to stretching and incorporation of the CNT fillers. However, the magnitude of the highest sample tested at the time of the report (5 wt% CNT loading, 0.27 W/m-K) was almost half of the calculated thermal conductivity of HDPE (0.45 W/m-K) when measured at 23°C. Increasing the blow up ratio and optimizing nanofiller incorporation are expected to give further increases in thermal conductivity creating highly oriented crystal structure that would exceed the values of HDPE.

In summary, the accomplishments of the SRNL and Virginia Tech team during FY 2014 were the following;

- 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 nearly void free bottles from base TLCPs that show reasonable tensile properties.
- 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.

FUTURE DIRECTIONS

- 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 high blow ratios.
- Demonstrate processing parameters to stretch blow mold modified TLCP blends.
- Continue measuring tensile and thermal properties of nanofiller modified stretch blow molded TLCP bottles.
- Document findings in final report to serve as a basis for future efforts in advanced liner materials.

FY 2014 PUBLICATIONS/PRESENTATIONS

1. McWhorter, S., Baird, D.B., Adams, T., Rawls, G. "Load-sharing Polymeric Liner for Hydrogen Storage Composite Tanks." *2014 US DOE Hydrogen and Fuel Cells Program Annual Merit Review.* Washington, DC: June 2014.

REFERENCES

1. James, B.D., Moton, J.M., Colella, W.G. "Hydrogen Storage Cost Analysis." *Proceedings of the 2013 US DOE Hydrogen and Fuel Cells Program Annual Merit Review.* Crystal City, VA: June 2013. [Online]. [Accessed July 2014] Available: http://www.hydrogen.energy.gov/pdfs/review13/st100_james_2013_o.pdf.

2. Ahluwalia, R.K., Hua, T.Q., Peng, J-K., Roh, H.S. "System Level Analysis of Hydrogen Storage Options" *Proceedings of the 2012 US DOE Hydrogen and Fuel Cells Program Annual Merit Review.* Crystal City, VA: June 2013. [Online][Accessed July 2014]. Available: http://www.hydrogen.energy.gov/pdfs/review12/st001_ahluwalia_2012_o.pdf.

3. Zhang, J., Fisher, T.S., Ramachandran, P.V., Gore, J.P. and Mudawar, I., "A Review of Heat Transfer Issues in Hydrogen Storage Technologies," J. of Heat Transfer (2005), 127: 1391.