CAAP Quarterly Report

July 15, 2025

Project Name: Selection and Development of Safer Polymer and Composite Pipeline Liners through Microstructural and Macroscopic Study of Materials and Designs

Contract Number: 693JK32250001CAAP

Prime University: Brown University

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Reporting Period: Q9

Project Activities for Reporting Period:

During this quarter in the Poling-Skutvik lab, samples under the NG2 gas mixture for different periods of time—7, 14, and 30 days—at elevated temperature (90 °C) and pressure (250 psi) were aged. We then completed measurements of the aged samples to assess their mechanical and thermal properties. The key difference between this gas mixture and NG1 is the presence of oxygen in NG2. Figure 1 shows the normalized modulus of the samples. Compared to NG1, although there is some fluctuation in the results, particularly for the PA sample, we observed an overall decrease in the modulus of the polymer samples. Figure 2 presents the activation energy of the polymers. It appears that under NG2, the activation energy reaches its minimum value after just 7 days, whereas under NG1, it took 30 days to reach a similar level. Beyond that point, the values plateau, indicating that the activation energy does not decrease further.

A paper titled "Environmental aging of polymers to evaluate their potential for remediating natural gas pipelines" was submitted for peer review for publication.

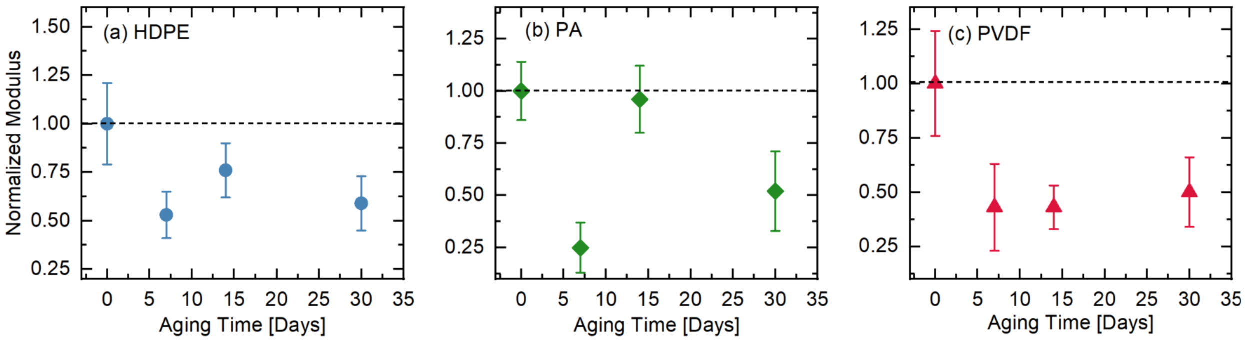

Figure 1: Normalized modulus of (a) HDPE, (b) PA and (c) PVDF.

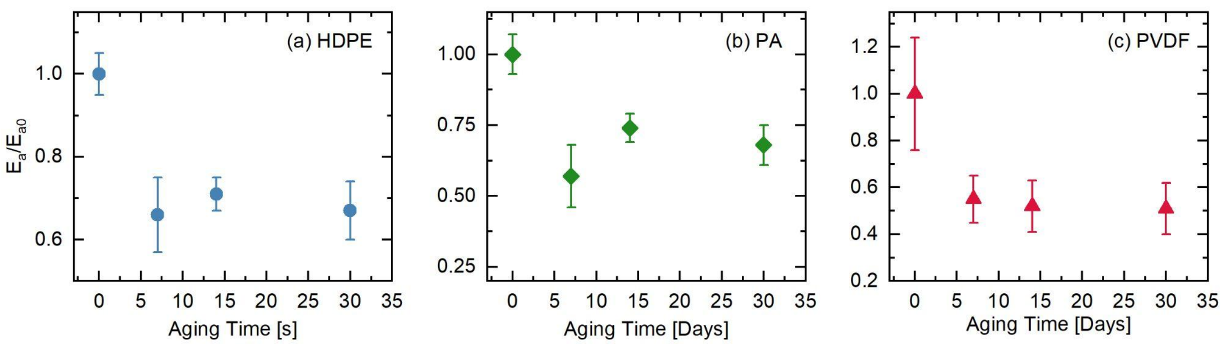

Figure 2: Activation energy of (a) HDPE, (b) PA and (c) PVDF.

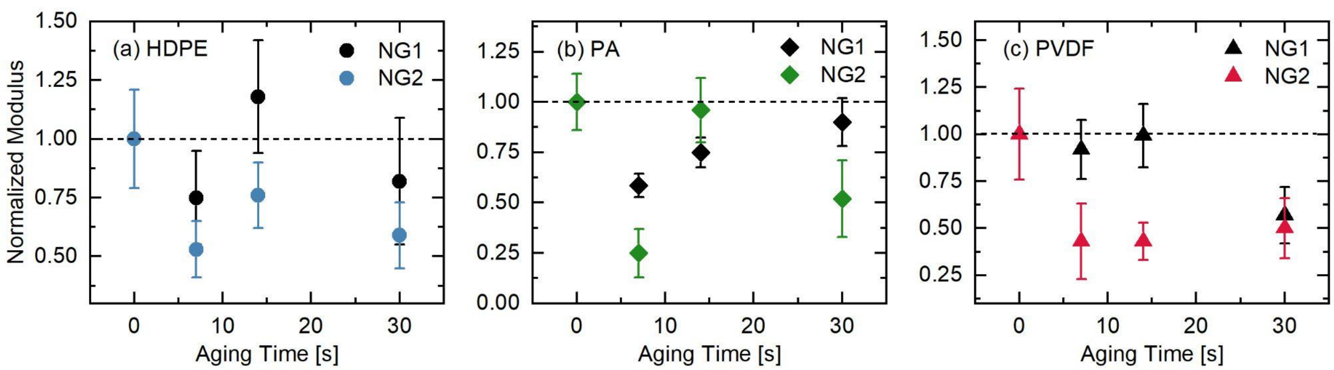

Figure 3: Comparing the normalized modulus of (a) HDPE, (b) PA and (c) PVDF for NG1 and NG2.

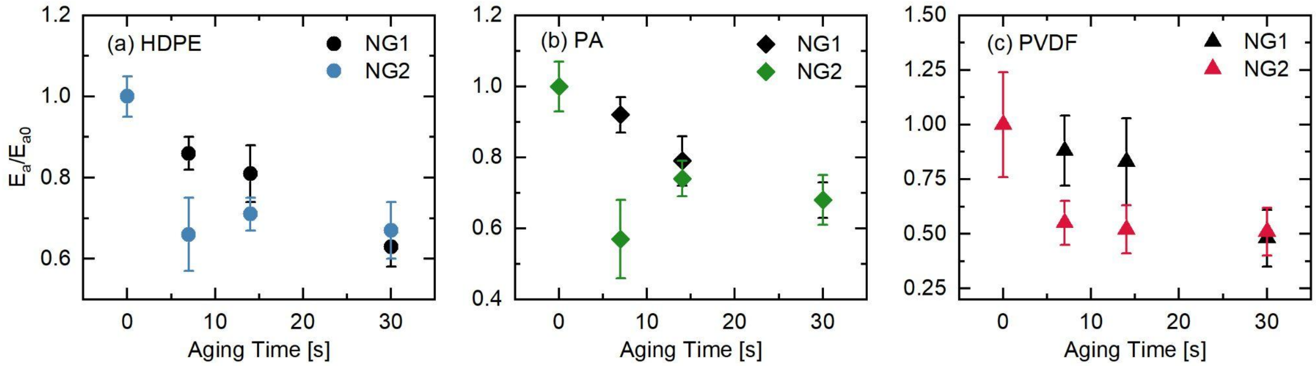

Figure 4: Comparing the activation energy of (a) HDPE, (b) PA and (c) PVDF for NG1 and NG2.

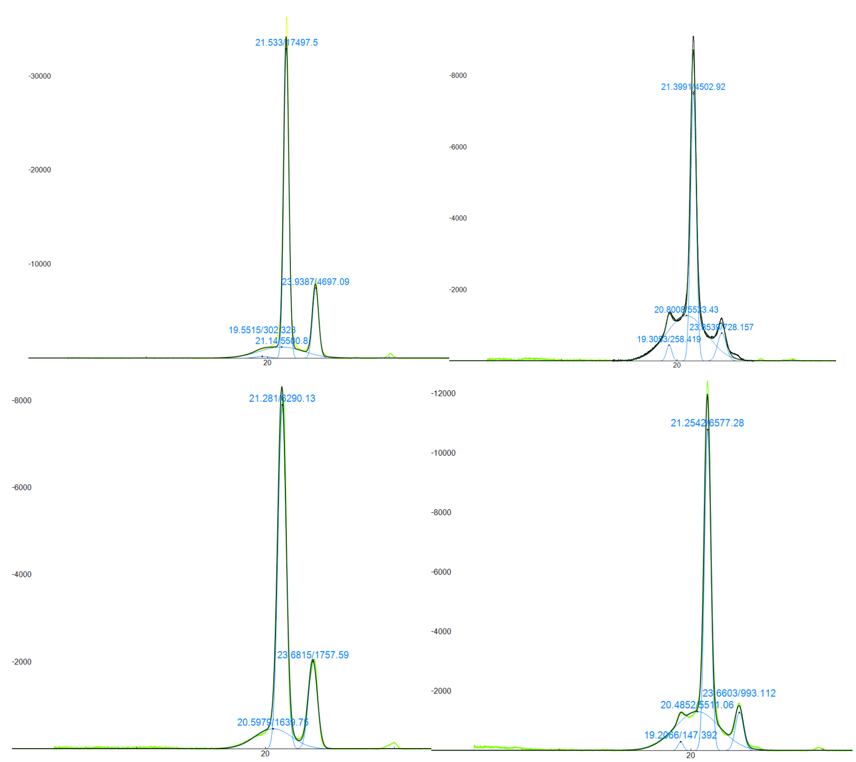

Figure 5**:** Unaged HDPE Notch (intact), Unaged HDPE Necking Region, 1 Month NG2 Notch (intact), 1 Month NG2 Necking Region

X-ray Diffraction (XRD) analysis was performed on high-density polyethylene (HDPE) samples to investigate the effects of natural gas aging on their crystalline structure, particularly in regions subjected to mechanical stress. Samples included both unaged and aged specimens (1 week, 2 weeks, and 1 month of exposure to natural gas), with scans conducted on both intact notched areas and the corresponding mechanical fracture surfaces.

All samples, including unaged and unfractured specimens, exhibited the two characteristic diffraction peaks of HDPE, typically observed around 2θ values of 21.5° and 24.0°.

In the necking region of both unaged and aged samples, a notable change in the diffraction pattern was observed. A distinct peak emerged at approximately $2\theta = 19.5°$, positioned to the right of the primary HDPE peak ($2\theta \approx 21.5°$). Concurrently, a decrease in the intensity of the secondary HDPE peak ($2\theta \approx 24.0°$) was evident. These observations are illustrated in Figure X, showing similar morphology in the notch areas of unaged and 1 month aged samples (XA and XC) and similar morphology in the fracture areas of these samples (XB and XD).

Across all mechanically broken (failed) sections, there was a general decrease in the intensity of diffractions corresponding to the crystalline regions, while the intensity of the amorphous halo remained relatively unchanged. Subsequent deconvolution of the XRD patterns confirmed this trend, revealing a consistent increase in the amorphous content within the mechanically fractured areas of the HDPE samples, regardless of aging duration. These findings suggest that mechanical deformation, particularly in the necking region, induces structural changes in HDPE, leading to a reduction in crystallinity and an increase in the amorphous phase. The appearance of the peak 19.3 2θ has been previously documented in literature, where significant deformation was experienced by HDPE samples[1]

During this quarter in the Srivastava lab, we conducted a detailed characterization of the deformation and fracture behavior of three polymers—HDPE, PA, and PVDF—through mechanical uniaxial tension tests. The polymer samples were exposed to the NG2 gaseous mixture at 90 ℃ and 250 psi for durations of 7, 14, and 30 days. To evaluate the deformation response of the aged polymers, tensile tests were conducted at three different strain rates (0.0005 s^{-1}, 0.005 s^{-1}, and 0.05 s^{-1}) using ASTM D638 Type V dogbone specimens. To investigate fracture behavior, additional tensile tests were performed on notched rectangular specimens at a loading rate of 0.0095 mm/s, where the samples were loaded until complete failure. To compare the changes in mechanical properties (Young's modulus and yield stress) over aging durations, one-way ANOVA was performed to assess statistical significance, indicated by p-values: $p < 0.05$ (*), $p < 0.01$ (**), and $p < 0.001$ (***). In Figures 6, 7, and 8, we present the variation of mechanical properties for HDPE, PA, and PVDF. Subfigures (a–c) show the Young's modulus, and (d–f) show the yield stress, both as functions of aging duration across increasing strain rates. Subfigure (g) depicts the force-displacement response of notched specimens for different aging durations. For HDPE, the deformation response remains largely consistent across aging durations. Although some statistically significant variations are observed in Figures 6(e) and 6(f), no clear trend emerges. We have also started to conduct fracture experiments on the notched HDPE samples. We are continuing to conduct additional tests on HDPE to get more data, which will be presented in future reports. For PA and PVDF, we observe statistically significant differences in Young's modulus and yield stress at the intermediate strain rate, differences that are not present at the lowest and highest strain rates. The force-displacement responses of the notched samples for both PA and PVDF when tested to fracture failure do not show any significant changes due to aging.

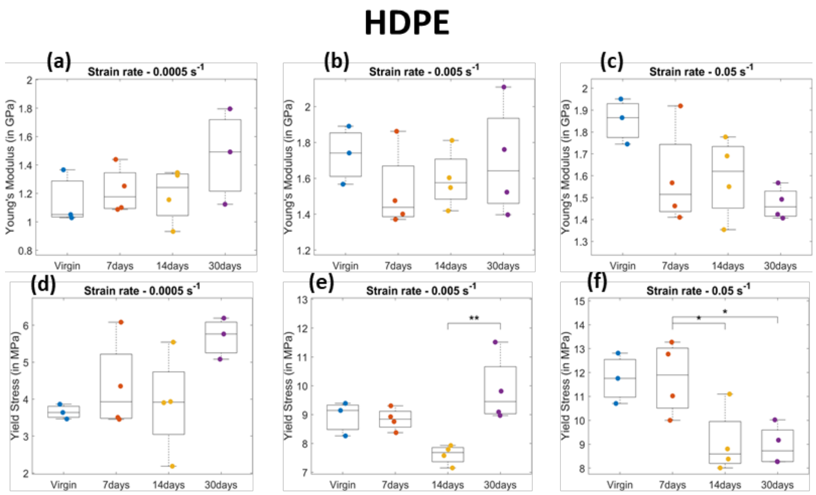

Figure 6: (a–c) Young’s modulus of HDPE measured at strain rates: (a) 0.0005 s⁻¹, (b) 0.005 s⁻¹, and (c) 0.05 s⁻¹
(d–f) Yield stress of HDPE measured at strain rates: (d) 0.0005 s⁻¹, (e) 0.005 s⁻¹, and (f) 0.05 s⁻¹

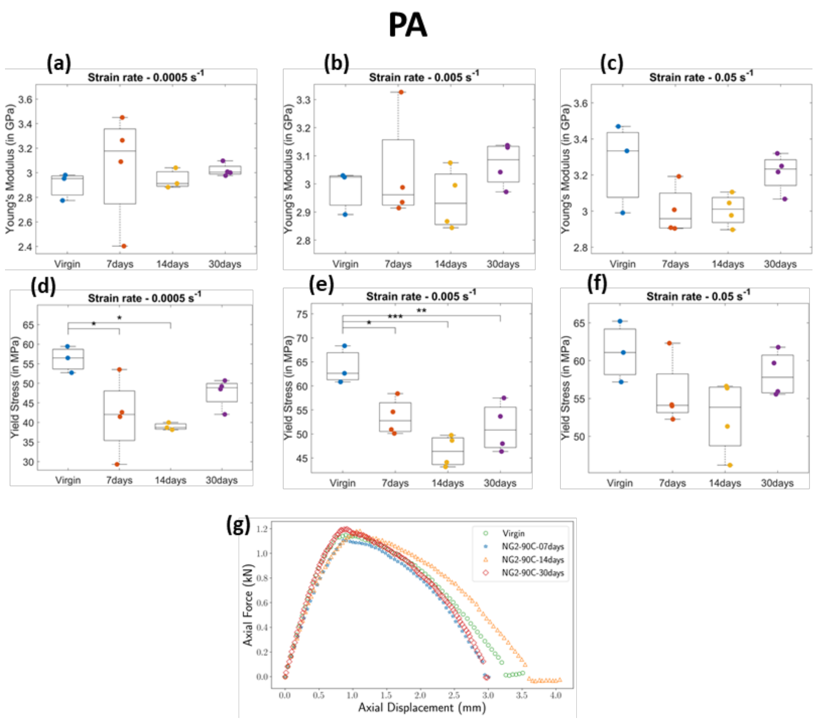

Figure 7: (a–c) Young’s modulus of PA measured at strain rates: (a) 0.0005 s⁻¹, (b) 0.005 s⁻¹, and (c) 0.05 s⁻¹
(d–f) Yield stress of PA measured at strain rates: (d) 0.0005 s⁻¹, (e) 0.005 s⁻¹, and (f) 0.05 s⁻¹
(g) Force-displacement response of PA over different aging durations

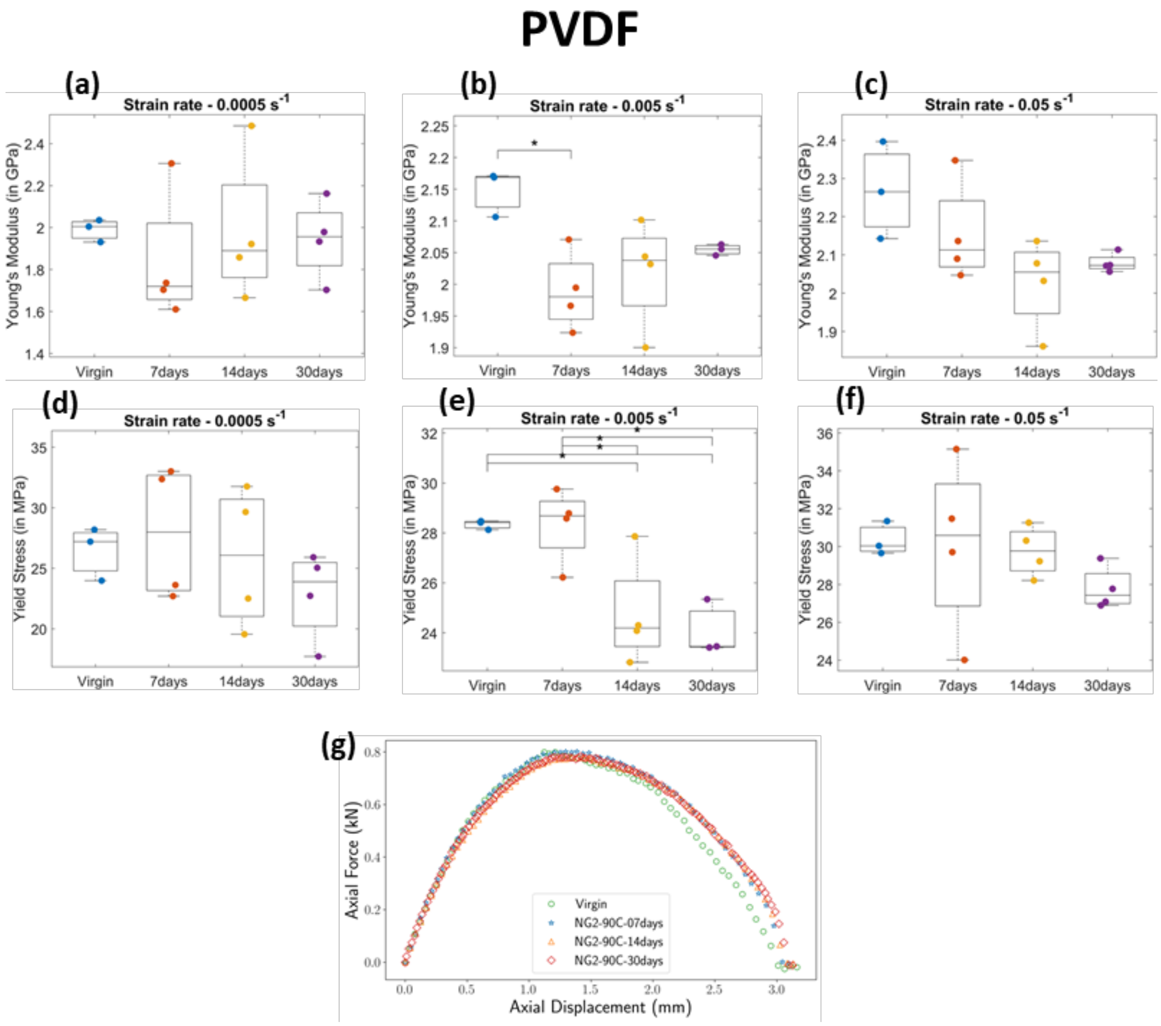

Figure 8: (a–c) Young's modulus of PVDF measured at strain rates: (a) 0.0005 s^{-1}, (b) 0.005 s^{-1}, and (c) 0.05 s^{-1}
(d–f) Yield stress of PVDF measured at strain rates: (d) 0.0005 s^{-1}, (e) 0.005 s^{-1}, and (f) 0.05 s^{-1}
(g) Force-displacement response of PVDF over different aging durations

Project Financial Activities Incurred during the Reporting Period:

Table 1 below summarizes the project financial activities incurred during the ninth quarter of the project.

Table 1 Summary of Q9 DOT Funded Spending Annual Report-03/28/2025-06/30/2025				
Institution		Amount ($)	Amount ($)	Subtotal ($)
Brown University	Category	Salary ($)	Fringe ($)	
	PI	3,120.03	920.41	4,040.44
	Co-PI	0.00	0.00	-
	Postdoc	0.00	0.00	-
	Graduate Students	15,297.51	529.40	15,826.91
	Undergraduate Students	0.00	0	-
	Graduate Student Fees			(2,553.88)
	Facility Usage			8,691.25
	Purchased Services			-
	Materials and Supplies			1,378.73
	Travel			-
	Equipment			-
	Total Direct			27,383.45
	Indirect			17,812.77
	Subtotal			**45,196.22**
University of Rhode Island	Personnel	Salary ($)	Fringe ($)	
	Salaries	6,909.00	949.98	7,858.98
	Operating Expenditures			57.78
	Travel			879.75
	Student Aid			-
	Total Direct			8,796.51
	Indirect			5,058.02
	Subtotal			**13,854.53**
Total				**59,050.75**

Table 2 Summary of Q9 Cost Sharing Spending Annual Report-03/28/2025-06/30/2025				
Institution		Amount ($)	Amount ($)	Subtotal ($)
Brown University	Category	Salary ($)	Fringe ($)	
	Graduate Student Tuition			18,067.84
	Subtotal			**18,067.84**
University of Rhode Island	Direct Costs			3,442.86
	Indirect			1,979.64
	Subtotal			**5,422.50**
Total				**23,490.34**

Project Activities with Cost Share Partners:

The universities continue to provide partial support for graduate students as per the cost-share agreement. Overall project cost share from URI and Brown University will be 20%.

Project Activities with External Partners:

The PI and Co-PI from Brown University met with the sub-awardee University of Rhode Island (URI) researchers several times this quarter to share the research results and discuss the outcomes. These meetings were also used to discuss future research steps. The team from URI and Brown University shared polymer samples for collaborative testing and characterization.

Potential Project Risks:

As more experimental data are collected, since this is a first study of its kind, there is a risk of unanticipated new findings. This risk will be managed by adjusting the research methods as new data comes. Inconsistencies across individual samples may make morphological conclusions for more macroscopic samples more challenging.

Future Project Work:

We plan to continue to age polymer samples using a hydrocarbon gaseous environment to observe how the properties change under these conditions. These samples will be tested to characterize their mechanical response and any microstructural changes. We will continue working towards publishing a journal paper based on our findings and continuing to test our samples after exposure to more corrosive gases, such as O_2, H_2S, and BTEX.

Potential Impacts to Pipeline Safety:

Previous testing established changes in samples that were established by X-ray diffraction. This method is impractical in the field, with XRD machines being bulky and immobile. If similar measurements can be made with an FTIR, which is a significantly more mobile tool, we can detect phase content changes that may be precursors to mechanical failure in the field.

Additionally, extensive testing of individual samples reveals changes in microstructural properties depending on the location within the sample. This could be an indicator of regions that were impacted differently by the aging process or significant heterogeneity in samples.

The fundamental understanding of liner polymer materials' response, materials properties, and safer liner material guidelines obtained through this collaborative research will help increase the understanding and safety of polymer liners for pipelines.