CAAP Quarterly Report

December 28, 2024

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

Prepared By: Ryan Poling-Skutvik, Edith Mathiowitz, and Vikas Srivastava

PI: Vikas Srivastava, Ph.D.
Email: vikas_srivastava@brown.edu
Phone: 401-863-2863

Co-PI: Ryan Poling-Skutvik, Ph.D.
Email: ryanps@uri.edu
Phone: 401-874-2627

Co-PI: Edith Mathiowitz, Ph.D.
Email: Edith_Mathiowitz@brown.edu
Phone: 401-863-1358

Reporting Period: (Q7)

Project Activities for Reporting Period:

In this quarter in Poling-Skutvik's lab, one of the focuses was preparation of a paper based on our findings so far. Figure 1 shows the storage modulus of HDPE, PA, and PVDF. No clear trend is observed, indicating that the mechanical properties of these materials are not affected by exposure to NG1, which is composed entirely of hydrocarbons.

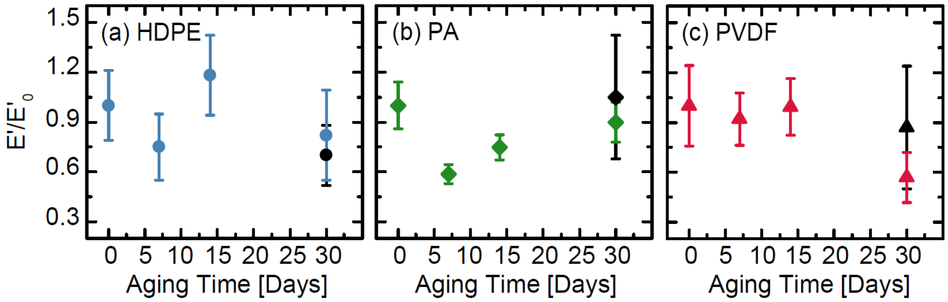

Figure 1- Storage modulus of (a) HDPE, (b) PA and (c) PVDF. Black symbols represent samples aged at 25°C.

However, Figure 2 shows a decreasing trend in the activation energy of these materials. This suggests that activation energy could be a useful indicator for predicting changes in the mechanical properties of polymeric materials.

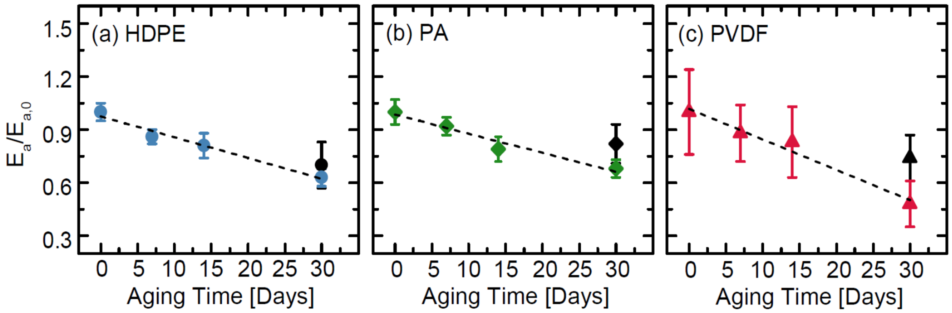

Figure 2- Activation Energy of (a) HDPE, (b) PA and (c) PVDF. Black symbols represent samples aged at 25°C.

This quarter at the Mathiowitz Lab, we began documenting trends across various polymer sample materials. The initial analyses were conducted on samples tested immediately after exposure to gases, aiming to detect the gases trapped inside, primarily using FTIR, before they had a chance to dissipate from the polymer.

In high-density polyethylene (HDPE), the polymer peaks corresponded and overlapped with those of the gas, which would typically be present in much smaller quantities. Comparisons of the C-C and C-H bands were attempted with the expectation that NG1 and NG2 would contribute more significantly to the C-H band intensity (Figure 3). Interestingly, the C-H band at 720 cm^-1 showed a notable increase in select scans, displaying a general upward trend. Similar analysis of the CH2 and CH band peak intensities revealed a small change in the relative intensities between groups, with certain samples—particularly those with the 720 cm^-1 band—showing significant increases compared to the neat samples. Additionally, some aged samples exhibited small peaks at 1640 cm^-1 (S1), indicative of alkene carbons, suggesting degradation of the polymer backbone. However, this phenomenon was inconsistent and warrants further investigation.

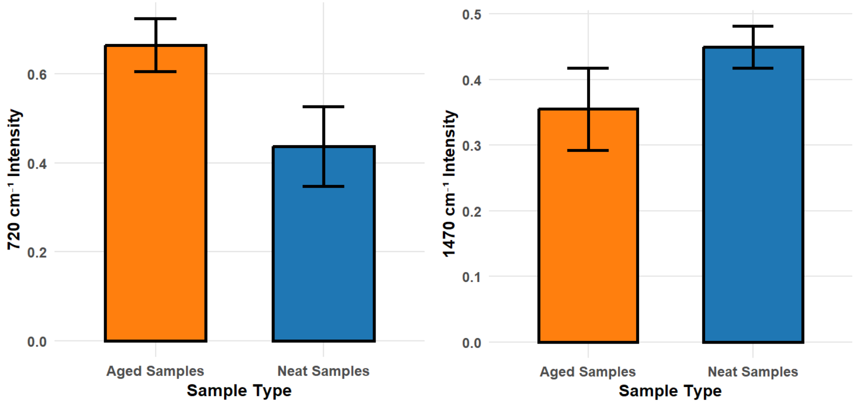

Figure 3: Comparison of the intensities of C-H rocking and C-H scissoring bands in HDPE

Polyamide, being a more complex polymer, presented challenges in analysis due to high noise and sample variability, making it difficult to establish clear relationships between peaks, as was done with polyethylene. Nevertheless, certain trends emerged (Figure 4). One of the most consistent observations was the significant effect of NG2 on the polyamide samples, leading to greater variation across the samples. The C-H bond peak at approximately 2930 cm^-1 was markedly increased in the NG2-aged samples, while it remained consistent across all other polyamide samples, including those aged for one month and the neat samples. Additionally, NG2 samples exhibited a peak at 1740 cm^-1 that was absent in the neat samples, which is indicative of oxidative degradation. NG2 differs from NG1 only in its 0.5% oxygen content, which could be facilitating polymer degradation and gas infiltration, although the extent of change observed suggests a significant amount of gas retention, which seems unlikely.

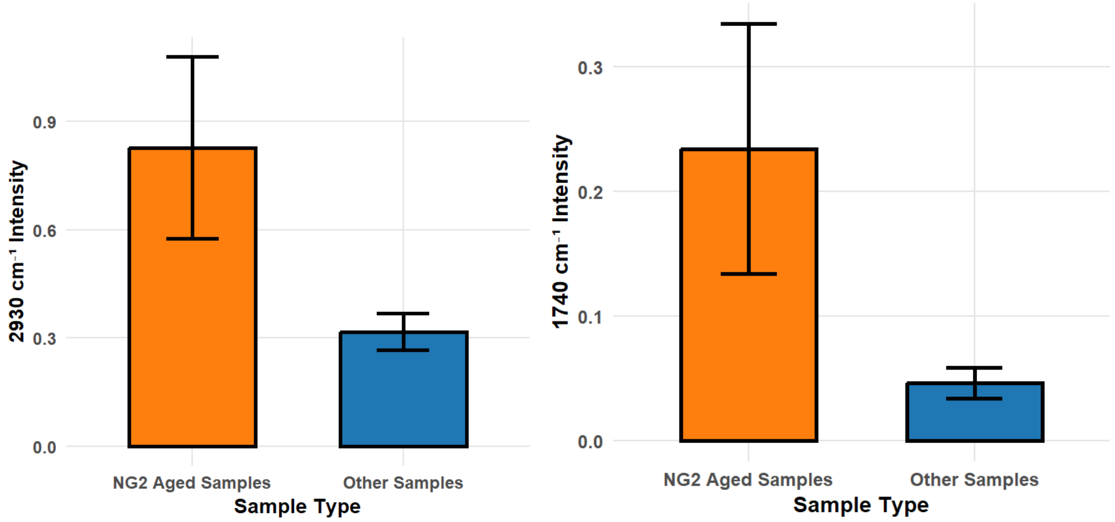

Figure 4: Comparison of the intensities of CH Strech and C=O streching bands

Polyvinylidene fluoride (PVDF) is also a complex polymer with numerous peaks overlapping with those of the gas. The trends observed in PVDF are challenging to interpret due to the presence of two distinct phases in most samples: a high-alpha phase, often seen in the central regions of the samples, and a higher-beta phase, typically observed at the edges. Additionally, a peak at approximately 2920 cm^-1, initially associated with natural gas infiltration, has since been detected in neat PVDF samples as well. The two morphologies are distinct, with samples typically exhibiting mixed morphological content—around 40% or more in the alpha phase and primarily beta phase samples with alpha phase content of less than 15%.

An additional factor in PVDF was the presence of degradation peaks around 1720 cm^-1, observed in a small minority of samples across various aging conditions (S3). Unlike polyamide, the gas composition did not appear to influence the observed changes in PVDF.

In this quarter in the Srivastava lab, we performed uniaxial tensile tests on dogbone shaped (ASTM D638 - Type V) polymer samples of HDPE, PA and PVDF. The tension tests were conducted at a rate of 0.0045 mm/s which corresponds to a very slow strain rate of 0.0001 s^{-1}. The polymer samples were exposed to two different gaseous mixtures at 90°C and approximately 250 psi pressure. The first mixture, namely NG1, contains purely hydrocarbons, whereas the second mixture, namely NG2, has some oxygen in addition to the hydrocarbons. The exposure time for NG1 has been 7, 14 and 30 days, whereas for NG2 till now, we have completed exposure times of 7 and 14 days. Here, we have compared the changes observed in the Young's modulus and yield stress of the polymer for the exposure conditions NG1-90°C-14days and NG2-90°C-14days.

A point to be noted here is that in Figure 5, in the legends, "Tested immediately" means that the samples were tested on the same day after it was taken out from the pressure vessel. For HDPE (Figure 5(a) and 5(b)) and PVDF (Figure 5(e) and 5(f)), we can observe that for both NG1 and NG2, there is a decrease in Young's modulus and yield stress compared to the virgin material. Moreover, NG2 has a potentially significant impact compared to NG1. In Figure 5(c) and 5(d), we can see that PA shows some interesting results. Both the samples exposed to NG1 and NG2 exhibit a higher modulus and yield compared to the virgin material. This, we believe, is the effect of subjecting PA to an elevated temperature of 90°C and pressure of 250 psi, which leads to some form of hardening, resulting in greater stiffness and yield. However, the effect of NG2 on PA when compared to NG1 is consistent with the other polymers.

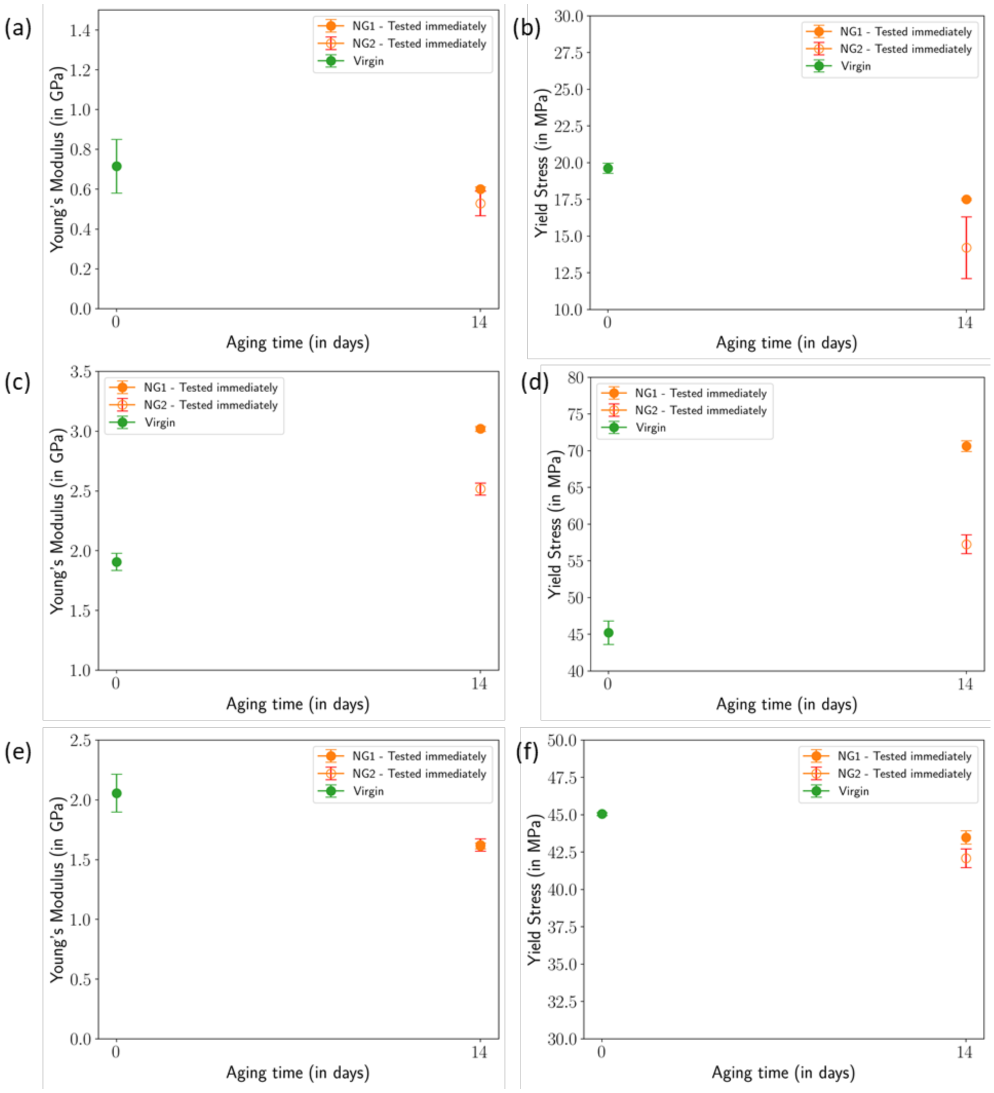

Figure 5**:** Young's Modulus - (a) HDPE, (c) PA and (e) PVDF.
Yield Stress - (b) HDPE, (d) PA and (f) PVDF.

Project Financial Activities Incurred during the Reporting Period:

Costs associated with Ph.D. graduate student support, research related travel, equipment, equipment operations, shared experimental paid facility use, materials and supplies for experimental research work for the project were supported.

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 URI researchers and Brown University researchers shared polymer samples for testing.

Potential Project Risks:

As the research progresses and more experimental data is collected, since the work and findings for liner polymer materials are new, there is a risk of unanticipated new findings. This risk will be managed by adjusting the research methods as new data is obtained through research work. Inherent inconsistencies across individual samples may make morphological conclusions for more macroscopic samples difficult.

Future Project Work:

Our future work will focus on publishing a 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 as XRD machines are bulky and immobile. If similar measurements can be made with an FTIR (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 shows changes in microstructure properties depending on the locations 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.