CAAP Quarterly Report

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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: Q6 (July 1 – Sep 30, 2024)

Project Activities for Reporting Period:

The researchers at the University of Rhode Island focused on measuring the activation energy of samples aged under different conditions and comparing the resulting changes with variations in the modulus of the samples. Figure 1 illustrates how activation energy changes in aged samples over time. The aging conditions involved exposure to pure hydrocarbon mixtures at 90°C and approximately 250 psi pressure. It is evident that activation energy decreases under these aging conditions; however, this decrease eventually stabilizes, exhibiting a plateau-like behavior. Notably, each test for each sample takes about four hours to complete, so measuring all samples after opening the pressure chamber requires considerable time. The procedures will be repeated with more precise experimental conditions to obtain accurate results for the samples immediately after aging.

Figure 2 shows the elastic modulus of the aged samples. In contrast to activation energy, the modulus of the polymer samples fluctuated significantly. Therefore, using modulus changes may not be an appropriate method for tracking the property degradation of these polymer liners.



Figure 2- Elastic modulus (a) HDPE sheets, (b) PVDF sheets and (c) PA sheets.

At Brown University, infrared spectroscopic analysis was conducted on Virgin, 1 Week and 2 Week Aged samples of PA, HDPE and PVDF, which can be seen in Figure 3. The polyamide used showed characteristic absorption peaks at 1632 cm⁻¹, 1535 cm⁻¹, and 1274 cm⁻¹ associated with the Amide I, Amide II, and Amide III bonds. The peaks seen at the other range of the spectrum at 3300, 3073, and 2933/2860 are associated with the Amide I, Amide B, and the C-H stretch. There are no notable changes in the intensities of the peaks, especially in the 2900-3000 region corresponding to the methane and ethane absorption bands if they were present in the sample. A similar peak profile is seen in HDPE with minimal changes in the 2915 and 2847 that correspond to the -CH stretch and the 1462 cm⁻¹ corresponding to the -CH scissor. In PVDF, we do see a significant change in several regions of the spectrum. The different spectrums were normalized to the 1178 peak, which corresponds to the CF₂ bond, acting as a constant. When normalized, there is a noticeable peak near 2920 cm⁻¹ that is only seen in the aged samples. This peak could correspond to the potential absorption of the hydrocarbons used in the aging process. Additionally, the peaks seen at 762 and 840 correspond to two distinct crystalline phases, specifically the alpha and beta, respectively, that show changes in intensity. The relative amounts of each phase were calculated from the intensity measurements and shown in Figure 4

Tension tests on cracked aged (aging condition: NG1-90C-243 psi-14 days) HDPE, PA and PVDF samples were also performed at Brown University. The uniaxial tension tests were conducted at a constant strain rate of 0.0005s⁻¹. The microstructural differences of the fractured surfaces were investigated under a Scanning Electron Microscope (SEM). The results are compared with virgin samples obtained in the last quarter.



Figure 3- FTIR of (a) PA, (b) HDPE and (c) PVDF. In each subfigure, top row- virgin, middle row- 1 week aged, bottom row- 2 week aged.



Figure 4- Alpha and Beta phase content of virgin and aged samples of PVDF.



Figure 5- Force vs. Displacement curve for cracked virgin and 1 week aged (a) HDPE, (b) PA and (c) PVDF.

In Figure 5(a), for HDPE, we can observe that in the early stage of loading until the peak load, the force-displacement response of the virgin and the aged sample are very close. However, after the peak load, the virgin sample fails before the aged sample. In Figure 5(b), we can observe that in the early stage of loading, the aged sample shows a stiffer response than the virgin sample. The aged sample fails much before the virgin sample, with a peak load less than that sustained by the virgin PA sample. The sharp drop in force as the crack propagates indicates that the fracture is brittle in nature for both the virgin and aged samples. In Figure 5(c), we observe that the virgin PVDF sample experienced some slipping during the tensile test. Therefore, comparing these two curves might lead to wrong conclusions regarding the difference in strength or the peak load sustained by the virgin and the aged sample. Hence, we need to repeat this set of experiments. However, the drop in the force follows the same trend in both the virgin and aged samples.

In Figure 6(i), we present the fracture morphology of the cracked virgin HDPE sample (1st row) and aged sample (2nd row). In Figures 6(i)(a) and 9(i)(d), we can observe that the surface near the initial crack tip is characterized by short fibrils and voids. Such short fibrils, accompanied by voids, characterize a craze-like failure. Crazing is often associated with brittle-like failure. Figures 6(i)(c) and 6(i)(f) show that as the crack progresses, the fibrils get stretched out, resulting in a final ligament. This is an indication of a brittle to ductile transition as the crack propagates. In Figure 6(i)(e), it can be seen that the craze-crack mechanism quickly transitions to a shear-yielding mechanism characterized by the dimple pattern, which indicates ductile failure. We can distinguish that the crazing mechanism of failure is more dominant in the virgin sample than in the aged sample. Hence, this results in the early failure of the virgin sample compared to the aged sample.

In Figure 6(ii), we present the fracture morphology of the cracked virgin PA sample (1st row) and aged sample (2nd row). Qualitatively, we don't see any distinct difference in the features of the fracture surface. In Figure 6(iii), we present the fracture morphology of the cracked virgin PVDF sample (1st row) and aged sample (2nd row). We don't observe a significant macroscopic difference in the morphology of the virgin and aged PVDF samples.



Figure 6: SEM images of the fracture surface of (i) HDPE - virgin (1st row), aged (2nd row), (ii) PA - virgin (1st row), aged (2nd row) and (iii) PVDF- virgin (1st row), aged (2nd row)

Project Financial Activities Incurred during the Reporting Period:

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

Table 1 Summary of Q6 Spending-07/01/2024-09/29/2024				
Institution		Amount (\$)	Amount (\$)	Subtotal (\$)
	Category	Salary (\$)	Fringe (\$)	
Brown University	Salaries	41,794.17	7,473.76	49,267.93
	Graduate Student Fees			23,099.00
	Facility Usage			1,871.50
	Purchased Services			
	Materials and Supplies			1,531.11
	Travel			
	Total Direct			75,769.54
	Indirect			31,338.99
University of Rhode Island	Subtotal			107,108.53
	Personnel	Salary (\$)	Fringe (\$)	
	Salaries	15,009.00	791.72	15,800.72
	Operating Expenditures			8,115.20
	Travel			1,278.45
	Student Aid			12,620.00
	Total Direct			37,814.37
	Indirect			14,486.76
	Subtotal			52,301.13
Total				159,409.66

Project Activities with Cost Share Partners:

Partial support for graduate students is provided by Brown University as per the cost-share agreement.

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 continuing risk of unanticipated new findings. This risk will be managed by adjusting the research methods as new data comes. All unanticipated findings will also be studied in depth to understand the underlying physical phenomenon. There are risks of experimental set-ups not working as expected and certain measurements having significant errors. This will be addressed by investigating the root cause of any errors and finding mitigating or alternative strategies.

Future Project Work:

We plan to continue to age polymer samples using more corrosive gases, such as oxygen, to observe how the properties change under these conditions. These samples will be further tested to characterize their mechanical response and any microstructural changes. We will address the issues related to slipping in some of our tensile test experiments. Progress on developing a theoretical gradient damage model for capturing the process in semi-crystalline polymers will continue.

Potential Impacts to Pipeline Safety:

Previous testing showed changes in materials 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, it is possible detect phase content changes that may be precursors to mechanical failure in the field.

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.