CAAP Annual Report

Date of Report:	04/14/2025
Prepared for:	U.S. DOT Pipeline and Hazardous Materials Safety Administration
Annual Period:	From (March 28, 2024) to (March 27, 2025)
Contract Number:	693JK32250001CAAP
Project Title : Liners through Micro	Selection and Development of Safer Polymer and Composite Pipeline ostructural and Macroscopic Study of Materials and Designs
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I. <u>Section A: Business and Activities</u>

A. Contract Activities

• Contract Modifications:

None

- Educational Activities:
 - Student mentoring:

PhD Student Mohammadjavad Hajirezaei has gained good expertise in the use of experimental techniques such as DSC, DMA and rheology. He has also been learning about the analysis of the data and time-temperature equivalence modeling. PhD Student Zakhar Lyakhovych has gained good expertise in experimental techniques, including DSC, XRD, PLM, and FTIR. He has laid out protocols for testing of meltcast and preprocessed samples. PhD student Deepro Ghosh has gained good expertise in the MTS servo-hydraulic mechanical testing for polymers. Another graduate student, Kevin LoGiudice, and a few undergraduate students have worked with Deepro and learned experimental design and characterization methods. Ph.D. student Deepro is also learning and working on different modeling and finite element simulation techniques for the project. Undergraduate students have been involved in the project topic and taught how to use XRD, FTIR and how to extract morphological information from the data. They are also taught polymer mechanical testing, characterization and experimental designs related to the project.

All students involved continue to learn significantly about experimental methods and have been contributing productively to this research project. The students involved in the project have been learning about pipeline materials, safety and integrity challenges, including rehabilitation considerations. You can find more detailed work by these students in the technical section of this report.

- Other:
- Publication:

A manuscript titled "Environmental aging of polymers to evaluate their use in remediating natural gas pipelines" is jointly developed and written by all the collaborators and students involved in this research project. The experimental outcomes are discussed with industry experts. This manuscript will be submitted for peer review and publication in the near future.

B. Financial Summary

• Federal Cost Activities:

Table 1 summarizes the involvement of the PI, co-PIs and students involvement, materials and supplies, equipment operational, shared facility use expenses, and travel for Brown University and the University of Rhode Island during project year 2.

• Cost share contribution:

Table 2 below details the cost share by Brown University and the University of Rhode Island for year 2 of the research project.

			8/2024-03/2//	2025
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Institution		Amount (\$)	Amount (\$)	Subtotal (\$)
	Category	Salary (\$)	Fringe (\$)	
	PI	13,104.14	3,865.72	16,969.86
	Co-PI	8,136.34	2,400.22	10,536.56
	Postdoc	2,996.19	883.87	3,880.06
	Graduate Students	59,510.11	861.13	60,371.24
	Undergraduate Students	6,368.64	438.98	6,807.62
Brown University	Student Fees			41,418.00
	Facility Usage			21,489.50
	Purchased Services			1,477.17
	Materials and Supplies			13,007.82
	Equipment			6,701.91
	Total Direct			182,659.74
	Indirect			80,051.39
	Subtotal			262,711.13
	Personnel	Salary (\$)	Fringe (\$)	
	Salaries	41,942.95	4,026.12	45,969.07
	Operating Expenditures			13,981.83
University of Phode Island	Travel			4,998.99
Oniversity of Knode Island	Student Aid			12,620.00
	Total Direct			77,569.89
	Indirect			37,346.23
	Subtotal			114,916.12
Total				377,627.25
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C. Project Schedule Update

- Project Schedule:
 - AIM 1: Collate Existing Data on Liner Materials
 - Liner materials' morphological and microstructural changes
 - X-Ray diffraction, FTIR and DSC were researched to see how aging changing in morphology could be detected. Aspects such as changes in crystallinity, gas permeation, and thermal properties were established to be feasibly detectable in the polymers we chose.
 - Liner material stability, degradation, microstructural properties
 - Scans of polymers from a variety of different commercial and research grades were procured from different research studies and used to create a framework of understanding experimental data.
 - Liner material mechanical/structural properties
 - Literature was reviewed to extract key mechanical parameters such as tensile strength, yield stress, and creep resistance for HDPE, PVDF and PA. Additionally, constitutive modeling approaches were looked to correlate microstructural changes with viscoelastic, viscoplastic, and fracture behavior in semi-crystalline polymers.
 - AIM 2: Characterization of Morphological, Microstructural and Mechanical Properties of Liner Materials
 - Experimental characterization of morphological behavior of liners
 - Characterization of PVDF, Polyamide and HDPE occurred for NG1 aging conditions with samples from an array of aging timepoints being tested.
 - Experiments to relate micromechanical changes to microstructure
 - Quantifiable parameters were analyzed for the three polymers and relationships to aging conditions were created. Trends seen in these in relation to aspects such as polymer crystallinity and were compared to mechanical properties. Dynamic Mechanical Analysis (DMA) was conducted on aged specimens to probe the viscoelastic properties of the liner materials. Subsequently, the method of Time-Temperature-Superposition (TTS) was employed to investigate viscoelastic relaxation of these materials.
 - Mechanical characterization of hydrocarbon and pressure-exposed liners
 - Uniaxial tensile testing was conducted on dogbone samples of PVDF, PA, and HDPE that had been exposed to a pure hydrocarbon environment (NG1) under elevated temperature and pressure conditions for several days. This

allowed us to evaluate the changes in mechanical properties such as Young's modulus and yield strength over exposure time.

- AIM 3: Liner and Rehabilitated Pipe Modeling & Simulations
 - Worked on early models for chemical and pressure-exposed liner materials
 - Started conducting finite element study of the rehabilitated pipes
- Corrective Actions:
 - We have started to work on including assessments of an epoxy bonded composite in the experimental plan We have begun preparing glass fiber epoxy composite specimens, which will be used for peel tests.
 - Continuing work on modeling of liner materials and finite element simulations of liner-pipe systems.

Tasks	YEAR 1		YEAR 2							YEAR 3																			
	1 2	2 3	4 :	5 6	6 7	8	9	10	11	12	1	2 3	3 4	5	6 7	8	9	10	11	12	1 2	2 3	4	56	6 7	8	9 1	0 1	1 12
AIM 1: Collate Existing Data on Liner Materials																													
Liner materials morphological and microstructural changes																													
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AIM 3: Liner and Rehabilitated Pipe Modeling & Simulations																													
Develop models for chemical and pressure exposed liner materials																													
Finite element study of the rehabilitated pipes																													

The chart above presents the research tasks and milestones that were worked on (in blue) and the projected research efforts that will be conducted during Year 3 (in orange). The blue boxes indicate work completed in Years 1 and 2, while the orange boxes represent planned activities based on our current research trajectory.

D. Status Update of the 8th Quarter Technical Activities

• Aging polymers under NG2

The aging processes of the polymers exposed to NG2 under different conditions have been initiated. In addition, all the data and measurements for NG1 have been collected and prepared to be presented in a paper.

• XRD and FTIR of bulk polymers

Quantitative analysis of NG1 aged polymers through FTIR and XRD was finalized. NG1 permeation and retention trends were recorded in FTIR and subsequent changes to crystal structure were recorded in XRD patterns.

• High Surface Area Analysis

Thin samples were created with high surface area to further look into NG1 and NG2 penetration in polymers of interest.



• Creep test of polymers

Figure 1. A creep test setup for selective comparison of properties measured through MTS

A creep test setup was put together, which could help us investigate some of the creep responses of the polymer following the detailed mechanical characterizations in the project. Polymer samples will be clamped between two rigid fixtures, and a constant load corresponding to approximately 30-80% of the material's yield strength is applied by hanging weights. To monitor the evolution of deformation over time, a camera mounted on a tripod captures periodic images of the samples throughout the test duration. A ruler placed adjacent to the polymer samples serves as a length scale, enabling pixel-tomillimeter conversion, which will could allow us to evaluate the elongation or creep strain of the samples over time. Currently, we are doing preliminary testing to ensure reliable and consistent strain measurements.

Peel tests of epoxy specimens



Figure 2: Peel test specimens

Peel test specimens were fabricated to evaluate the adhesive strength between a flexible composite layer and a rigid substrate using the 180° peel test. The intention behind these specimens was to mimic the cured-in-place (CIP) pipeline liners. The flexible member was prepared by saturating fiberglass fabric in a cycloaliphatic amine-based epoxy resin system, followed by overnight curing. It was then bonded to cast iron coupons using a solvent-free two-component epoxy adhesive. The bonded region was clamped and cured overnight under pressure at room temperature. At present, a few preliminary tests are being performed on these specimens to ensure consistent results.

• Development of a model of liner material exposed to a chemical and pressure environment

We have started working on a diffusion-reaction model for mechano-chemical degradation of the liner material.

II. Section B: Detailed Technical Results in the Report Period

A. Background and Objectives in the 2nd Annual Report Period

1. Background

Aging cast iron and steel pipelines used in natural gas distribution pose serious integrity and safety concerns due to corrosion caused by the presence of impurities such as carbon dioxide (CO₂) and hydrogen sulphide (H₂S). To address these issues, internal polymeric and composite liners offer a promising trenchless rehabilitation solution instead of the high costs and risks associated with the open excavation and replacement of these deteriorating pipes. However, a comprehensive understanding of how these liner materials respond to long-term exposure to the natural gas environment under elevated temperatures and pressures and the changes that are induced in the microstructure and the morphology of these polymers, are missing. In the second year of this project, we focused on exposing polymer samples of high-density polyethylene (HDPE), polyamide (PA), and polyvinylidene fluoride (PVDF) to a purely natural gas (NG) environment. Subsequently, a series of tests were conducted to characterize the macroscopic mechanical properties and microstructural changes over several days of exposure time.

2. Objectives in the 2nd Annual Report Period

a) Mechanical Characterization of Aged Polymers

To investigate the effect of exposure to a natural gas environment under elevated temperature and pressure on the mechanical properties of polymer liners used in pipelines. This was carried out through tests such as Dynamic Mechanical Analysis (DMA) and uniaxial tensile tests, which probe the changes in viscoelastic behavior, stiffness and strength over exposure time.

b) Microstructure Characterization

To quantify changes in the polymer microstructure that were established in the previous annual report. Spectral regions where any hydrocarbon absorption would be seen and were assessed as well as any other trends in polymer chemical composition or alignment that can be seen.

c) Characterization of Thermal Properties

Detect changes in thermal properties that have been previously established for the polymers through Differential Scanning Calorimetry (DSC). Observe any changes to thermal events and calculate level of order changes as a result of aging conditions.

d) Theoretical Development of liner material model

We aim to begin our modeling effort with a simplified diffusionreaction framework that captures the transport and consumption of chemical species within the pipeline liner. This model will form the basis for linking permeation of any chemical species to material degradation.

B. Experimental Program in the 2nd Annual Report Period

1. Experimental Design

a) Sample Preparation

Commercially available sheets of high-density polyethylene (HDPE), polyamide (PA), and polyvinylidene fluoride (PVDF) were purchased from McMaster. Dog bone tensile specimens were machined using a Mill Computer Numerical Control (CNC) according to ASTM D638-V. Rectangular samples measuring 12.7 mm in length by 3.2 mm in thickness were fabricated for dynamic mechanical analysis (DMA) following ASTM D790-17 standard. In addition, very small samples (~15mg), were cut from the stock sheet material, which were then subsequently pressed at 10000 lbs for 5 minutes resulting in a thin flat disk with a diameter of approximately 10 mm.

b) Aging Protocol

Samples were placed inside a pressure vessel using a custom-made holder to hold the samples in an upright position and ensure good contact with the gaseous environment. Then, the vessel was evacuated under vacuum to remove air after which, it was filled with a natural gas mixture consisting of 80% methane, 10% ethane, 7% propane and 3% n-Butane (we will refer to this mixture as NG1 in the rest of the report). The aging process was conducted at a temperature of 90°C and a pressure of 200 PSI for durations of 7, 14, and 30 days.

2. Test Procedure

a) Dynamic Mechanical Analysis

Dynamic Mechanical Analysis (DMA) was conducted on a TA Instruments HR-20 rheometer to characterize the viscoelastic moduli of the materials across a range of frequencies. A pre-load force of $5N \pm 0.1N$ was applied before initiating the frequency

sweep at each temperature to ensure sufficient contact between the instrument and the sample. The frequency sweep was performed over a range of f = 0.01 to 10 Hz at temperatures ranging from 25°C to 105°C in increments of 10°C. Samples were allowed to equilibrate for 10 minutes after each temperature change to ensure uniform temperature within the sample.

b) Uniaxial Tensile Experiments

Uniaxial tensile tests using an MTS Bionix Servohydraulic testing machine were performed. A 25 kN load cell is used to measure the force, which is then converted to the nominal stress. To measure the nominal strain in our experiments we employ the Digital Image Correlation (DIC) software MatchID 2D, which is integrated with a FLIR Blackfly S USB3 camera that captures images of the sample as it is deforming in the tensile test. The uniaxial tension tests at room temperature, at a nominal strain rate of $\dot{\varepsilon} = 2 \times 10^{-4} s^{-1}$ by loading the samples until the point of necking. Specifically, these tests are used to calculate relevant properties such as Young's modulus, yield strength, and strain at yield. The Young's modulus was obtained by fitting a straight line to the initial elastic region of the stress-strain curve. The yield strength, as well as the strain at yield, were obtained using the 0.2% offset method as seen in Figure 3.



Figure 3. Representative engineering stress vs engineering strain plots for (a) HDPE, (b) PA, and (c) PVDF.

c) Fourier Transform Infrared Spectroscopy

Samples were used as given and tested as soon as they were removed from the aging chamber. The FTIR was set up with an Attenuated Total Reflectance attachment that allowed rapid scanning of samples surfaces. Scanning was conducted over wavelengths ranging from 4000 to 500 cm⁻¹ with a resolution of 4 cm⁻¹. To assess changes in polymer composition with gas exposure, the spectra were normalized to characteristic peaks with Spectragryph, a post-spectral processing software.

d) X-Ray Diffraction

Structural properties of samples were investigated by X-ray diffractometer equipped with a Cu radiation source (D8 DISCOVER, Bruker) within the diffraction angle (2 θ) range 10 to 60° step-wise operating at 40 kV and 40 mA. Background subtraction was conducted at 1.00 curvature and 0.20 threshold. Deconvolution and peak separation was conducted with Fityk peak fitting software.

C. Results and Discussions

1. Mechanical Properties

We observed that the mechanical properties of the samples, specifically Young's modulus and tensile strength, do not show significant changes after exposure to the natural gas environment (Fig. 1). These results are consistently confirmed through both DMA and tensile measurements across all three polymer chemistries. Both measurements exhibit some fluctuations in mechanical properties; however, there is no clear evidence of degradation, even after one month of aging at 90°C for any of the polymers. Furthermore, these properties appear to be independent of temperature, as can also be seen in Figure 4.



Figure 4. Normalized Young's modulus determined from DMA (solid) and tensile tests (open) and and normalized yield stress as function of aging time at 90°C for (a) and (d) HDPE, (b) and (e) PA, (c) and (f) PVDF. Black symbols represent measurements taken after aging at 25°C.

For completeness of the presentation of the results obtained from the uniaxial tensile tests, we have also tabulated the absolute value of the following properties - Young's Modulus, Yield Stress and Yield Strain.

Aging	Young's Modulus	Young's Modulus
Days	Mean (in GPa)	Std (in GPa)
Virgin	0.72	0.165
7	0.81	0.009
14	0.60	0.015
30	0.50	0.139
30-RT	0.52	0.156

Table 1: Young's Modulus Data for HDPE

Aging	Young's Modulus	Young's Modulus
Days	Mean (in GPa)	Std (in GPa)
Virgin	2.55	0.195
7	3.12	0.046
14	3.02	0.024
30	2.44	0.053
30-RT	2.82	0.021

Table 2: Young's Modulus Data for PA

Aging	Young's Modulus	Young's Modulus
Days	Mean (in GPa)	Std (in GPa)
Virgin	2.06	0.194
7	1.66	0.074
14	1.72	0.127
30	1.42	0.024
30-RT	2.00	0.021

Table 3: Young's Modulus Data for PVDF

Aging	Yield Stress	Yield Stress
Days	Mean (in MPa)	Std (in MPa)
Virgin	11.99	1.672
7	11.43	0.290
14	11.23	0.179
30	6.89	2.869
30-RT	7.79	1.573

Aging	Yield Stress	Yield Stress
Days	Mean (in MPa)	Std (in MPa)
Virgin	50.24	2.62
7	50.64	1.73
14	52.62	1.044
30	47.67	0.627
30-RT	54.54	0.426

Table 4: Yield Stress Data for HDPE

Table 5: Yield Stress Data for PA

Aging	Yield Stress	Yield Stress
Days	Mean (in MPa)	Std (in MPa)
Virgin	30.27	2.077
7	24.08	0.476
14	26.14	1.182
30	28.23	1.121
30-RT	29.77	0.630

Table 6: Yield Stress Data for PVDF

Aging	Yield Strain	Yield Strain
Days	Mean	Std
Virgin	0.019	0.0020
7	0.016	0.0004
14	0.021	0.0002
30	0.015	0.0023
30-RT	0.017	0.0021

Aging	Yield Strain	Yield Strain
Days	Mean	Std
Virgin	0.022	0.0004
7	0.018	0.0005
14	0.019	0.0003
30	0.022	0.0002
30-RT	0.021	0.0002

Table 7: Yield Strain Data for HDPE

Table 8: Yield Strain Data for PA

Aging	Yield Strain	Yield Strain
Days	Mean	Std
Virgin	0.017	0.0023
7	0.018	0.0004
14	0.017	0.0015
30	0.022	0.0009
30-RT	0.017	0.0003

Table 9: Yield Strain Data for PVDF

2. Time-Temperature-Superposition (TTS)

We previously discussed the mechanism of TTS in past reports, and a summary of this approach is presented in Fig. 5. Our motivation for applying TTS arose because, while both Young's modulus and yield stress characterize the mechanics of solids, polymer melts are inherently viscoelastic. Therefore, even if natural gas does not produce any detectable effects on these properties, it may still influence the viscoelastic relaxations of these materials. To investigate this, we performed DMA at various temperatures to construct a master curve for each polymer (Fig 5. (a) and (b)). Using a master curve, we can plot the shift factor (aT) versus the inverse of temperature (Fig 5.(b)) and calculate activation energy Ea by using the following equation:

$$log(a_T) = \frac{E_a}{2.303R} (\frac{1}{T} - \frac{1}{T_{ref}})$$



Figure 5. (a) Storage (solid line) and loss (dash line) moduli as a function of frequency for HDPE. (b) HDPE master curve obtained by TTS with shift factors. (c) Shift factors for HDPE as a function of inverse temperature.

As exposure time increases, the slope of the Arrhenius plots decreases, indicating a decline in activation energy over the course of aging, as shown in Fig. 6. This behavior implies that natural gas molecules slowly penetrate the polymer matrix, functioning as plasticizers and lowering the energy barriers required for molecular mobility.



Figure 6. Shift factors for (a) HDPE, (b) PA and (c) PVDF as function of inverse temperature after different aging periods.

A clear trend of decreasing normalized activation energy is observed in the polymers as the aging duration increases, as shown in Fig. 7 (left panels). However, to determine whether this reduction is reversible, additional tests were conducted after allowing the samples to rest for a period of time following their removal from the chamber. Noticeably, the activation energy shows a clear trend of recovery as the samples are left in the ambient laboratory environment for longer periods, as illustrated in Fig. 6 (right panels). This recovery behavior clearly indicates that natural gas molecules slowly diffuse out of the polymer matrices without causing any lasting chemical alterations. The uniform recovery patterns observed in all three polymers further validate that the interaction between natural gas and the polymer is physical rather than chemical.



Fig 7. Normalized Arrhenius activation energy and the recovery tests of aged samples for (a) and (b) HDPE, (c) and (d) PA and (e) and (f) PVDF. Black symbols represent measurements taken after aging at 25°C. Dashed lines are guides to the eye.

3. Microstructure Characterization

a) ATR-FTIR

Fourier Transform Infrared (FTIR) spectroscopy was used to provide critical insights into the chemical and structural changes of polymers. The analysis focuses on the 2913 cm⁻¹ and 1465 cm⁻¹ wavelengths, corresponding to C-H stretching and CH₂ bending vibrations, respectively. These peaks are intrinsic to the aliphatic segments in both polymers, with 2913 cm⁻¹ representing asymmetric CH₂ stretching and 1465 cm⁻¹ reflecting CH₂ scissoring or bending modes. These wavelengths are characteristic of hydrocarbon-based materials.

In HDPE, a hydrocarbon polymer dominated by CH₂ groups, the peaks at 2913 cm⁻¹ and 1465 cm⁻¹ are primary features of the hydrocarbon backbone, so detecting changes was challenging due to overlap with the polymer's intrinsic bands.

Both polyamide and PVDF showed changes in the intensities at these two wavelengths. In polyamide, the 2913 cm⁻¹ and 1465 cm⁻¹

bands exhibited increased intensity after 30 days, but no significant changes were observed at 1 or 2 weeks. This may indicate that NG1 infiltration occurs over longer time scales. Additionally, the stressinduced orientation of CH₂ groups during gas permeation could enhance dipole alignment, intensifying IR absorption.

In PVDF, there was an immediate rise in the intensity of the two bands, which plateaued after 1 week and remained elevated. Interestingly, the 1465 cm⁻¹ band did not show as significant an increase. These samples also displayed higher variability compared to other polymers tested, though this aligns with previously observed trends.



Figure 8: FTIR absorbance normalized to peak intensity at 1613 cm-1 corresponding to C—O stretching for (a) PA and at 1178 cm-1 corresponding to C–F stretching for (c) PVDF. Black curves are neat samples and colored curves have been aged at 90 °C for 30 days. (b,d) Normalized absorbance of peaks at 1495 cm-1 (open) corresponding to asymmetric C–H stretching and 2915 cm-1 corresponding to C–H stretching as a function of aging time at 90 °C.

b) XRD

Using X-ray diffraction, we attempted to detect changes to polymer morphology that would result in different X-ray spectra compared to unaged controls. In the polymeric dog bone samples, sections were scanned and compared unaged samples. After exposure we see limited changes in the polymer crystallinity. While some changes were observed, over time there was no consistent trend or change in samples, as seen in Figure 9.



Figure 9: Crystallinity of polymer samples after various aging timepoints in NG1

Additionally, due to the bulk nature of the samples, higher-surfacearea samples were prepared. The sample creation was suspected to alter properties compared to unaged dogbone samples, which was confirmed by XRD scans. As observed, significant morphological differences emerged between unaged thin samples and unaged dogbone samples for PA and PVDF. HDPE showed minimal changes between neat and thin samples, as well as between unaged and 2-week-aged thin samples.

Polyamide XRD patterns revealed a decrease in crystallinity in thin samples, marked by a broad amorphous region. In aged samples, an increase in crystallinity was observed alongside a pronounced rightward shift in diffraction peaks. PVDF scans of unaged thin samples showed a significant rise in amorphous content and a mixture of crystalline phases (α , β , and γ). Both aged PVDF samples exhibited a sharp increase in crystallinity, with a growing predominance of the α -phase—indicated by an intensified secondary peak near 26.5° (2 θ).



Figure 10: XRD graphs of HDPE, Polyamide, and PVDF (A, B, C; respectively) thin samples that are unaged, aged 2 weeks in NG1, and aged 2 week in NG2 (bottom to top of each graph, respectively)

c) DSC

Differential Scanning Calorimetry (DSC) was used to investigate changes in thermal transitions due to aging. After 1 week, all three polymers showed minimal changes in enthalpy and the overall shape of their thermal profiles. This result aligned with expectations, given the limited crystallinity changes observed in XRD scans. No significant thermal events—such as outgassing or material relaxation from absorbed gas escape—were detected.



Enthalpy Changes in NG1 Aged Samples

Figure 11: Changes in the delta H of HDPE, Polyamide, and PVDF after 1 week of aging at NG1 at 90 °C and 200 psi.

4. Liner Degradation Model

We follow [1], to establish a framework for degradation and damage of liner material after exposure to a chemical and pressure environment. The choice of this framework is motivated from the fact that presence of oxidising agents in the natural gas being carried through the pipelines can permeate into the liner which can induce oxidative degradation [2]. Oxidative degradation induced chain scission can cause a reduction in toughness and molecular weight, which results in embrittlement leading to premature brittle fracture.



Figure 12: Schematic of a pipe carrying natural gas at a pressure of p_i where the concentration of the oxidising agent is C_{∞} .

The transport of the oxidative agent into the polymer pipe wall is governed by a diffusion-reaction equation:

$$\frac{\partial C}{\partial t} = D\left(\frac{\partial^2 C}{\partial x^2}\right) - S$$

where -

- C(x, t) is the concentration of the oxidant at x and time t.
- *D* is diffusion coefficient
- $S = k_R C$ is the reaction sink term, representing the rate of oxidant consumption via reaction with the polymer

Now the initial condition and boundary condition are as follows:

- Initial condition C(x, 0) = 0
- Boundary condition -
 - \circ $\;$ At the outer boundary $\;$ C(L,t)=0

• At the inner boundary -
$$k \left[C_{\infty} - C(0,t) \right] = -D \left. \frac{\partial C}{\partial x} \right|_{x=0}$$

Now the deterioration of the polymer liner is realised through chain scission owing to the oxidative reaction with the diffused oxidant. This is quantified using a degradation variable ω which is defined as follows:

$$\omega(t) = 1 - \frac{M_n(t)}{M_{n,0}},$$

where $M_n(t)$ current number-average molecular weight and $M_{n,0}$ is the number-average molecular weight of the original polymer. The degradation parameter ω ranges from 0 to 1, where ω is 0 for the virgin material, and ω equals to 1 for the fully degraded material. Here, it is assumed that the rate

of increase of the degradation parameter is a monotonic function of S, which is the rate of oxidant consumption. Hence, the degradation parameter ω is given as follows:

$$\omega(r,t) = \int_0^{t-t_{\text{OIT}}} k_\omega S \, dt = k_\omega k_R C_\infty \int_0^{t-t_{\text{OIT}}} \frac{C(x,t)}{C_\infty} \, dt$$

where k_{ω} is the kinetic coefficient of degradation and t_{OIT} represents the oxidation induction time, that is when $t \leq t_{OIT}$, the degree of degradation ω is zero. Subsequently, the deterioration in the mechanical properties of the liner material is manifested through a decrease in the specific fracture energy (SFE), which represents the energy required to form a new surface through cracking per unit area. If the SFE of the virgin material is given by $2\gamma_0$, then the degraded SFE 2γ is as follows:

$$\frac{2\gamma}{2\gamma_0} = (1-\omega)^{n_\omega},$$

where n_{ω} is a constant exponent for the degradation kinetics of SFE.

D. Future work

We have acquired all the gas compositions that induce a harsher environment, particularly due to the presence of gases such as H₂S and BTEX. We will continue investigating changes in mechanical properties and polymer chemistry as the polymer samples are exposed to and aged in these harsher environments. These experiments will help refine and enhance our modeling approach. Ultimately, the resulting material models will serve as the foundation for finite element analyses of the liner–pipe systems.

We will conduct a quantitative analysis of the differences in FTIR and XRD spectra between thin polymer samples to determine whether their structural characteristics, such as increased surface area, enhance gas penetration within the polymer matrix. This approach will provide clearer insights into the extent of gas diffusion and its relationship to material morphology. In FTIR analysis, we anticipate observing intensified spectral peaks corresponding to absorbed gas components, which may indicate higher gas uptake. For XRD, we will quantify crystalline phase alterations and peak shifts to assess whether these trends persist under varying environmental conditions, thereby elucidating the stability of structural changes during aging.

Additionally, we will conduct thermal characterization of thin samples to compare melting points, enthalpy changes, and compositional variations across aging stages. Special attention will be given to identifying anomalies, such as outgassing or structural relaxation phenomena, to establish their correlation with the polymer's aging behavior under natural gas exposure.

E. References

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