CAAP Quarterly Report

July 15, 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

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

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

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

Reporting Period: (Q5)

Project Activities for Reporting Period:

At the University of Rhode Island, Poling-Skutvik lab received two gas cylinders for aging samples. The first cylinder contains a mixture of 80% methane, 10% ethane, 7% propane, and 3% n-butane. The second cylinder contains 82.5% methane, 10% ethane, 7% propane, and 0.5% oxygen. A safety operation procedure (SOP) was prepared to safely utilize these gas cylinders. This SOP includes four main sections: general information, storage and handling, regulators and operation, and a step-by-step guide. This was crucial to ensure that the aging process is conducted in a safe and repeatable manner. Subsequently, polymer samples were aged under the conditions specified in Table 1.

| Exposure | Gas composition | Temperature range (°C) | Pressure (psi) | Aging time | Polymers |
|-------------------------|---|---------------------------|-------------------|---------------|-------------------|
| Hydrocarbon mixtures | 80% Methane, 10% Ethane, 7% Propane, 3% N Butane | 9 0 | 245 | 1 week | HDPE, PVDF, PA |

We hypothesized that the activation energy controlling Time-Temperature Superposition (TTS) could be influenced by the aging of polymers. This hypothesis allows us to benchmark polymer performance and degradation. TTS was performed on aged samples to observe changes in activation energy. Figure 1 presents the TTS experimental results for the aged samples, while Figure 2 displays the shift factor for these samples. There is a minor reduction in activation energy, as we had hypothesized.



Figure 1: (a) HDPE master curve, (b) PVDF master curve and (c) PA master curve.



Figure 2: (a) HDPE shift factor, (b) PVDF shift factor and (c) PA shift factor.

At Brown University, we were able to begin taking polarized light microscopy images of the samples for polymers that are relevant as pipeline liner materials. Aged samples have been received and are in the process of being analyzed. Thermal analysis and X-ray diffraction were carried out on several aged samples and different process morphologies of other polymeric samples. Literature pointed to mechanical links to certain morphologies, and so a Gaussian deconvolution procedure was developed to separate different crystalline phases in complex crystalline samples.



Figure 3: X-ray diffraction scan of quenched polyamide 12 samples (left) and melt cast polyamide sample.

A quenched meltcast polyamide 12 sample was created by quenching molten polymer in ice water and analyzed. According to literature, this creates a γ ' and amorphous morphology¹. These two phases were represented with Gaussian peaks and fit to the experimental data resulting in a fit with an R²= 0.998 as seen in Figure 3. The amorphous peak location height and width were noted and overlaid with other polyamide samples that underwent different conditions. Additional crystalline phases were added according to the possible crystalline formations, such as a, a', and γ .

| Sample | Alpha Area | Alpha Area | Gamma Area | Gamma' Area | Amorphous Area | Crystallinity | gamma/alpha ratio |
|----------|---------------|---------------|---------------|----------------|-------------------|---------------|----------------------|
| Quenched | 0 | 0 | 0 | 997 | 3793 | 0.21 | 1 |
| Meltcast | 1424 | 492 | 3012 | 35 | 3793 | 0.57 | 1.6 |
| 165C | 703 | 580 | 4918 | 10 | 3793 | 0.62 | 3.8 |
| 170C | 839 | 885 | 6746 | 202 | 3793 | 0.70 | 4.0 |
| 175C | 216 | 225 | 2157 | 83 | 3793 | 0.41 | 5.1 |
| 180C | 59 | 27 | 1878 | 27 | 3067 | 0.39 | 22.2 |
| 185C | 582 | 660 | 4754 | 281 | 3793 | 0.62 | 4.1 |
| 190C | 194 | 315 | 3157 | 0 | 3793 | 0.49 | 6.2 |
| 195C | 3.8 | 41 | 1175 | 41 | 2490 | 0.34 | 27.1 |
| 200C | 32 | 3 | 1149 | 34 | 1627 | 0.43 | 33.8 |

Table 2: XRD of processed PA12 Samples.

Studies show polyamides have different tensile strengths with different crystalline phase contents. These phases can morph into one another, but some transitions are one way. γ ' phase is known to transform into the mechanically inferior a phase, but γ , which is mechanically superior to both phases, will not transform. The presence of γ ' crystalline structures could be indicative of eventual long-term failure. A summary of different processing conditions and the phase contents in each is shown in Table 2. The highlighted sample is an anomaly that showed a distinctly high gamma ratio.



Figure 4: XRD of polyamide 6 and aged polyamide 6 for 7 days at 90C.



Figure 5: Control PVDF and Aged PVDF.



Figure 6: Control HDPE and Aged HDPE.

The polyamide 6 sample had a primarily alpha structure as can be seen in Figure 4. There is also an unknown crystalline formation that can be seen in the two broader peaks flanking the sharp crystalline alpha peaks potentially a result of the rarely considered beta state of polyamide 6. A summary of the crystalline phase content of a control and aged sample can be seen in Table 3.

X-ray diffraction of PVDF is often difficult due to the variety of crystalline phases that are often present in close proximity to one another. We were able to use numerous examples in the existing literature to determine locations to place peaks and followed general conventions when placing the amorphous peak (Figure 5). One note was the addition of a second amorphous location at 26.5° as a result of the prominence of the peak and the broadened structure that were accounted for with two unknown peaks in addition to a third unknown peak seen at 17.7 which appears earlier than other crystal phases are expected in PVDF.

In Figure 6, the scan shows that the aging process had very little effect on the crystalline structure of the HDPE. Both primary peaks, 21.5 and 24 degrees, were seen with very comparable sizes. One note is the minor shift in peak locations seen in the aged sample, but due to its presence equally over the three peaks seen, this is likely a result of the limits of the XRD.

In this quarter at Brown University, we also worked on the development of a gradientdamage theory to model the failure in semi-crystalline polymers that are subjected to mechanical loading. Semi-crystalline polymers are important polymers as pipeline liner material. A gradient damage approach is chosen [2, 3]. The basic framework for deriving this theory is being laid out. Moreover, uniaxial tension tests at constant rates were performed on notched ASTM D638 - Type V samples of HDPE, PA and PVDF and the microstructure of their fractured surfaces were studied under a Scanning Electron Microscope (SEM).

Theoretical Framework for Polymer Failure

Kinematics

We consider a macroscopically homogeneous body B identified with the region of space it occupies in a fixed reference configuration. We denote by X an arbitrary material point of B. A motion of B is then a smooth one-to-one mapping of $\mathbf{x} = \chi(\mathbf{X}, t)$. The deformation gradient, velocity and velocity can be given respectively as:

$$\mathbf{F} = \nabla \chi, \ \mathbf{v} = \dot{\chi}, \ \mathbf{L} = \text{grad} \ v = \dot{\mathbf{F}}\mathbf{F}^{-1}$$

By using the Kroner-Lee decomposition of the deformation gradient, we get,

$$\mathbf{F} = \mathbf{F}^e \mathbf{F}^p$$

 $\mathbf{L} = \mathbf{L}^e + \mathbf{F}^e \mathbf{L}^p \mathbf{F}^{e-1}.$

where \mathbf{F}^{e} , \mathbf{F}^{p} represent the elastic and inelastic distortion, respectively. The velocity gradient now becomes:

where $\mathbf{L}^e = \dot{\mathbf{F}}^e \mathbf{F}^{e-1}, \ \mathbf{L}^p = \dot{\mathbf{F}}^p \mathbf{F}^{p-1}$

Damage Variable

We introduce a damage variable:

$$d(\mathbf{X},t) \in [0,1],$$

where d = 0 represents that the material point is intact and d = 1 means that the material point is fractured.

Principle of virtual power

We denote by P an arbitrary region of the reference body B with the outward normal \mathbf{n}_R on the boundary $\partial \mathbf{P}$ of P. Additionally, we allow for power to be expended internally on P by scalar microscopic stress ω , vector microscopic stress $\boldsymbol{\xi}$ over d and ∇d , respectively.

Hence the internal power is given by:

$$\mathcal{W}_{int}(P) = \int_{P} (\mathbf{T}_{R} : \dot{\mathbf{F}} + \omega \dot{d} + \boldsymbol{\xi} . \nabla \dot{d}) dv_{R}$$

Here, T_R is the Piola-Kirchhoff (PK) stress defined as: $T_R = JTF^{-T}$

We allow for power to be expended externally on P by a scalar microscopic traction $\xi(\mathbf{n}_R)$ that expends power over \dot{d} on the boundary.

So the external power is,

$$\mathcal{W}_{ext}(P) = \int_{\partial P} \mathbf{t}_R(\mathbf{n}_R) \cdot \dot{\chi} \, da_R + \int_P \mathbf{b}_R \cdot \dot{\chi} \, dv_R + \int_{\partial P} \xi(\mathbf{n}_R) \dot{d} \, da_R$$

Here, $\mathbf{t}_R(\mathbf{n}_R)$ is the surface traction and \mathbf{b}_R is the external body force. Now, through the standard arguments of the arbitrary nature of P and virtual velocity fields, and power balance, $(\mathcal{W}_{int}(P) = \mathcal{W}_{ext}(P))$ we get the following force balance:

- Macroscopic force balance: $\text{Div}\mathbf{T}_R + \mathbf{b}_R = 0$
- Microscopic force balance: $Div \boldsymbol{\xi} \omega = 0$

Free Energy Imbalance

Let us define the free energy per unit reference volume as ψ_{R} . Now, we define two new stress measures: Elastic second PK stress: $\mathbf{S}^{e} = J\mathbf{F}^{e-1}\mathbf{T}\mathbf{F}^{e-T}$, Mandel stress: $\mathbf{M}^{e} = J\mathbf{F}^{eT}\mathbf{T}\mathbf{F}^{e-T}$ We define the list $\mathcal{V}: \mathcal{V} = (\mathbf{C}^{e}, d, \nabla d)$

From the free energy imbalance, we formulate the following constitutive relations:

$$\mathbf{S}^{e} = 2J^{p-1} \frac{\partial \hat{\psi}_{R}(\mathcal{V})}{\partial \mathbf{C}^{e}}, \ \boldsymbol{\xi} = \frac{\partial \hat{\psi}_{R}(\mathcal{V})}{\partial \nabla d}$$

We also decompose the scalar microscopic stress ω into an energetic part ω_{en} and a dissipative part ω_{dis} ,

$$\omega = \omega_{en} + \omega_{dis},$$

Where the energetic part is given by,

$$\omega_{en} = \frac{\partial \tilde{\psi}_R(\mathcal{V})}{\partial d}$$

SEM images of fractured surfaces of HDPE, PA and PVDF

In Figures 7(a), 7(b) and 7(c), we see the fracture morphology of the full fractured surface of HDPE at a strain rate of 0.0005s⁻¹, 0.005s⁻¹ and 0.05s⁻¹, respectively. The white arrows denote the direction of crack propagation. In the middle row (Figure 7(d), 7(e) and 7(f)), we focus on the local fracture morphology near the initial crack tip corresponding to the red outlined box in the top row. Similarly, in the last row (Figure 7(g), 7(h) and 7(i)), we focus on the fracture morphology away from the initial crack tip, denoted by the yellow outlined box in the top row. Qualitatively, for all 3 strain rates, we can observe that short fibrils and voids characterize the surface near the initial crack tip, whereas as we move away, we can see that the fibrils get stretched out. Numerous short fibrils, along with voids, are characteristic of craze-like failure. As the crack propagates, the samples exhibit more ductile failure, resulting in a final ligament. On comparing the effect of strain rate on the evolution of the fracture morphology, we observe that the area of the region near the initial crack tip, marked by a craze-crack mechanism characterized by numerous fibrils and voids, reduces significantly with increasing strain rate.



Figure 7: SEM images of the fracture surface of notched HDPE samples at a strain rate of: (left column-a,d,g) 0.0005s⁻¹, (middle column-b,e,h) 0.005s⁻¹ and (right column-c,f,i) 0.05s⁻¹.

At the fastest loading rate $(0.05s^{-1})$, in Figure 7(c), fracture progression is characterized by a transition from a craze-crack mechanism to a shear-yielding mechanism with a dimple pattern (Figure 7(i)) [4]. An interesting observation is the development of two distinct parabolic crack fronts, which might be a result of how the notch was induced using a razor.



Figure 8: SEM images of the fracture surface of notched PA samples at a strain rate of (a) $0.0005s^{-1}$, (b) $0.005s^{-1}$ and (c) $0.05s^{-1}$.

In Figures 8(a), 8(b) and 8(c), we see the fracture morphology of the full fractured surface of PA at a strain rate of 0.0005s⁻¹, 0.005s⁻¹ and 0.05s⁻¹, respectively. In a qualitative sense, there is no distinct difference in the fracture morphology of PA due to increasing loading rate, as seen in Figures 8(a), 8(b) and 8(c). Macroscopically, the PA samples had an appearance of brittle fracture as they displayed no plastic deformation (necking) in response to crack propagation.

In Figures 9(a), 9(b) and 9(c), we see the fracture morphology of the full fractured surface of PVDF at a strain rate of $0.0005s^{-1}$, $0.005s^{-1}$ and $0.05s^{-1}$, respectively. Similarly, as was seen in the case of PA, there is no distinct change in the morphology of the full fractured surface, as seen in Figures 9(a), 9(b) and 9(c), as we increase the strain rate of the tensile test. Crazing is not observed. However, the size of voids increases as we increase the strain rate.



Figure 9: SEM images of the fracture surface of notched PVDF samples at a strain rate of (a) $0.0005s^{-1}$, (b) $0.005s^{-1}$ and (c) $0.05s^{-1}$.

Project Activities with External Partners:

The PI is in discussion and planning to visit Houston to present the ongoing research and findings with relevant industry partners.

Project Financial Activities Incurred during the Reporting Period:

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

Project Activities with Cost Share Partners:

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

Potential Project Risks:

As the research progresses and more experimental data is collected, since the work and findings for liner polymer materials will be new, there could be a risk of unanticipated new findings. This risk will be managed by adjusting the research methods as new data comes.

Future Project Work:

The polymer samples will be aged in the coming months and quarters. The researchers will continue to conduct additional polarized light microscopy of different samples to detect surface morphology. Preliminary DSC results have shown changes in thermal events between control and aged samples that will be correlated to specific crystal structures seen in XRD results.

We will continue to develop the damage model, where we intend to specify the exact form of the free energy function, which will incorporate the physics of the deformation and the mechanism of failure for polymers. For mechanical characterization, we will perform tension tests on unaged and aged ASTM D638 Type V samples, followed by bending tests on aged specimens.

Potential Impacts to Pipeline Safety:

We have been able to use Gaussian deconvolution to detect various crystal phases in polyamide and PVDF. We are able to adjust the content of different phases with certain processing methods. These phases are associated with different mechanical integrities and could be indicative of longterm stability. The detection of these phases in aged samples could be a precursor to mechanical failure. This is an example of research findings that can help improve the integrity management of polymer liner materials.

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.

References

[1] Ma, N., Liu, W., Ma, L., He, S., Liu, H., Zhang, Z., ... & Zhu, C. (2020). Crystal transition and thermal behavior of Nylon 12. e-Polymers, 20(1), 346-352.

[2] Narayan, Sooraj, and Lallit Anand. "Fracture of amorphous polymers: A gradient-damage theory." Journal of the Mechanics and Physics of Solids 146 (2021): 104164.

[3] Narayan, Sooraj, and Lallit Anand. "A gradient-damage theory for fracture of quasi-brittle materials." Journal of the Mechanics and Physics of Solids 129 (2019): 119-146.

[4] Pan, Huanyu, Sheila Devasahayam, and Sri Bandyopadhyay. "Study of microstructure and fracture properties of blunt notched and sharp cracked high density polyethylene specimens." *Scientific Reports* 7.1 (2017): 6096.