

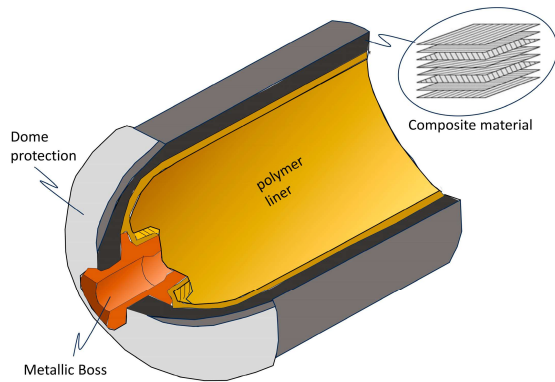
A diffusion-coupled thermomechanical constitutive model for polymers in a hydrogen environment

20th European Mechanics of Materials Conference
EMMC 2026
May 27-29, 2026, Florence, Italy

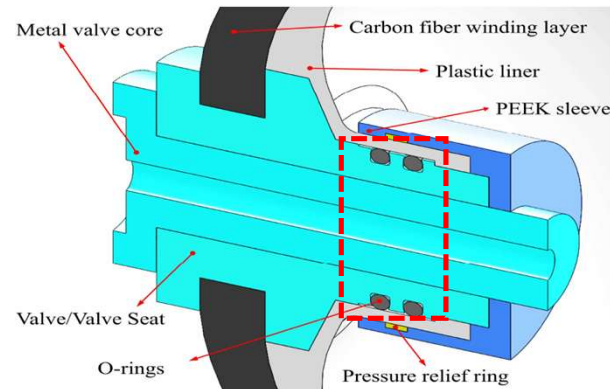
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This research was performed within the project HYPOLFAIL - Hydrogen-Induced Damage to Polymers at High Pressure: Understanding Interaction and Failure Mechanisms, selected under the M-ERA.NET Joint Transnational Call 2024. HYPOLFAIL is coordinated by SCIOFLEX Hydrogen GmbH (AT), with consortium partners GDTech S.A. (BE), Seal Maker Produktions- und Vertriebs GmbH (AT), MATELIOS (IT), University of Pannonia (HU), Université de Liège - CM3 (BE), and Johannes Kepler University Linz - IPPE (AT). The project is funded by the respective national and regional funding organizations: FFG-Mobility (Austria), SPW (Belgium), PR Calabria FESR-FSE+ 2021–2027 (Italy), and NKFIH (Hungary).

Polymers in H₂ storage tanks



Type 4 Hydrogen tank [Piraino 2024]

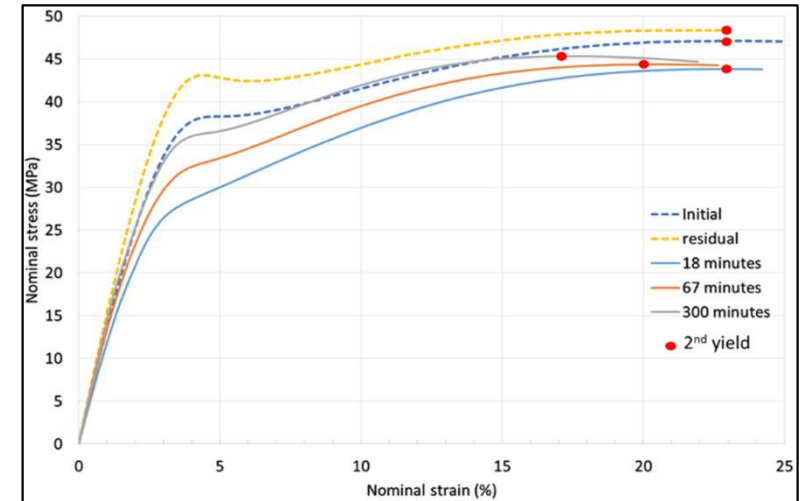


O-rings in Metallic Boss [Zhang 2025]

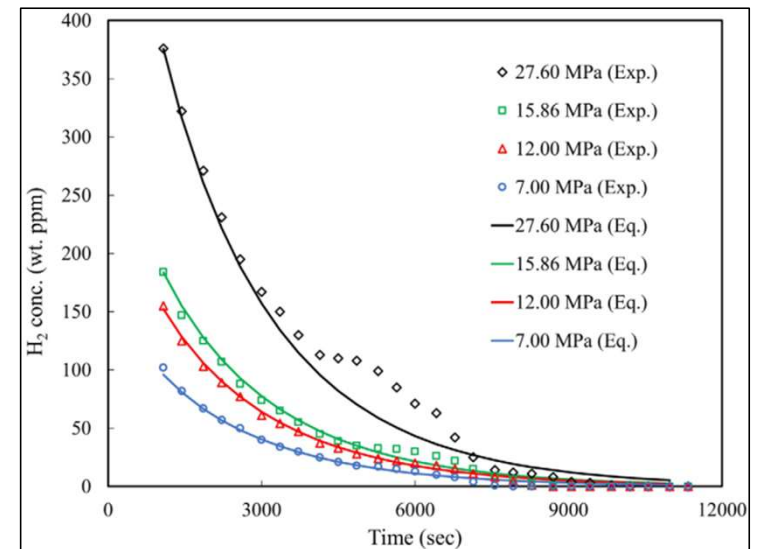
Challenges

- Polymer liners and O-rings -> Coupled H₂-diffusion-non-linear mechanical response
- Changes to amorphous phase during diffusion -> Lower glass transition temperature -> Plasticized response
- Square root mass outflow -> Fickian diffusion process

Objective: Model to capture Fickian diffusion coupled deformation in polymers - qualitatively show plasticisation in Thermoplastic Urethane (TPU) !



PA11 in H₂ - Ex-situ tensile tests [Talleduc 2024]



Fickian Diffusion of H₂ in EPDM [Kulkarni 2021]

Strong Form of Diffusion Thermomechanics

Force balance

$$\text{Div } \mathbf{P} = \mathbf{0}$$

Heat equation

$$c_p \dot{\theta} = \text{Div}(k \nabla \theta) + W$$

Fluid continuity

$$\frac{\partial c}{\partial t} = \text{Div}(D \nabla c)$$

Variables

$\mathbf{P}$ - 1st PK stress

θ - Temperature

c - H₂ concentration

W - Heat source

k - Thermal Conductivity

D - Diffusion coefficient

Issues

- 1st PK Stress $\mathbf{P}$ - Relaxation in viscoelasticity and viscoplasticity

- Swelling induced deformation

$$E_{\Delta c} = 3\alpha_c(c - c_0)$$

where $E_{\Delta c}$ is a log strain

$$\alpha_c = 1.5e - 4/\text{wt.ppm}$$

- Units of concentration [wt.ppm]

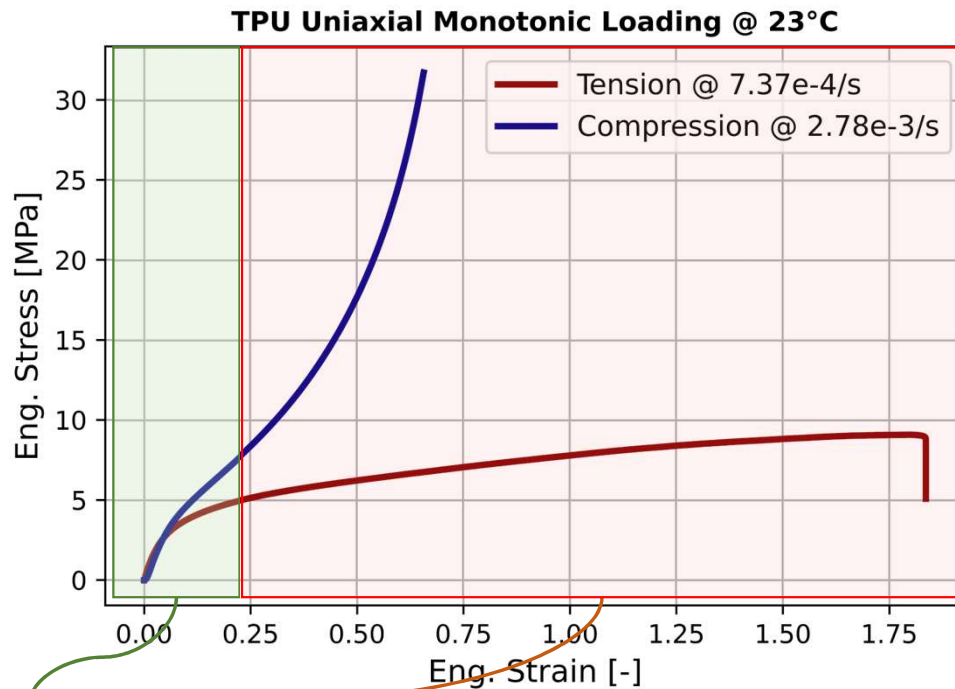
$$= \frac{\text{parts of H}_2}{\text{million parts of polymer}}$$

- **Assumptions:**

1. W only consists of mechanical heating, but not diffusion-related terms
2. No influence of $\mathbf{P}$ on fluid continuity
3. Constant $D = 4e-4 \text{ mm}^2/\text{s}$

Diffusion-Thermo(visco)mechanics

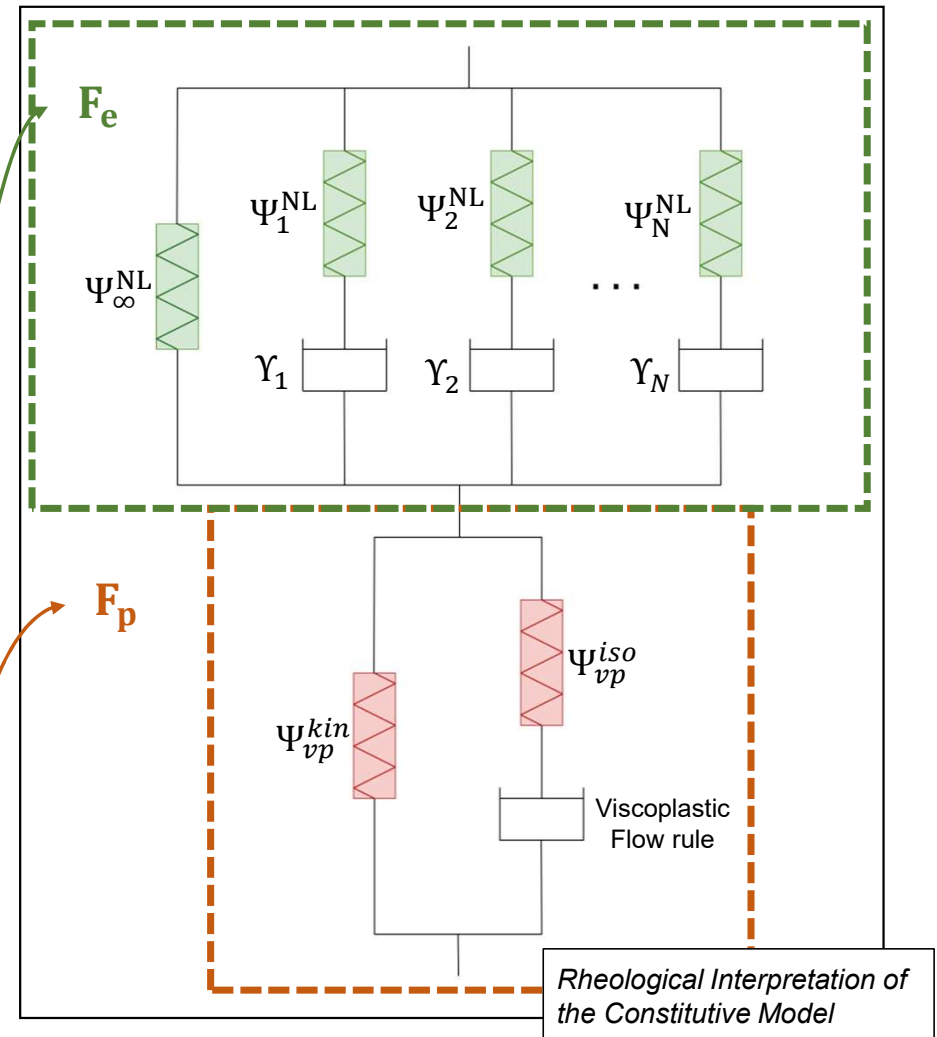
- TPU Perspective [Jinaga 2025]



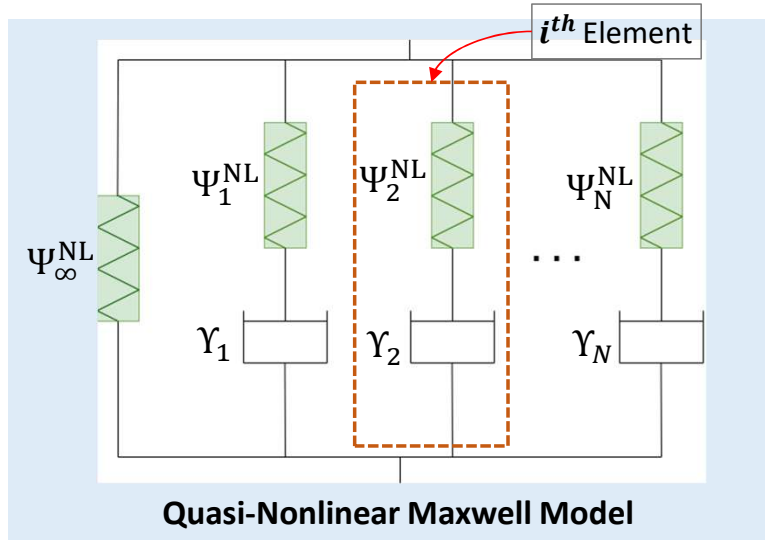
Viscoelasticity - Quasi-nonlinear Maxwell Model

Viscoplasticity - Power Law OF + Perzyna Flow

Mullin's Effect + Self heating



Quasi-Nonlinear (Diffuso-Thermo-)Viscoelasticity (TVE)



For the i^{th} Maxwell element, in Linear Viscoelasticity [Govindjee 1993]

- Rate equations solved for i^{th} spring strain ($\mathfrak{E}_i$) in shifted time (Δt^*) using time-temperature superposition (TTSP)

$$\mathfrak{E}_i = \mathfrak{E}_i(\mathbf{E}_e, \Delta t^*) \Rightarrow \Delta t^* = \int_n^{n+1} \frac{1}{a(\epsilon)} d\epsilon$$

- WLF shift factor + Dolittle Expression from DMA Master Curves

$$a = \exp\left(-\frac{C_1(\theta - \theta_{ref})}{C_0 + \theta - \theta_{ref}}\right) \exp\left(-\frac{D_1 D_2 c}{D_3(JD_3 + D_2 c)}\right)$$

“Quasi-Nonlinear Viscoelasticity”

Linear viscoelasticity -> Newtonian Dashpots with Separable rate equations

+

Strain-dependent moduli -> Nonlinear functions in terms of log strains $\mathbf{E}_e, \mathfrak{E}_i$

Non-linearity in stress [Jinaga 2025]

- Convenient form of Corotational Kirchhoff stress ($\boldsymbol{\tau}_i$),

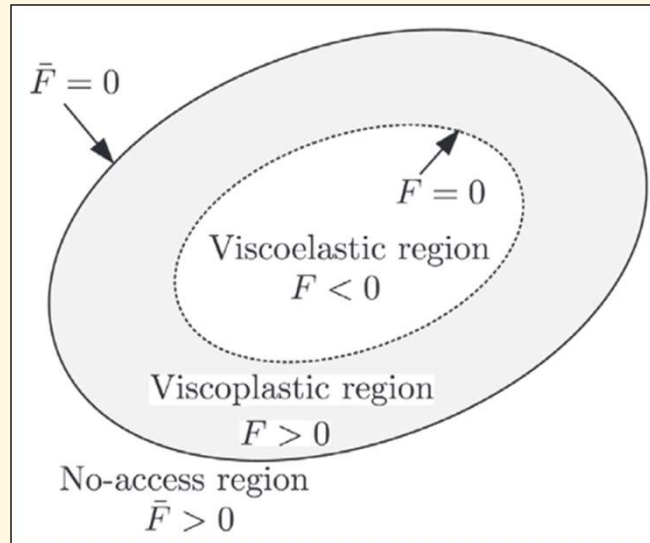
$$\boldsymbol{\tau}_i = K_{i0} \mathbf{A} \text{tr } \mathfrak{E}_i \mathbf{I} + G_{i0} \mathbf{B} \text{dev } \mathfrak{E}_i$$

non-linearity induced using strain-dependent scalars $\mathbf{A}$ and $\mathbf{B}$

Here, $K_{\infty 0}, K_{i0}$ and $G_{\infty 0}, G_{i0}$ are the initial moduli from DMA Master Curves

(Diffuso-Thermo-) Viscoplasticity (TVP)

- Extended Drucker-Prager Power Yield Function ($\bar{F}$) in various regimes [Nguyen 2016]



where

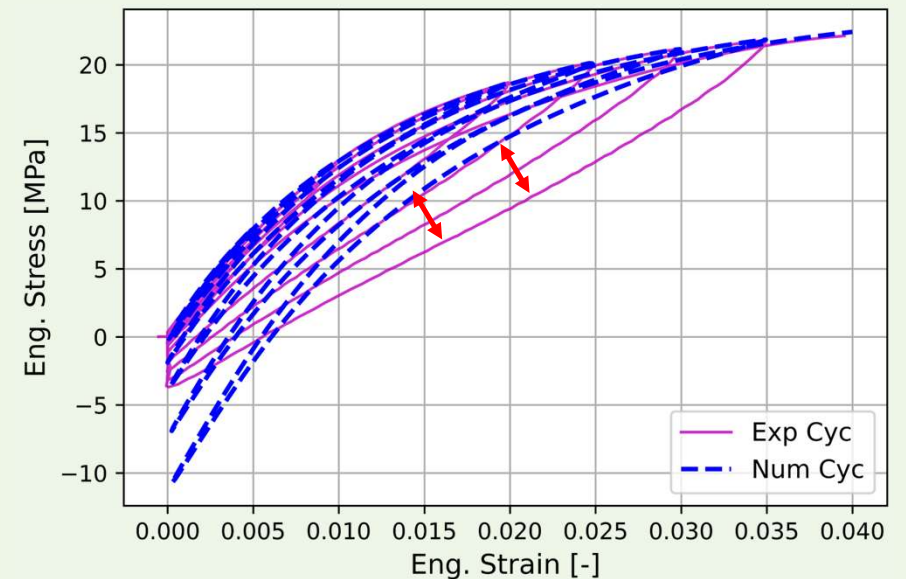
$$\bar{F} = \bar{F}(\tau, \Gamma, \Delta\gamma, T, c)$$

is in flow parameter (Γ) and equivalent plastic strain ($\Delta\gamma$) driven by Perzyna Flow

Simplifying Assumption: Hardening laws in $\bar{F}$ are constant with concentration

Mullin's Effect

- Linear Scaler (ζ) in cyclic loading



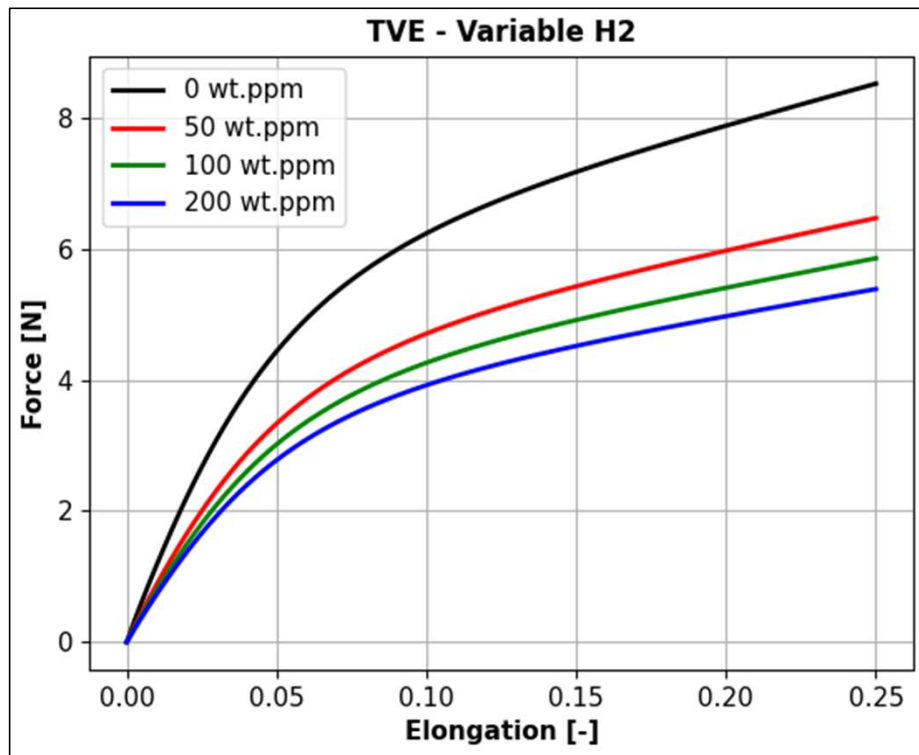
where

$$\zeta = 1 - z \left(1 - \frac{\psi}{\psi_{\max}} \right)$$

Simplifying Assumptions: z is constant with concentration, ψ is only a function of viscoelastic deformation energy

Stress Response with constant H₂ concentrations

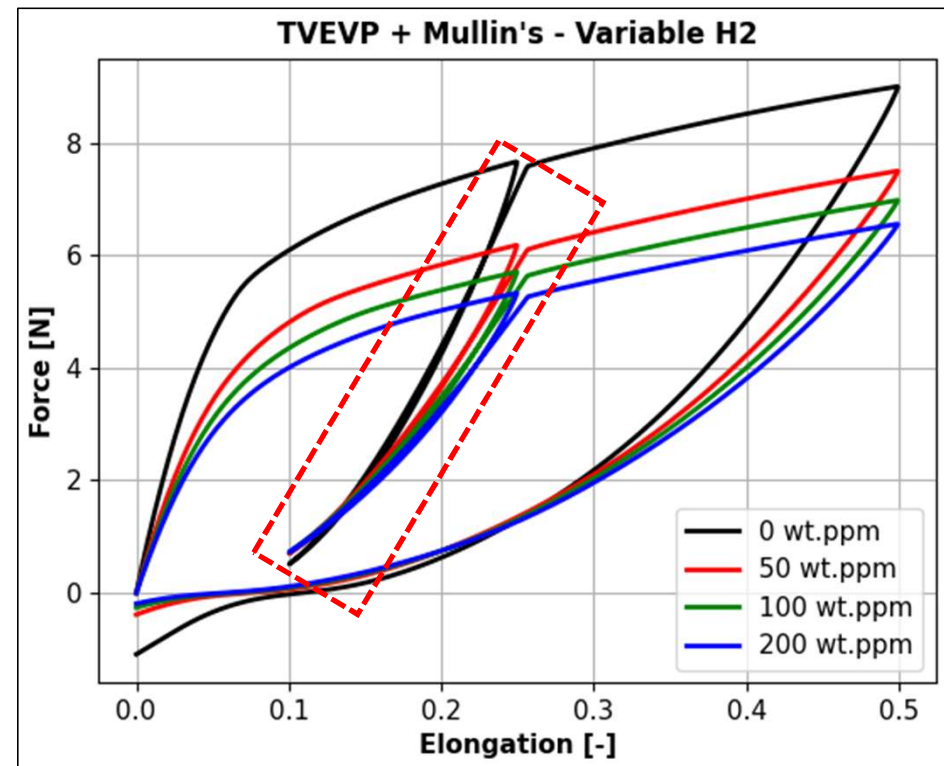
- UTT Response [TPU data from Jinaga 2025]



- Combined Shift factor – WLF temperature with Dolittle concentration shifts in relaxation modulus

$$a = \exp\left(-\frac{C_1(\theta - \theta_{ref})}{C_0 + \theta - \theta_{ref}}\right) \exp\left(-\frac{D_1 D_2 c}{D_3(JD_3 + D_2 c)}\right)$$

Assumed Values - D₁ = 0.025, D₂ = 1, D₃ = 4e-4



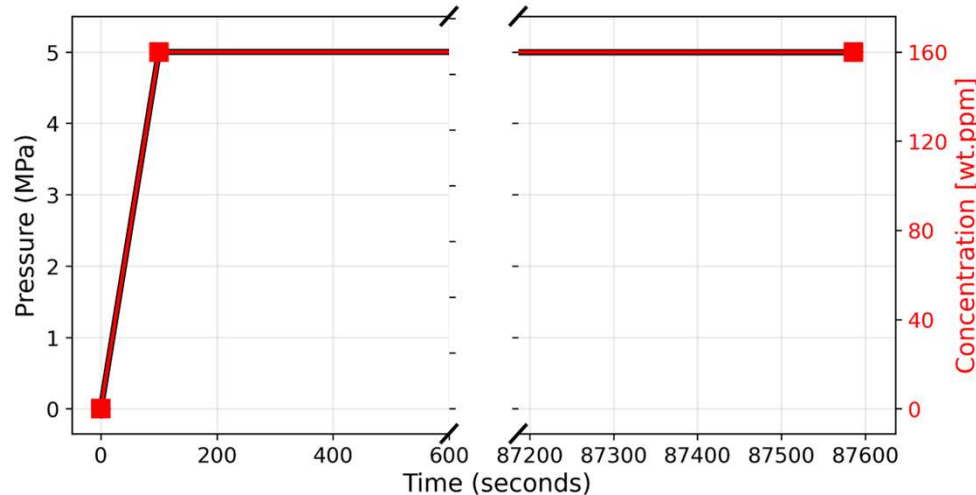
Transient Uniaxial Test – Fick's Diffusion in a Membrane 1

Features

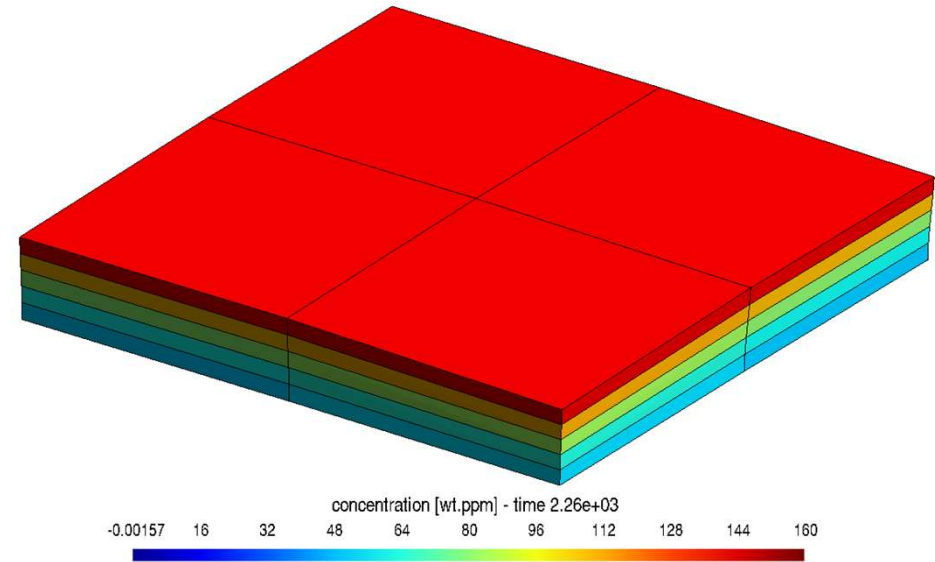
- Pressure (p) ramp of 5 MPa for 10 secs, held for 1 day
- Pressure-concentration (p-C) relation
 - Henry's law : $c = S p$

where $S = 32 \text{ wt.ppm/MPa}$ [Kulkarni 2021]

To show: Transient parabolic profiles and concentration effect on creep



p-C ramp and hold profile



Numerical Setup

1. Top surface is loaded and held flat
2. Rest of the surfaces are adiabatic
3. Sides constrained in uniaxial stress

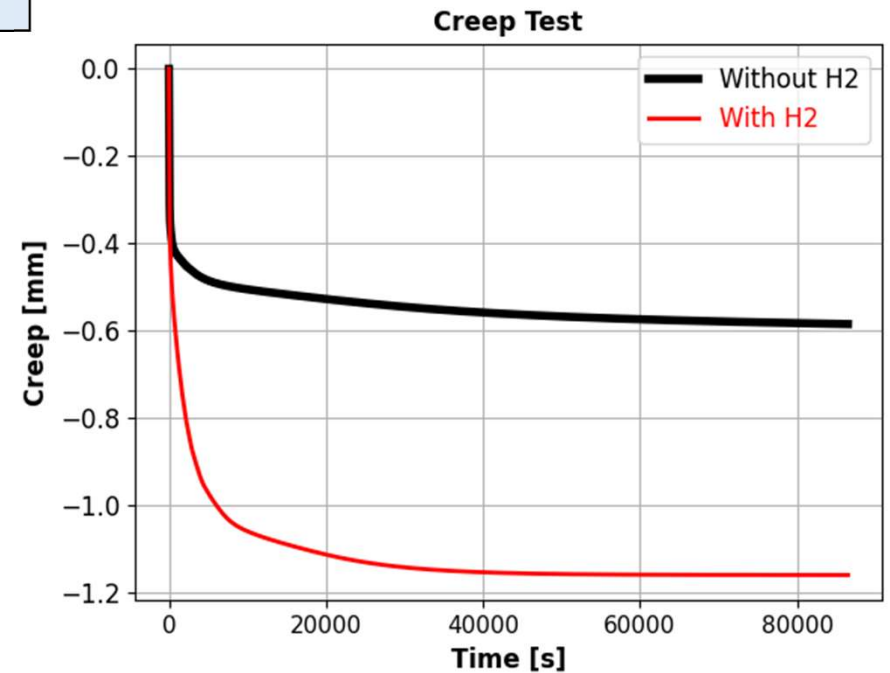
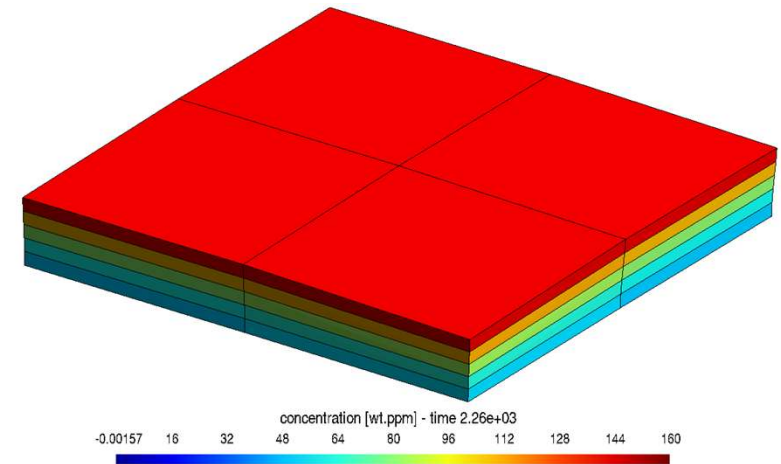
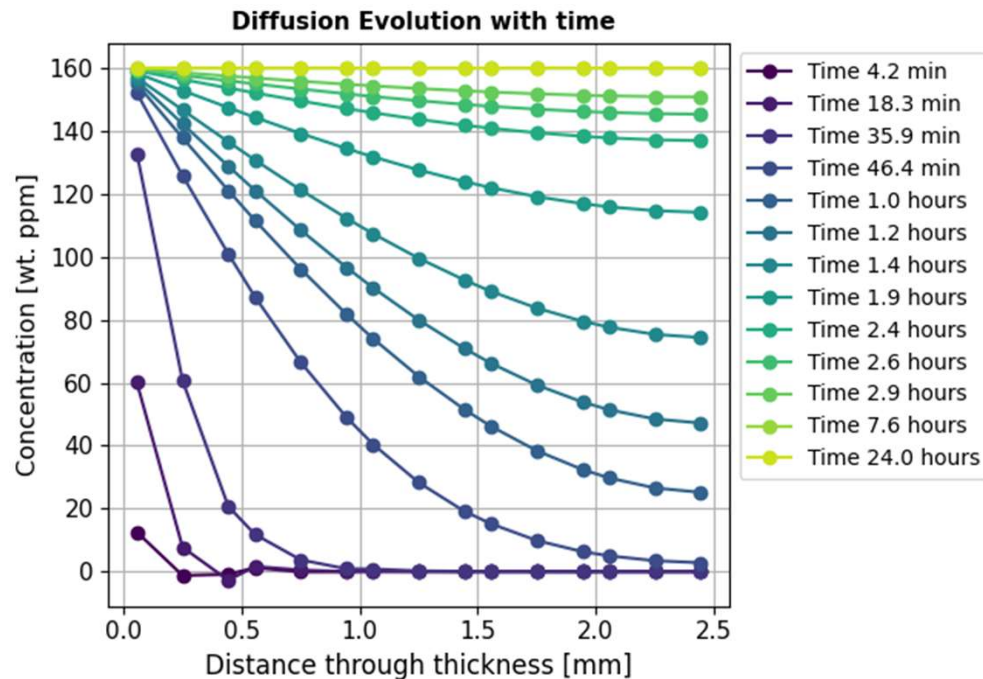
Transient Uniaxial Test – Fick's Diffusion in a Membrane 2

Features

- Pressure (p) ramp of 5 MPa for 10 secs, held for 1 day
- Pressure-concentration (p-C) relation
 - Henry's law : $c = S p$

where $S = 32 \text{ wt.ppm/MPa}$ [Kulkarni 2021]

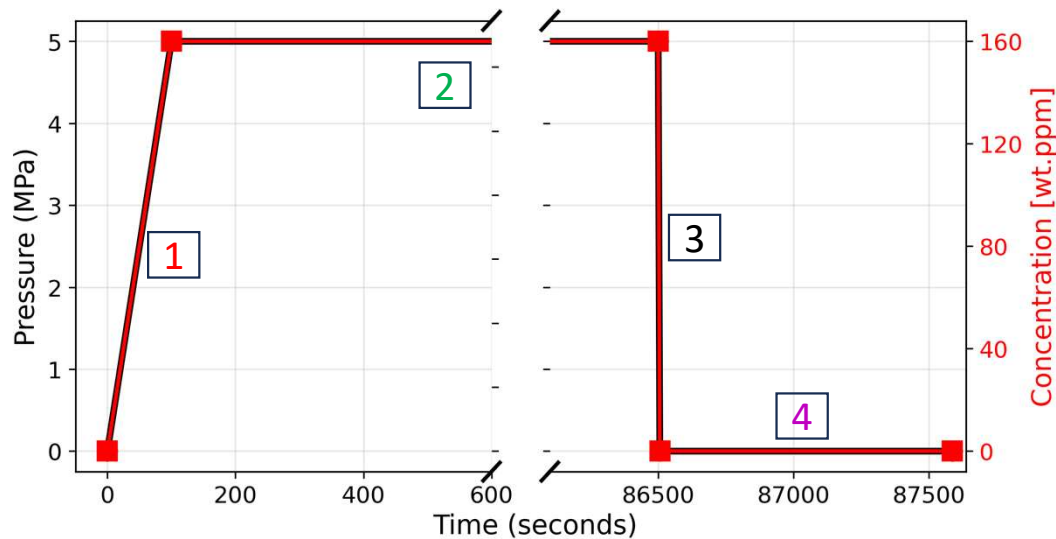
To show: Transient parabolic profiles and concentration effect on creep



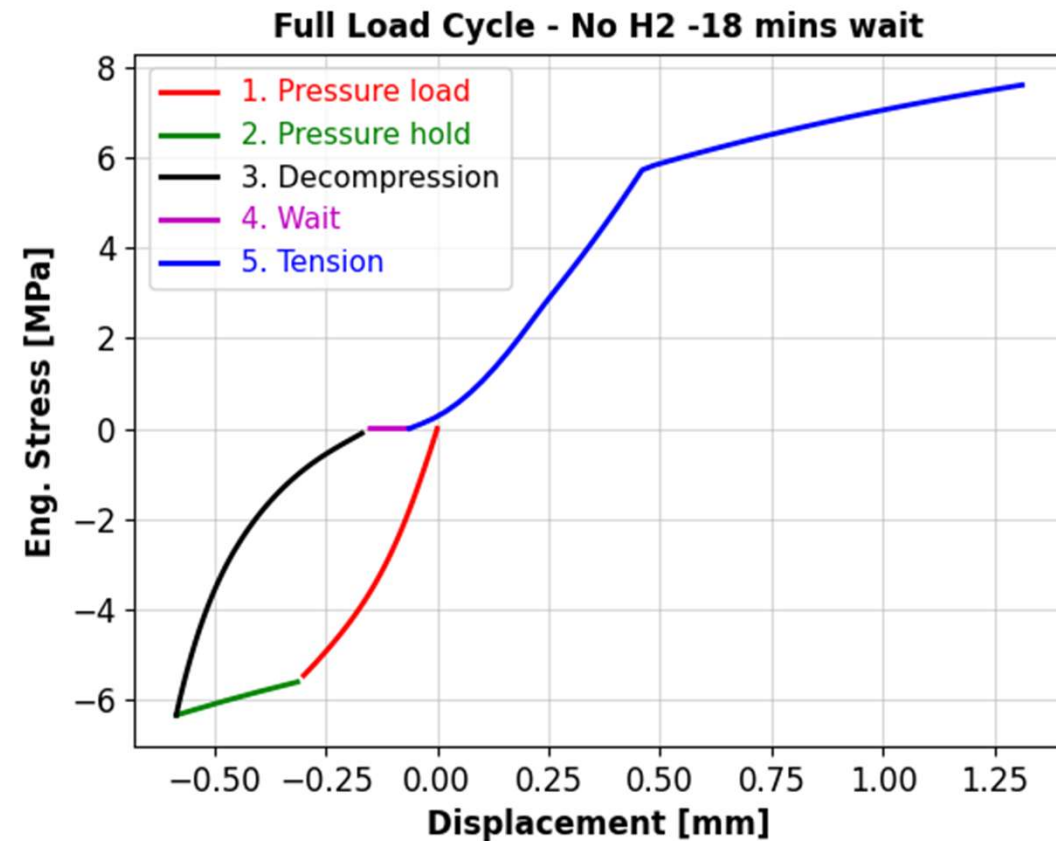
Complex Transient Test – Post-Decompression Tensile Loading 1

Loading Steps

1. Pressure load - ramps of 5 MPa - 160 wt.ppm for 100 secs
2. Pressure hold for 24 hours
3. Decompression in 6 secs
4. Wait for variable time – 18/67/300 mins/ 24 hours
5. Tension ~50 % elongation



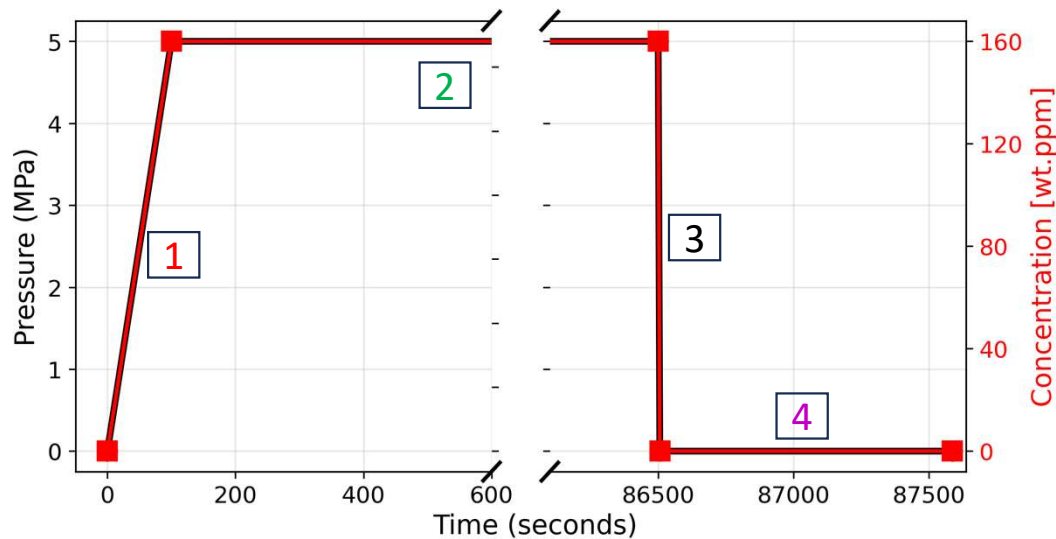
Pressure-concentration loads in steps 1-4



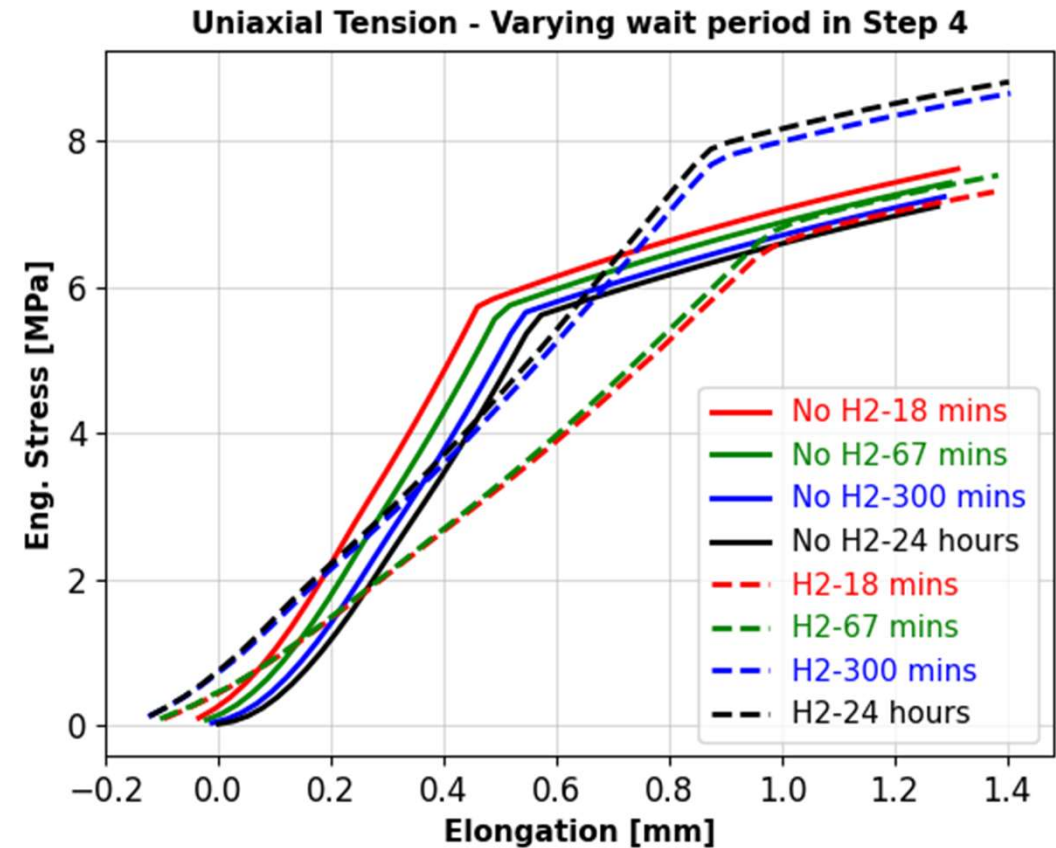
Complex Transient Test – Post-Decompression Tensile Loading 2

Loading Steps

1. Pressure load - ramps of 5 MPa - 160 wt.ppm for 100 secs
2. Pressure hold for 24 hours
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4. Wait for variable time – 18/67/300 mins/ 24 hours
5. Tension ~50 % elongation



Pressure-concentration loads in steps 1-4



More compliant reloading curves and hardened plastic state post step 4 diffusive outflux

Conclusions and Perspectives

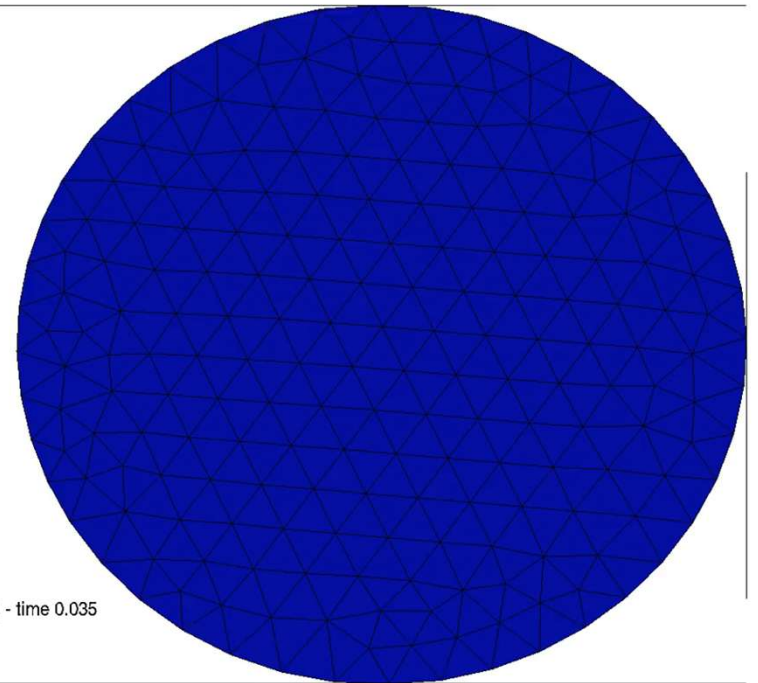
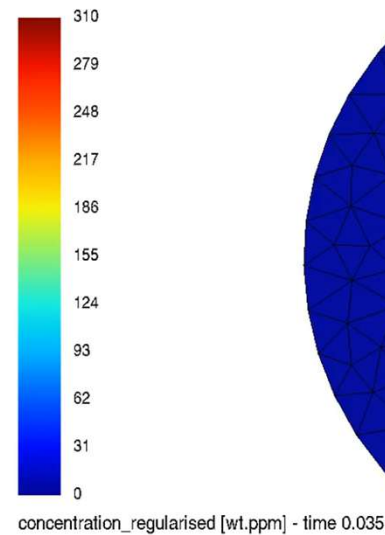
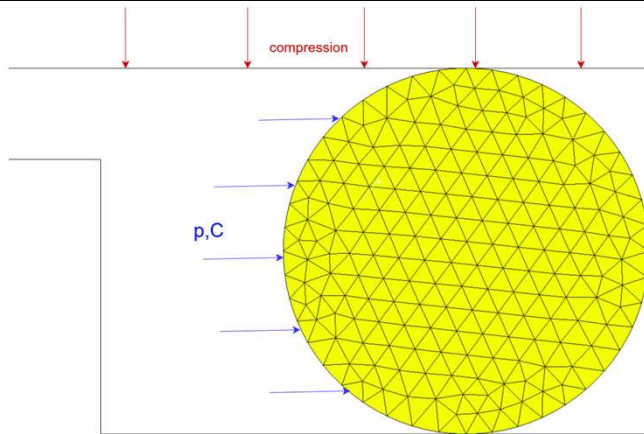
- Constitutive model to capture direct influence of concentration on stress – combined shift factor
- Plasticisation of polymer with increasing hydrogen content demonstrated - steady state and transient
- Effects of Fickian diffusion on polymer relaxation demonstrated
- Incorporation of strain gradient coupling in advanced diffusion models - Application to O-rings

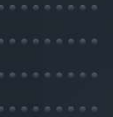
2D O-ring (under development) Setup: RT, high strain rate and *Discontinuous Galerkin formulation* [Nguyen 2016]

Load Steps:

1. **Compression to engage contact** (in black)
2. **Pressure and concentration ramps**

[Yamabe 2009]





Thank you for your attention!

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Conclusions and Perspectives

- Constitutive model to capture direct influence of concentration on stress – combined shift factor
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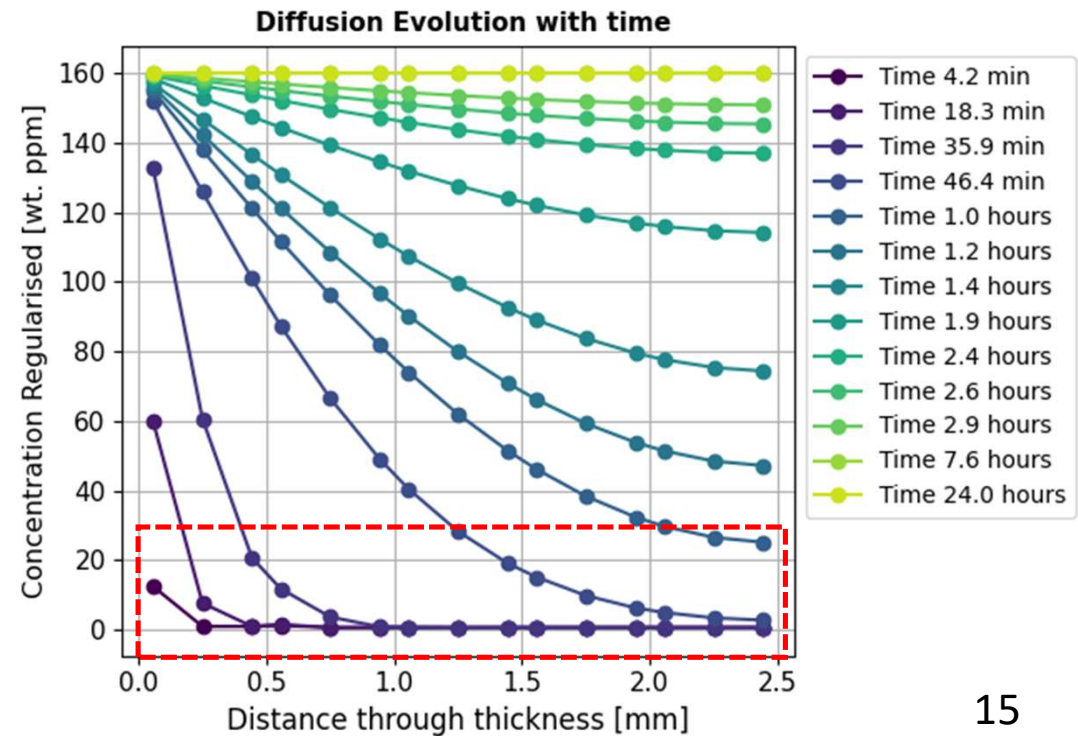
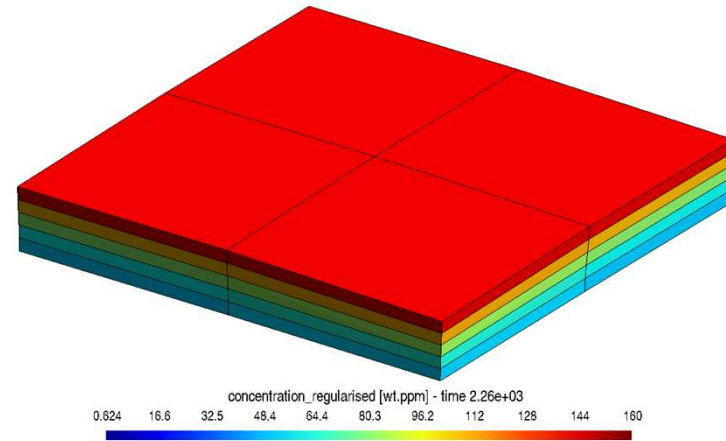
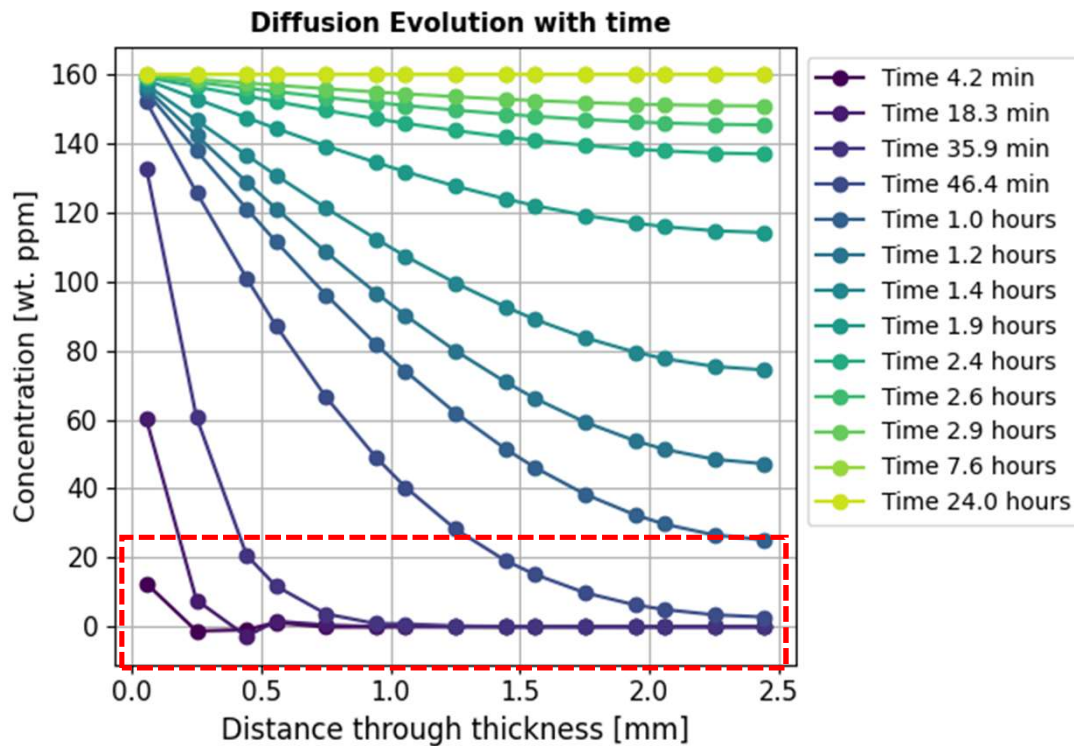
References

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Appendix - Regularised Concentration 1

Issue: 2nd order mesh at 0 wt.ppm -> negative concentration values

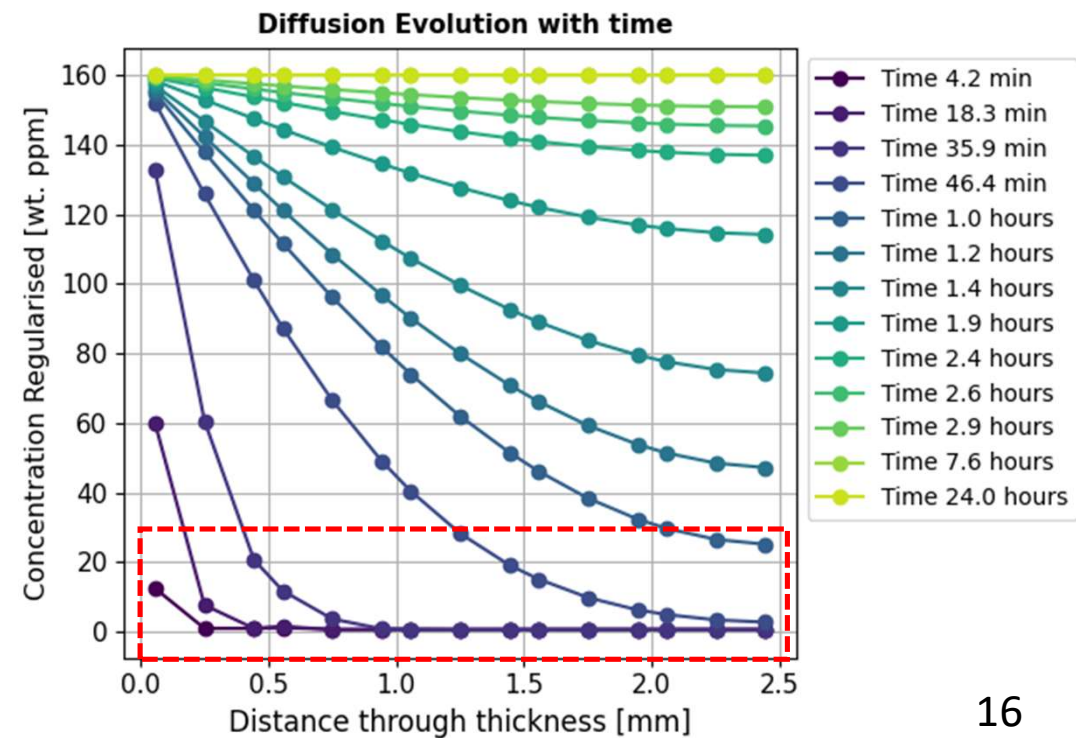
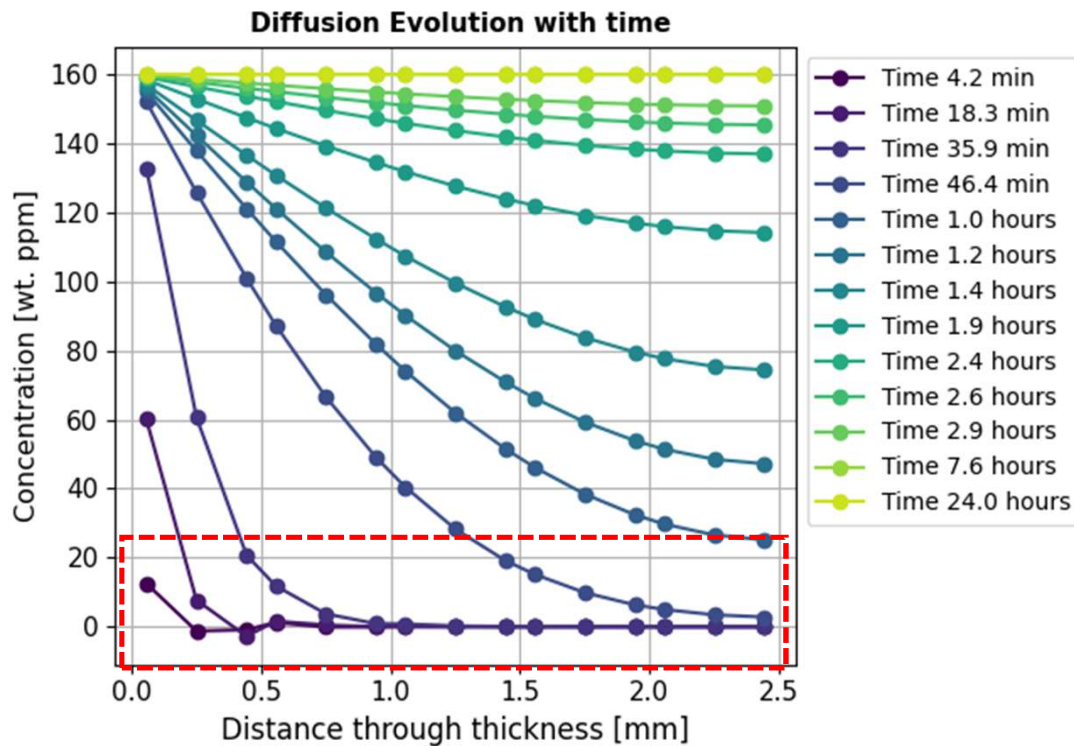
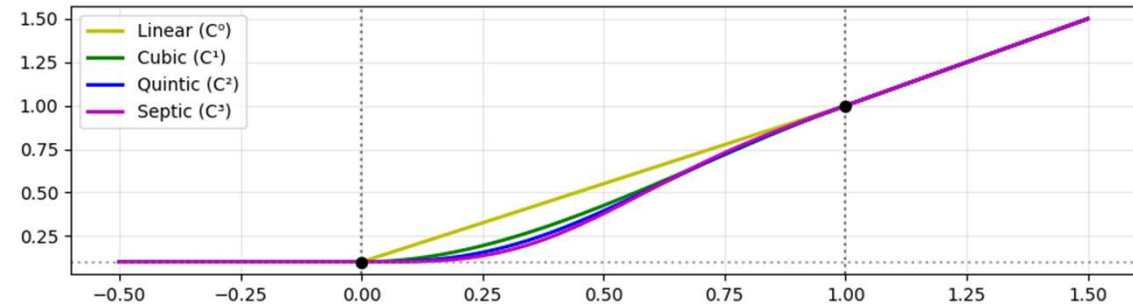
Solution: Hermitian interpolation (C2 quintic) -> min. positive regularised value -> Consistent diffusive flux



Appendix - Regularised Concentration 1

Issue: 2nd order mesh at 0 wt.ppm -> negative concentration values

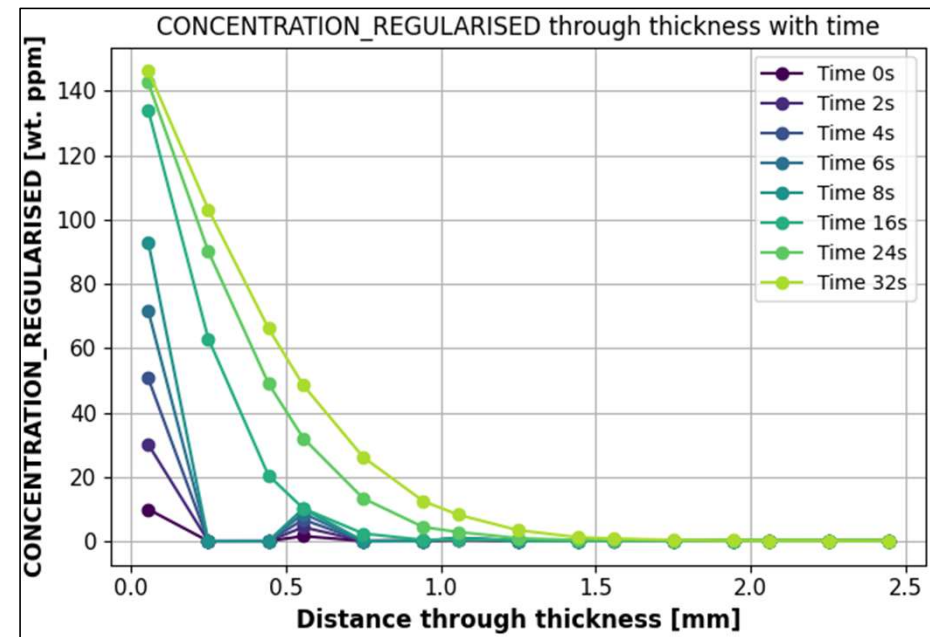
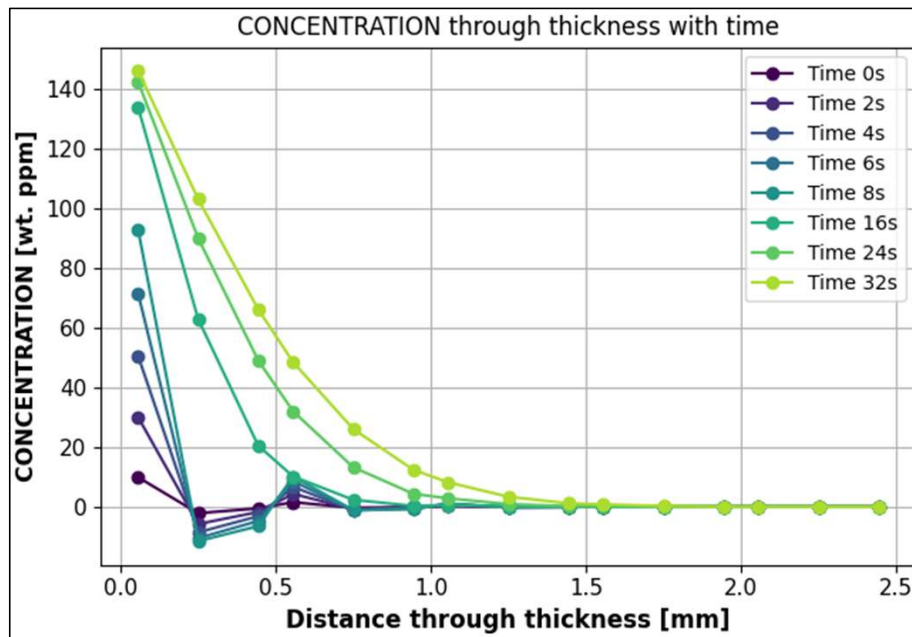
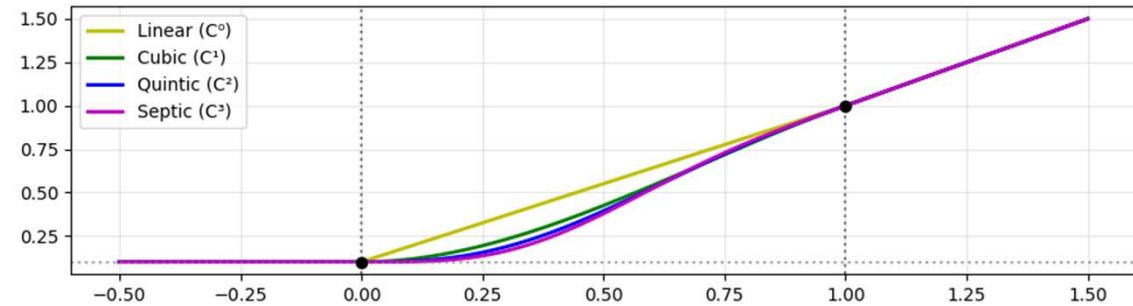
Solution: Hermitian interpolation (C2 quintic) -> min. positive regularised value -> Consistent diffusive flux



Appendix - Regularised Concentration 2

Issue: 2nd order mesh at 0 wt.ppm -> negative concentration values

Solution: Hermitian interpolation (C2 quintic) -> min. positive regularised value -> Consistent diffusive flux



Appendix - Numerical Example

- 2D O-ring 1

Setup: Transient 2-step deformation and realistic diffusion at room temperature, high strain rate, 0 wt.ppm; Only TVE.

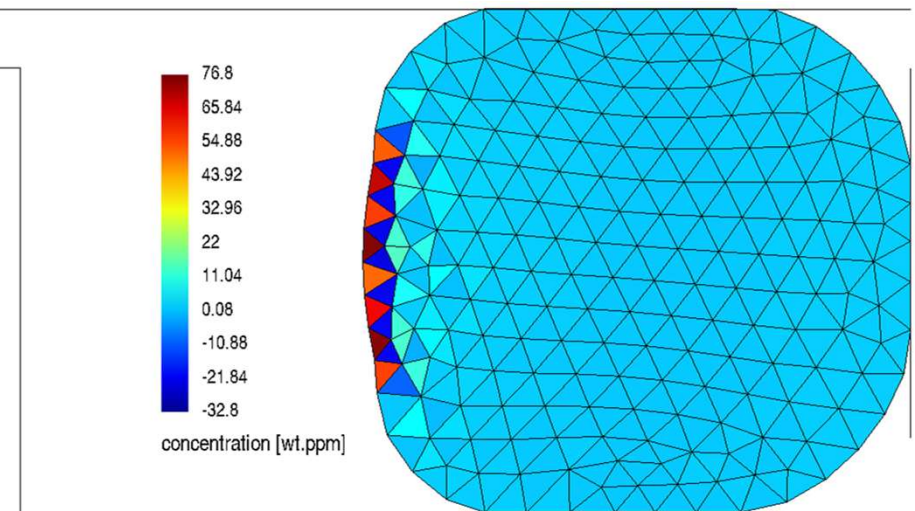
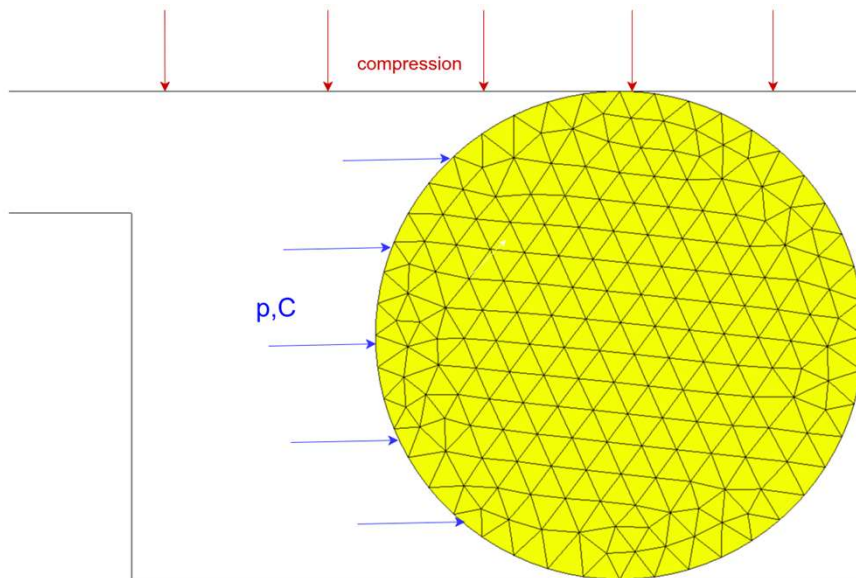
Load Steps:

1. **Compression to engage contact** (in black)
2. **Pressure and concentration ramps**

[Yamabe 2009]

Issues: For slow diffusion (low D),

- Solution front contains unrealistic values of concentration
- Exacerbated in case of irregular meshes
- Unstable using Hermitian regularisation



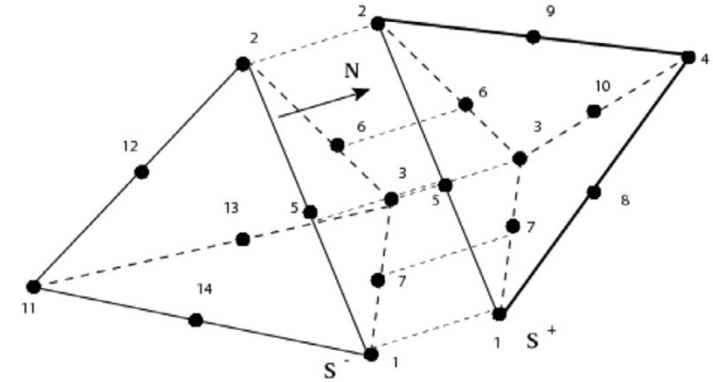
Unrealistic conc. distribution from the solver

Appendix - Revised Weak Form of Diffusion Thermomechanics

Discontinuous Galerkin Formulation

- Inter-element interfaces with weakly constrained C0 independent variables [Nyugen 2013, Homsy 2019]
- 2nd order-like stabilisation terms with $\mathbb{C}^0$ and $\mathbb{D}^0$, initial stiffness and diffusion tensor (also, conductivity for temperature field, not shown)

Where, across interfaces, $[[\cdot]]$ - jumps only in independent variables, $\langle \cdot \rangle$ - mean operator



Interface element between tetrahedral elements
(Nyugen 2013)

Force balance

$$\int_{\Omega} \mathbf{P} : \delta \mathbf{F} d\Omega + \int_{\partial_I} [[\delta \mathbf{u}]] \cdot \langle \hat{\mathbf{P}} \rangle \cdot \mathbf{N}^- d\partial\Omega + \int_{\partial_I} [[\mathbf{u}]] \cdot \langle \hat{\mathbf{P}}(\delta \mathbf{u}) \rangle \cdot \mathbf{N}^- d\partial\Omega + \int_{\partial_I} [[\mathbf{u}]] \otimes \mathbf{N}^- : \left\langle \frac{\beta}{h} \mathbb{C}^0 \right\rangle : [[\delta \mathbf{u}]] \otimes \mathbf{N}^- d\partial\Omega = \int_{\partial_N} \mathbf{T} \cdot \delta \mathbf{u} d\partial\Omega$$

Fluid continuity

$$\int_{\Omega} (\mathbf{Q} \cdot \delta \nabla c + \dot{c} \delta c) d\Omega + \int_{\partial_I} [[\delta \nabla c]] \cdot \langle \hat{\mathbf{Q}} \rangle \cdot \mathbf{N}^- d\partial\Omega + \int_{\partial_I} [[\nabla c]] \cdot \langle \hat{\mathbf{Q}}(\delta \nabla c) \rangle \cdot \mathbf{N}^- d\partial\Omega + \int_{\partial_I} [[\nabla c]] \cdot \mathbf{N}^- : \left\langle \frac{\beta}{h} \mathbb{D}^0 \right\rangle : [[\delta \nabla c]] \cdot \mathbf{N}^- d\partial\Omega = \int_{\partial_N} Q \delta c d\partial\Omega$$

Variables

$\mathbf{P}$ - 1st PK stress
 $\mathbf{T}$ - Traction
 c - H₂ concentration
 $\mathbf{Q}$ - Diffusive flux
 $\mathbf{N}^-$ - Interface normal
 Q - Scalar flux BC

Appendix - Numerical Example

- 2D O-ring 2

Setup: Transient 2-step deformation and realistic diffusion at room temperature, high strain rate, 0 wt.ppm; Only TVE -> **with DG formulation**

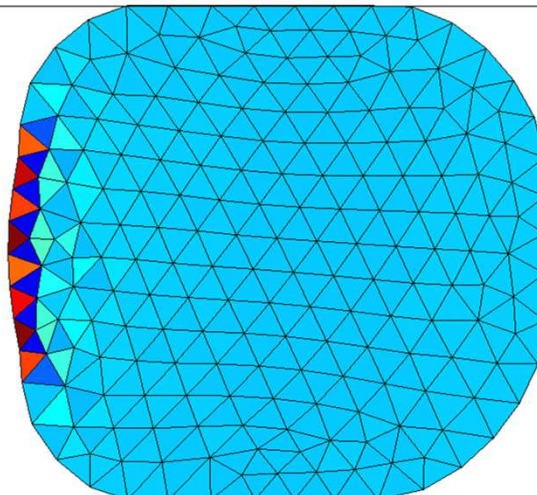
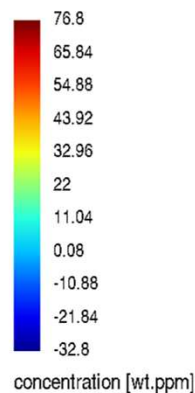
Load Steps:

1. **Compression to engage contact** (in black)
2. **Pressure and concentration ramps**

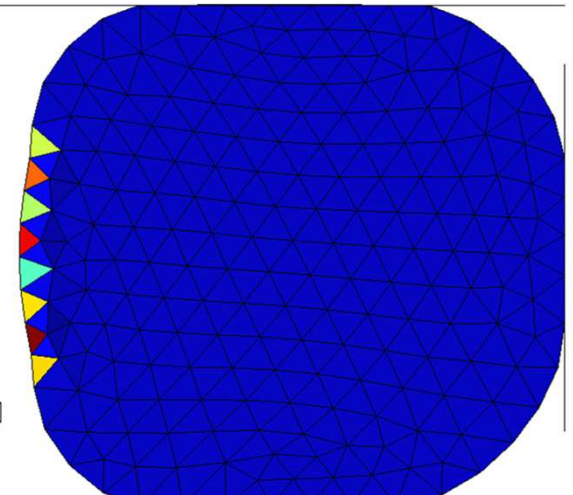
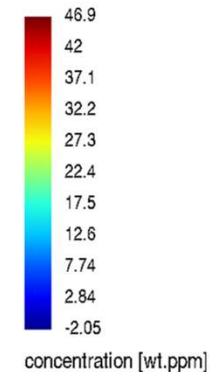
(Refs: IPPE and Yamabe 2009)

Resolved: For slow diffusion (low D),

- Concentration profiles are realistic with DG formulation!
- Caveat: Additional numerical expenditure of interface elements



With Continuous Galerkin (CG)



With Discontinuous Galerkin (DG)

Appendix - Numerical Example

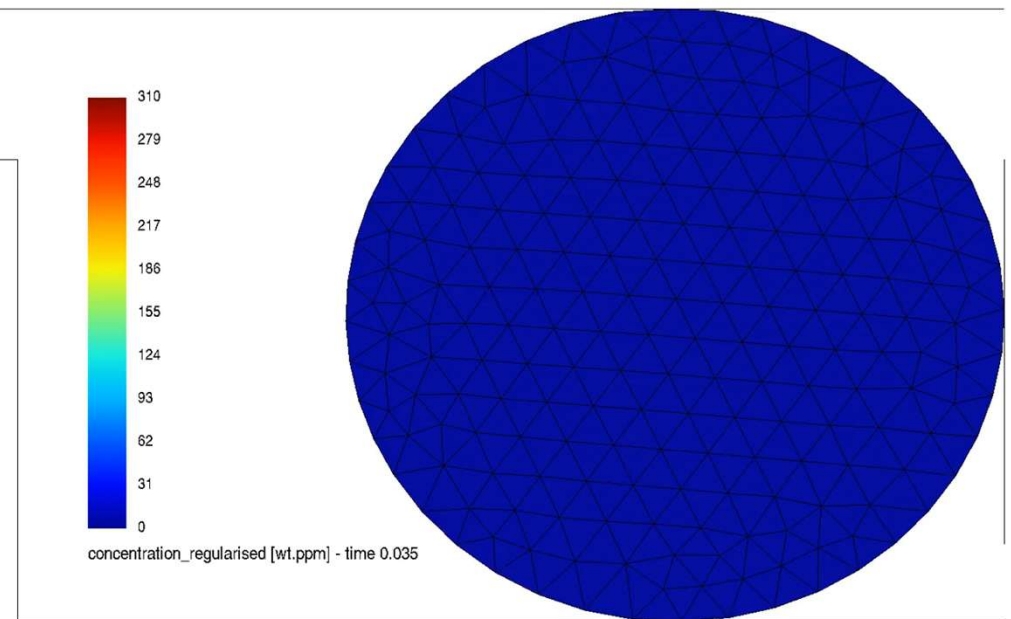
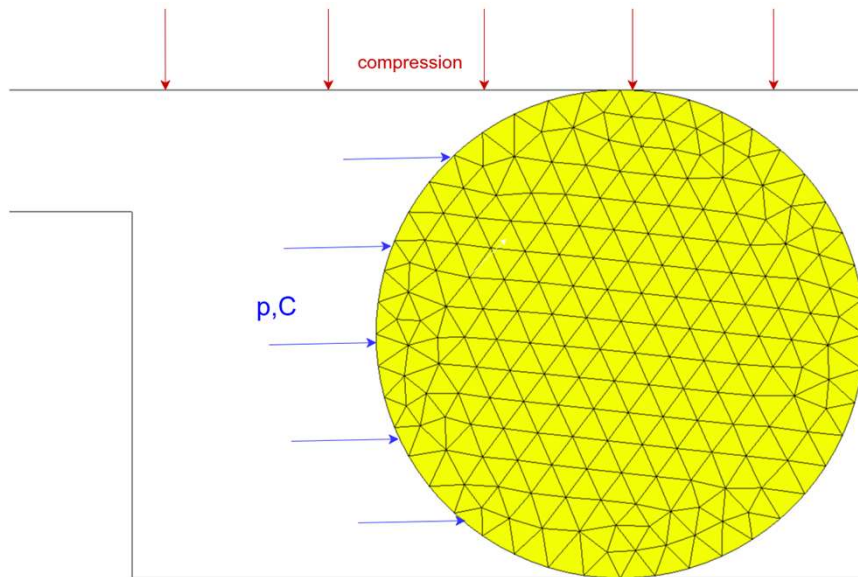
- 2D O-ring (under development)

Numerical Setup: RT, high strain rate and *Discontinuous Galerkin formulation* [Nguyen 2016]

Load Steps:

1. **Compression to engage contact** (in black)
2. **Pressure and concentration ramps**

[Yamabe 2009]



Realistic concentration distributions in coarse unstructured meshes with Discontinuous Galerkin (DG) Formulation

Appendix - Numerical Example

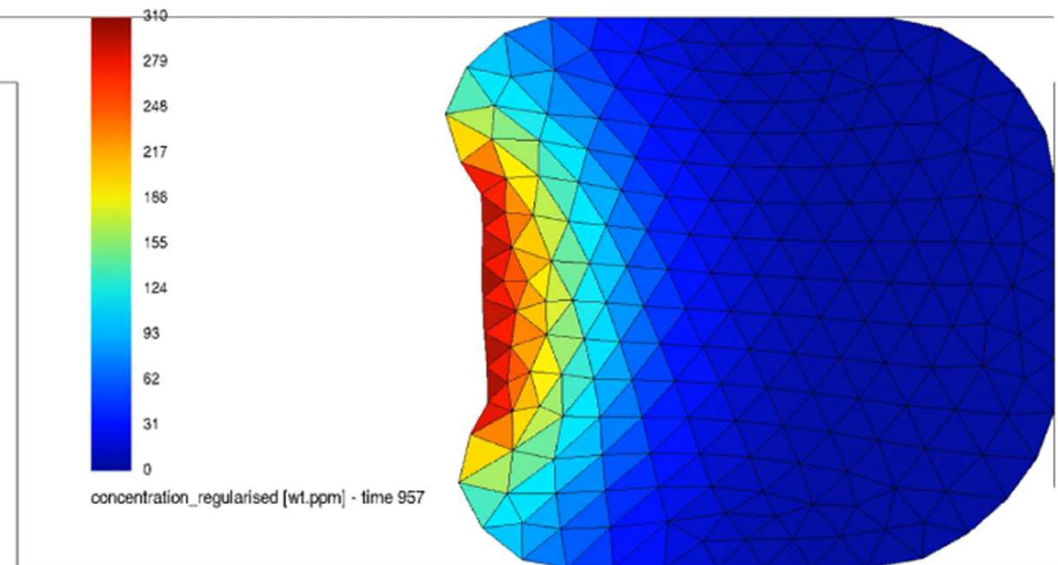
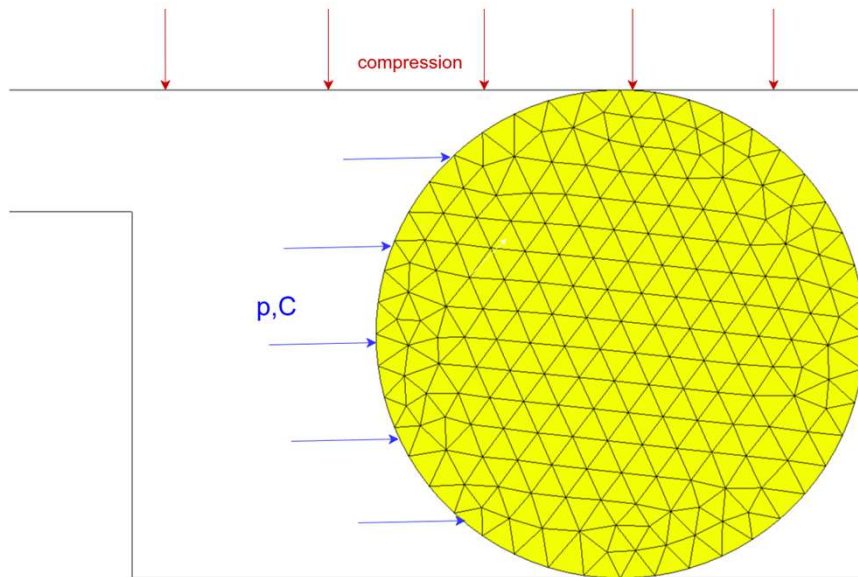
- 2D O-ring (under development)

Numerical Setup: RT, high strain rate and *Discontinuous Galerkin formulation* [Nguyen 2016]

Load Steps:

1. **Compression to engage contact** (in black)
2. **Pressure and concentration ramps**

[Yamabe 2009]



Realistic concentration distributions in coarse unstructured meshes with Discontinuous Galerkin (DG) Formulation

Appendix - Advanced Diffusion Thermomechanics

Force balance

$$\text{Div } \mathbf{P} = \mathbf{0}$$

Heat equation

$$c_p \dot{\theta} = \text{Div}(k \nabla \theta) + W$$

Fluid continuity

$$\frac{\partial c}{\partial t} = \text{Div}(m \nabla \mu)$$

Variables

$\mathbf{P}$ - 1st PK stress
 $\mathbf{F}$ - Deformation gradient
 θ - Temperature
 c - H₂ concentration
 μ - chemical potential
 H - Heat source
 k - Thermal Conductivity
 m - Mobility coefficient

Advancements

- Thermodynamic foundation – influence of stress on diffusion
- Mobility Coefficient m - dependence of diffusion coefficient on temperature and concentration
- Chemical potential - $\mu = \frac{\partial \psi}{\partial c}$ -> mixing and strain dependence

(ψ is free energy)

$$\mu = R\theta \left(\log \frac{\lambda \alpha_D c}{1 + \lambda \alpha_D c} + \frac{\lambda \alpha_D c}{1 + \lambda \alpha_D c} + \frac{\chi}{(1 + \lambda \alpha_D c)^2} \right) + \mu_{\text{VEVP}}(\mathbf{F}, \theta, c)$$

[Chester 2011]

- $\nabla \mu = \nabla \mu(\mathbf{F}, \theta, c, \nabla \mathbf{F}, \nabla \theta, \nabla c)$
 - Strain Gradient ($\nabla \mathbf{F}$) - To accommodate C1 terms in the formulation

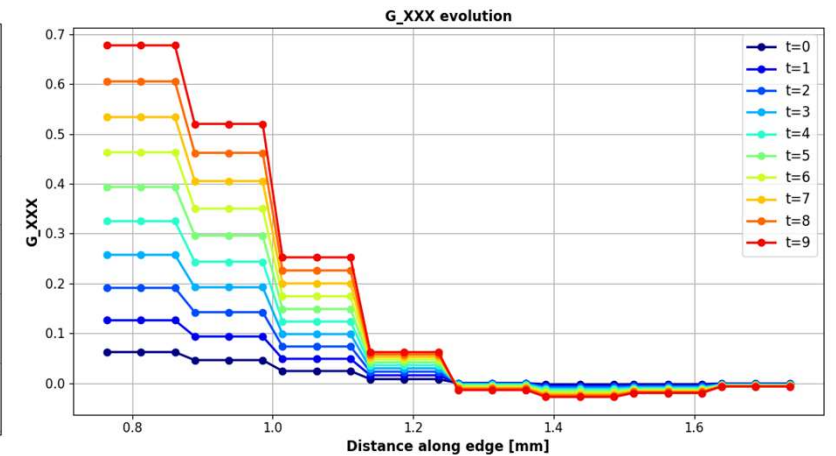
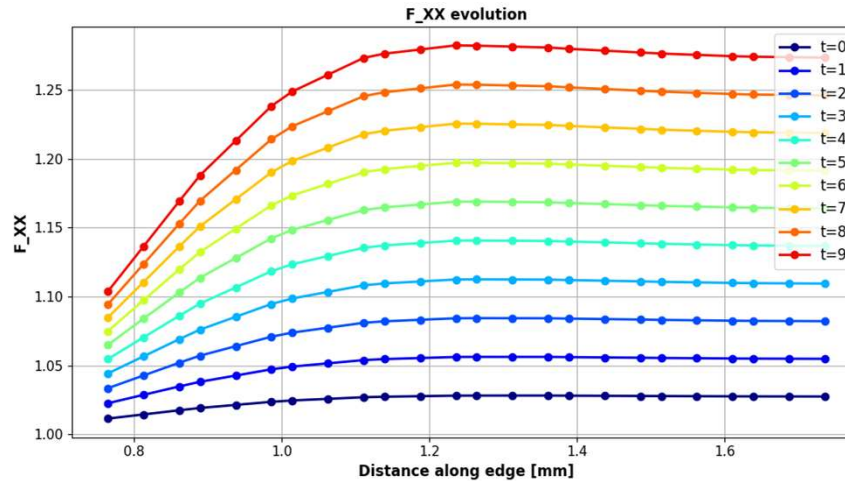
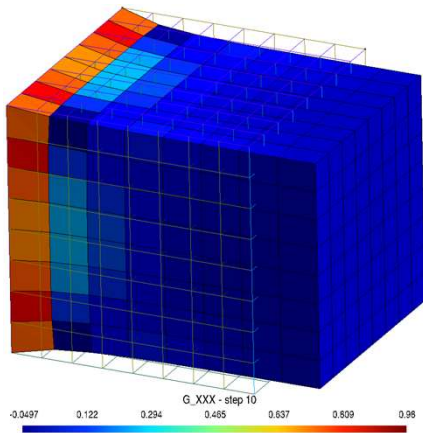
Appendix - Revised Weak Form of Advanced Diffusion Thermomechanics

Enhanced Discontinuous Galerkin Formulation

- Additional stabilisation term for strain gradient $\nabla \mathbf{F}$ with higher order initial stiffness $\mathfrak{J}^0$ in force balance – weak C1
- Higher order stress is 0
- Formulation remains C0 with a finite L2 norm – continuous strains and piecewise continuous gradients.

Force
balance

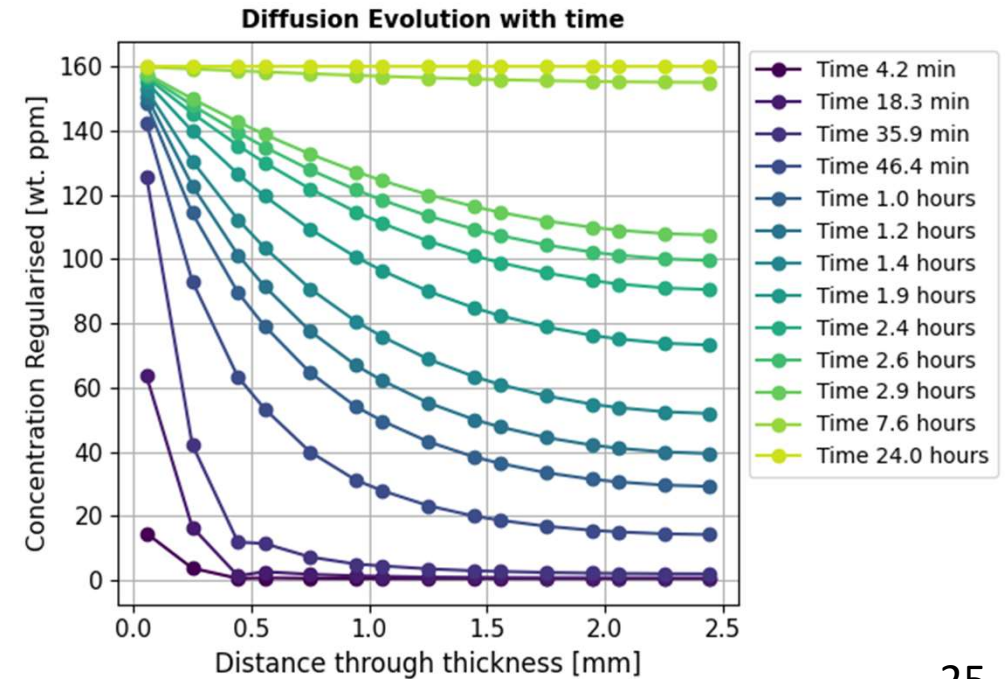
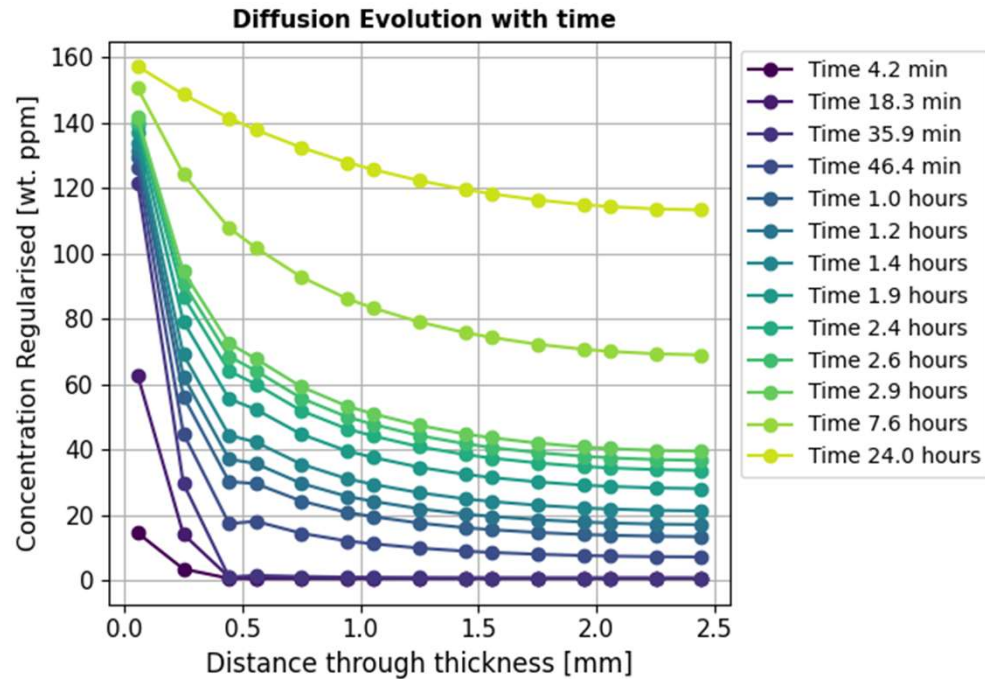
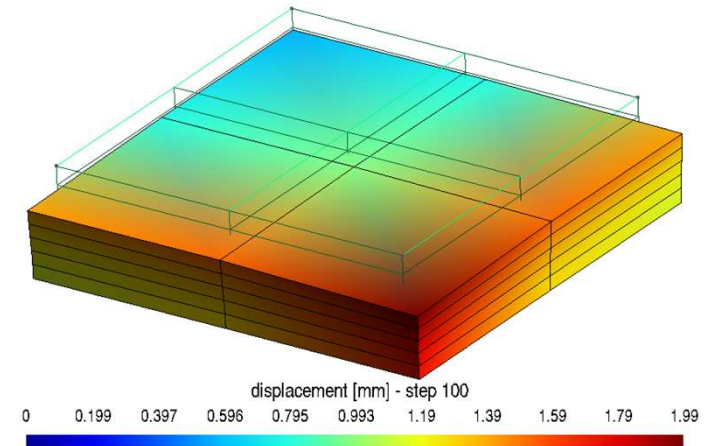
$$\begin{aligned}
 & \int_{\Omega} \mathbf{P} : \delta \mathbf{F} \, d\Omega + \int_{\partial_I} [[\delta \mathbf{u}]] \cdot \langle \hat{\mathbf{P}} \rangle \cdot \mathbf{N}^- \, d\partial\Omega \\
 & + \int_{\partial_I} [[\mathbf{u}]] \cdot \langle \hat{\mathbf{P}}(\delta \mathbf{u}) \rangle \cdot \mathbf{N}^- \, d\partial\Omega \\
 & + \int_{\partial_I} [[\mathbf{u}]] \otimes \mathbf{N}^- : \left\langle \frac{\beta}{h} \mathbb{C}^0 \right\rangle : [[\delta \mathbf{u}]] \otimes \mathbf{N}^- \, d\partial\Omega \\
 & + \int_{\partial_I} [[\mathbf{u} \otimes \nabla]] \otimes \mathbf{N}^- : \left\langle \frac{\beta}{h} \mathfrak{J}^0 \right\rangle : [[\delta \mathbf{u} \otimes \nabla]] \otimes \mathbf{N}^- \, d\partial\Omega \\
 & = \int_{\partial_N} \mathbf{T} \cdot \delta \mathbf{u} \, d\partial\Omega
 \end{aligned}$$



Appendix - Transient Uniaxial Test – Advanced Diffusion in a Membrane

Features

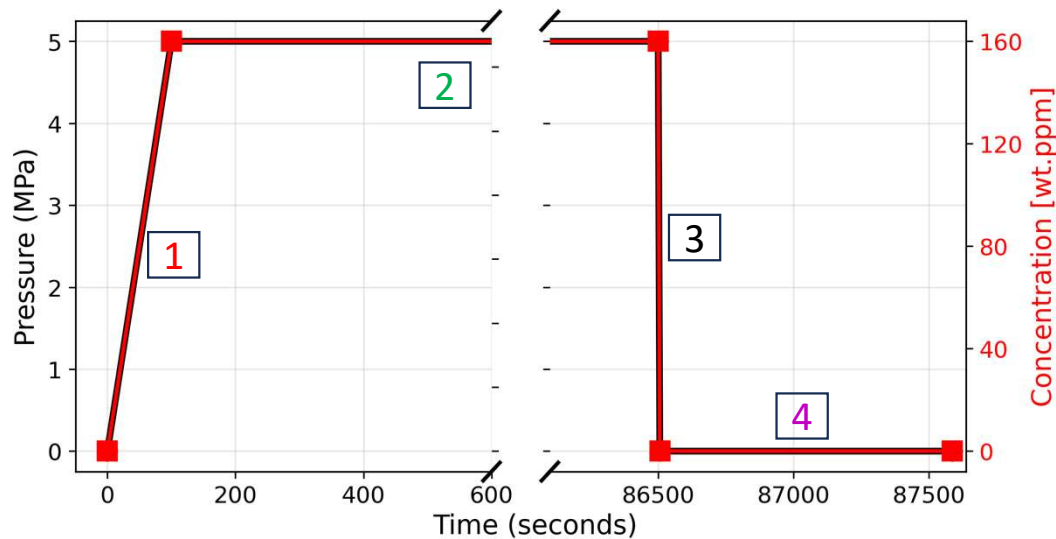
- Pressure (p) ramp of 5 MPa for 10 secs, held for 1 day
- Advanced diffusion model with chemical potential
- Varying $\lambda = 100$ and 1,



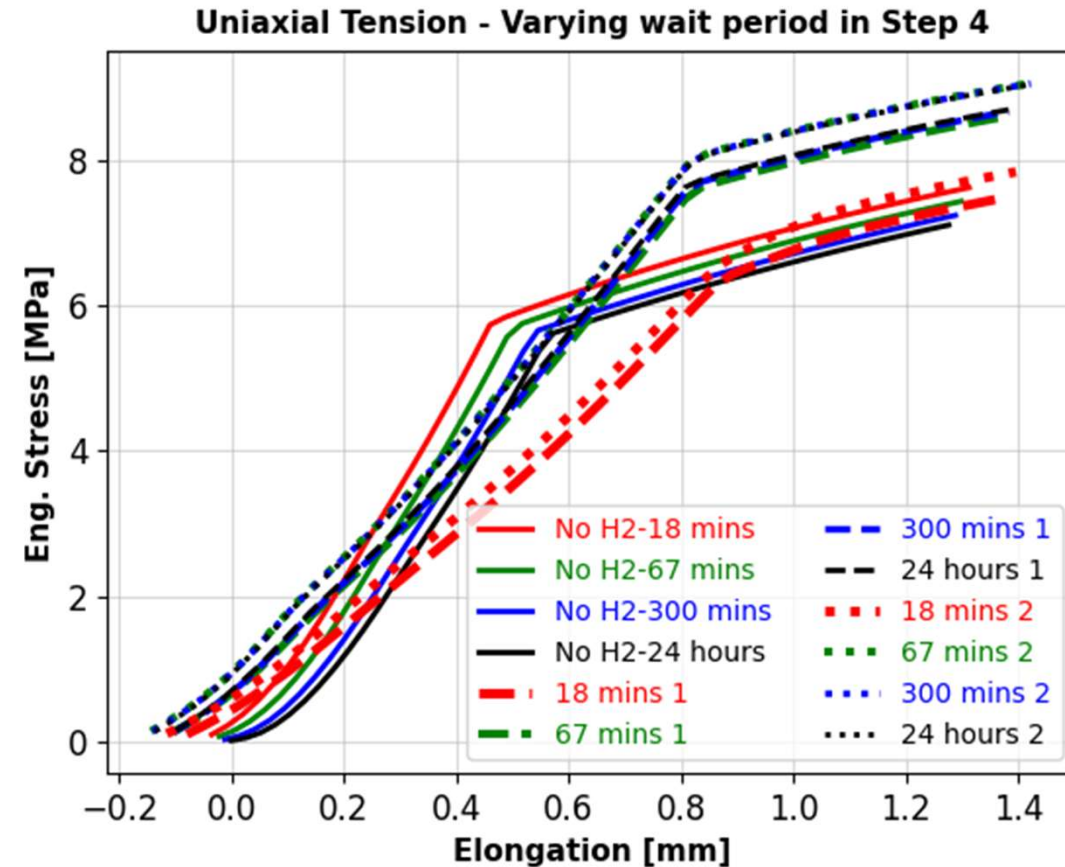
Appendix - Complex Transient Test with Advanced Diffusion

Loading Steps

1. Pressure load - ramps of 5 MPa - 160 wt.ppm for 100 secs
2. Pressure hold for 24 hours
3. Decompression in 6 secs
4. Wait for variable time – 18/67/300 mins/ 24 hours
5. Tension ~50 % elongation

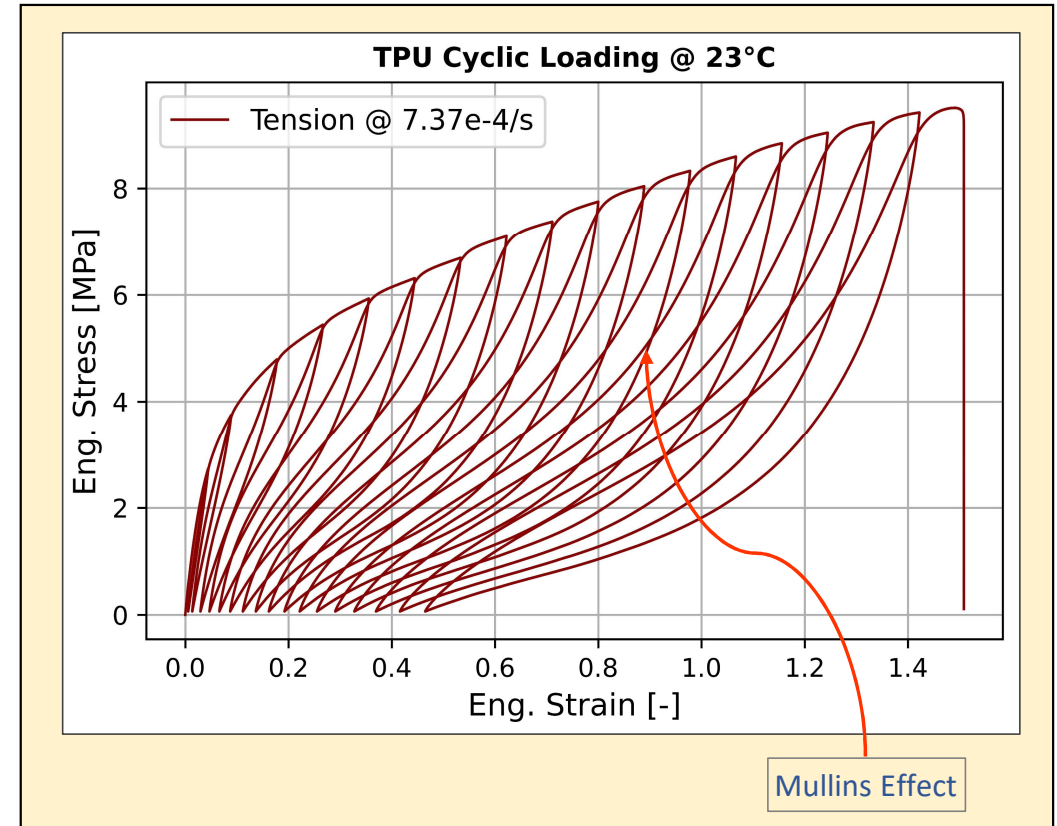
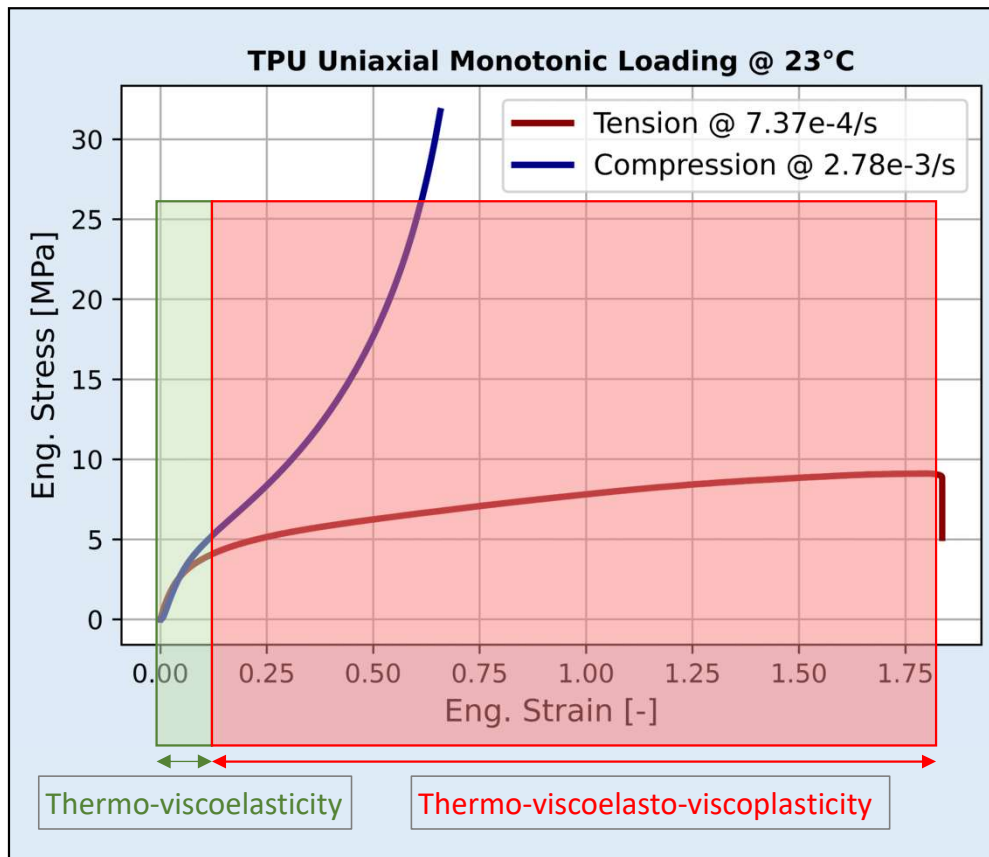


Pressure-concentration loads in steps 1-4



Appendix - Thermo(visco)mechanics

- TPU Perspective

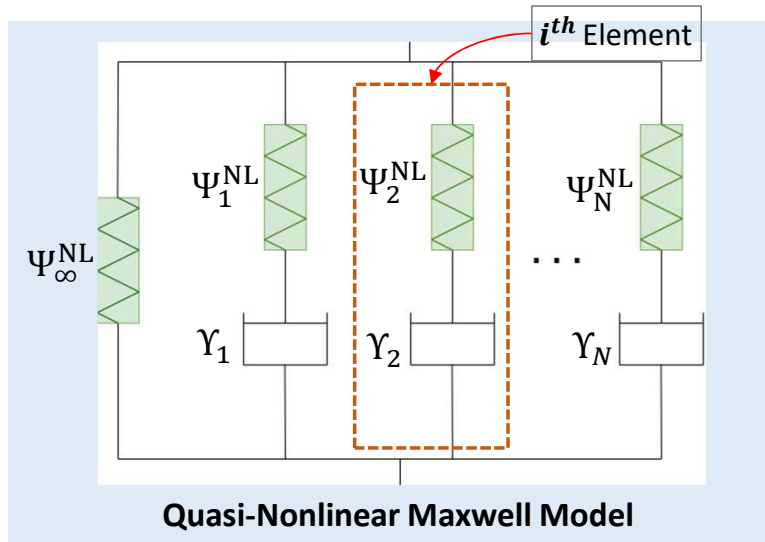


Objectives

1. Non-linear Thermoviscoelasticity
2. Thermoviscoplasticity – Isotropic and Kinematic hardening
3. Mullin's Effect to capture unloading curves

Thermodynamically consistent Formulation!!

Appendix - Quasi-Nonlinear TVE Abridged



“Quasi-Nonlinear Viscoelasticity”

Linear viscoelasticity -> Newtonian Dashpots with
Separable rate equations

+

Strain-dependent moduli -> Nonlinear functions in terms
of log strains $\mathbf{E}_e$, $\mathfrak{E}_i$

For the i^{th} Maxwell element, in Linear Viscoelasticity:

- Rate equations solved for i^{th} spring strain ($\mathfrak{E}_i$), in shifted time using time-temperature superposition (TTSP), (deviatoric shown below)

$$\text{dev } \mathfrak{E}_i = \exp\left(-\frac{\Delta t^*|_{ref}}{g_i}\right) \text{dev } \mathfrak{E}_i^n + \exp\left(-\frac{\Delta t^*|_{mid}}{g_i}\right) (\text{dev } \mathbf{E}_e - \text{dev } \mathbf{E}_e^n)$$

- Relaxation in shifted time using WLF shift factor from DMA Master Curves.

$$\Delta t_n^* = \int_{t_n}^{t_{n+1}} \frac{1}{a_T(\epsilon)} d\epsilon \quad \rightarrow \quad a_T = \exp\left(-\frac{C_1(T - T_{ref})}{C_2 + T - T_{ref}}\right)$$

Quasi Non-linearity in stress:

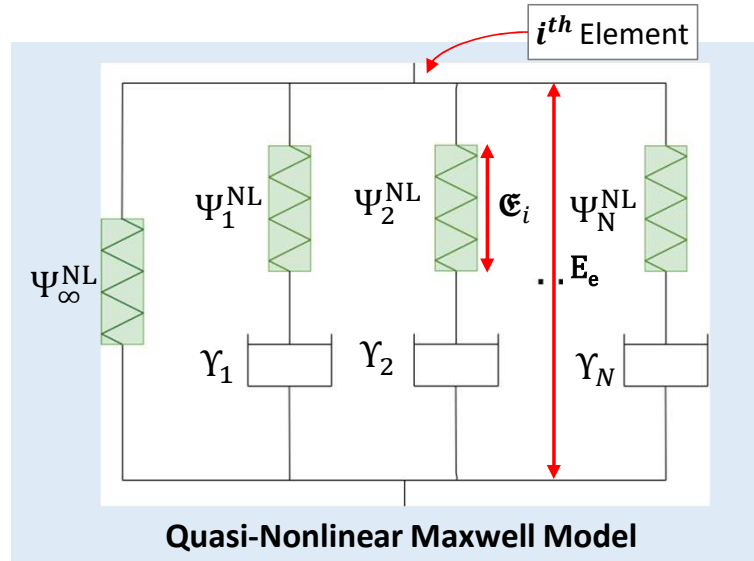
- Form of Corotational Kirchhoff stress ($\hat{\tau}_i$) is preserved,

$$\begin{aligned} \hat{p}_i &= K_{i0} \text{tr } \mathfrak{E}_i \\ \text{dev } \hat{\tau}_i &= 2G_{i0} \text{dev } \mathfrak{E}_i \end{aligned} \quad \rightarrow \quad \begin{aligned} \hat{p}_i &= K_{i0} A_{v_c} \text{tr } \mathfrak{E}_i \\ \text{dev } \hat{\tau}_i &= 2G_{i0} B_{d_c} \text{dev } \mathfrak{E}_i \end{aligned}$$

induced non-linearity using strain-dependent scalars A_{v_c} and B_{d_c} .

Here, $K_{\infty 0}$, K_{i0} and $G_{\infty 0}$, G_{i0} are the initial moduli from DMA Master Curves.

Appendix - Quasi-Nonlinear Thermoviscoelasticity 1



“Quasi-Nonlinear Viscoelasticity”

Linear viscoelasticity -> Newtonian Dashpots and Hookean springs

+

Strain-dependent moduli -> Nonlinear functions in terms of log strains $\mathbf{E}_e$, $\mathfrak{E}_i$

Linear Viscoelasticity for the i^{th} Maxwell element:

- Rate equations in terms of the strain in the i^{th} spring ($\mathfrak{E}_i$),

$$\dot{\mathfrak{E}}_i = f(\mathbf{E}_e, \mathfrak{E}_i, k_i, g_i)$$

where, $\mathbf{E}_e$ is the logarithmic strain in the intermediate configuration, k_i and g_i are the bulk and shear relaxation times for the i^{th} branch.

- Corotational Kirchhoff stress ($\hat{\boldsymbol{\tau}}_i$) of the i^{th} element in pressure and deviatoric components,

$$\begin{aligned} \hat{p}_i &= K_i \text{tr } \mathfrak{E}_i \\ \text{dev } \hat{\boldsymbol{\tau}}_i &= 2G_i \text{dev } \mathfrak{E}_i \end{aligned}$$

where, K_i and G_i are the bulk and shear moduli for the i^{th} branch.

Strain-dependent moduli:

- Corotational Kirchhoff stress ($\hat{\boldsymbol{\tau}}_i$) in the i^{th} branch retains its form,

$$\begin{aligned} \hat{p}_i &= K_i (\text{tr } \mathfrak{E}_i, V_j) \text{tr } \mathfrak{E}_i \\ \text{dev } \hat{\boldsymbol{\tau}}_i &= 2G_i (||\text{dev } \mathfrak{E}_i||, D_j) \text{dev } \mathfrak{E}_i \end{aligned}$$

where, K_i and G_i functions contain the non-linearity, V_j and D_j are treated as material parameters.

Appendix - Quasi-Nonlinear Thermoviscoelasticity 2

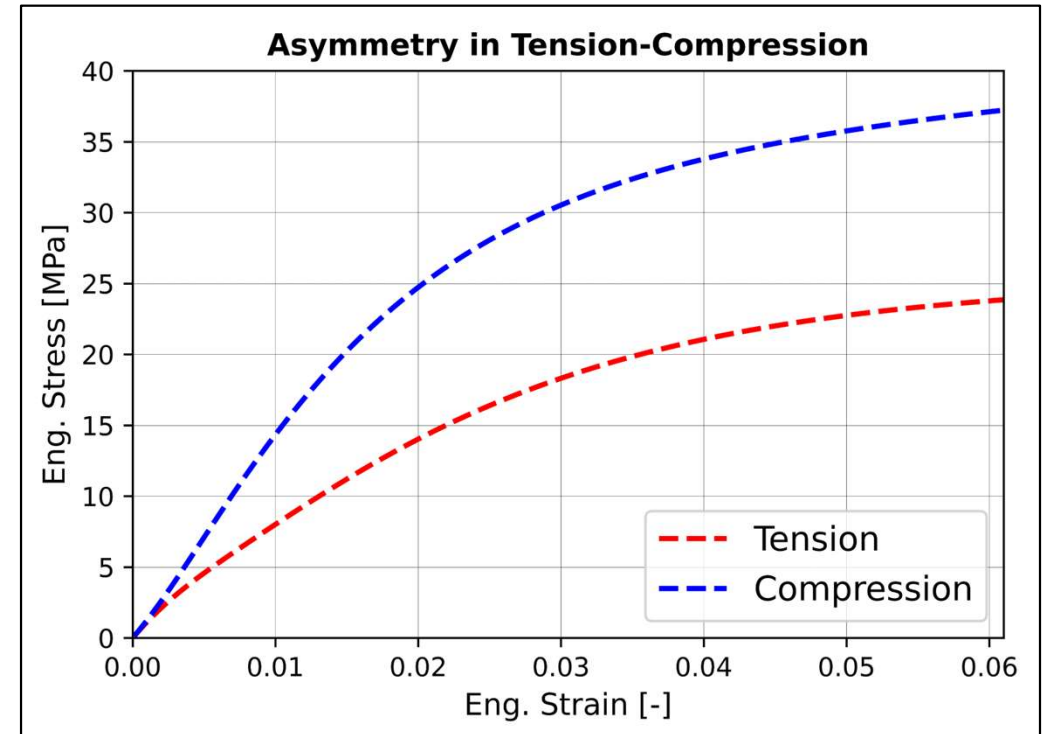
Strain-dependent moduli:

- Corotational Kirchhoff stress ($\hat{\boldsymbol{\tau}}_i$) in the i^{th} branch retains its form,

$$\begin{aligned}\hat{p}_i &= K_i (\text{tr } \boldsymbol{\mathfrak{E}}_i, V_j) \text{tr } \boldsymbol{\mathfrak{E}}_i \\ \text{dev } \hat{\boldsymbol{\tau}}_i &= 2G_i (||\text{dev } \boldsymbol{\mathfrak{E}}_i||, D_j) \text{dev } \boldsymbol{\mathfrak{E}}_i\end{aligned}$$

where, K_i and G_i functions contain the non-linearity, V_j and D_j are treated as material parameters.

- Features** - Non-linearity in viscoelastic regime at low strains, large tension-compression asymmetry in stiffness.
- To calibrate:** V_j and D_j are calibrated from uniaxial tension and compression tests at different temperatures.



Numerical Setup: Uniaxial stress and quasi-steady tension-compression sweeps using quasi-nonlinear elasticity.

Appendix: Strain-Dependent Functions in QNL TVE

General Form

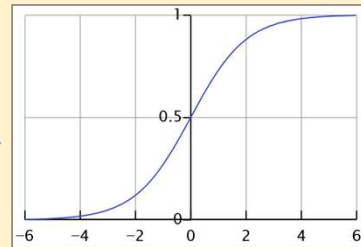
- Moduli expressed as $K_i = K_{i0} A_{vc}$ and $G_i = G_{i0} B_{dc}$
- Large tension-compression asymmetry in moduli at low strains without a slope discontinuity

$$\begin{aligned} A_{vc} &= f(\text{tr } \mathfrak{E}_i) A_{vi1} + C_i (1 - f(\text{tr } \mathfrak{E}_i)) A_{vi2} \\ B_{dc} &= f(\text{tr } \mathfrak{E}_i) B_{di1} + C_i (1 - f(\text{tr } \mathfrak{E}_i)) B_{di2} \end{aligned}$$

Where, A_{vi1} , B_{di1} activate in tension and A_{vi2} , B_{di2} in compression; C_i is the compression scaler.

- f is the logistic function

$$f = \frac{1}{1 + \exp(-m \text{tr } \mathfrak{E}_i)}$$



Where, m (>100) is a numerical regularisation parameter.

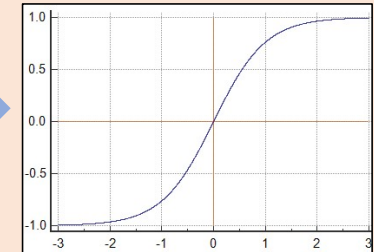
Explicit Form

- Strain-dependent scalars for every branch -> Scalable sigmoid shape of moduli

$$\begin{aligned} A_{vi} &= \frac{1}{\sqrt{V_1 \text{tr } \mathfrak{E}_i^2 + V_2}} + V_0 (1 + V_3 \tanh(\text{tr } \mathfrak{E}_i^2)) \\ B_{di} &= \frac{1}{\sqrt{D_1 \text{dev } \mathfrak{E}_i : \text{dev } \mathfrak{E}_i + D_2}} + D_0 (1 + D_3 \tanh(\text{dev } \mathfrak{E}_i : \text{dev } \mathfrak{E}_i)) \end{aligned}$$

- The first terms are sigmoidal in " $A_{vi} \text{tr } \mathfrak{E}_i$ " and " $B_{di} \text{dev } \mathfrak{E}_i$ "

$$\begin{aligned} A_{vi} \text{tr } \mathfrak{E}_i &= \frac{\text{tr } \mathfrak{E}_i}{\sqrt{V_1 \text{tr } \mathfrak{E}_i^2 + V_2}} \\ B_{di} \text{dev } \mathfrak{E}_i &= \frac{\text{dev } \mathfrak{E}_i}{\sqrt{D_1 \text{dev } \mathfrak{E}_i : \text{dev } \mathfrak{E}_i + D_2}} \end{aligned}$$



and the second terms with tanh allow additional stiffness at higher strains.

- V_j and D_j are treated as material parameters ≥ 0 .

Appendix - QNL TVE – Compression

Concept

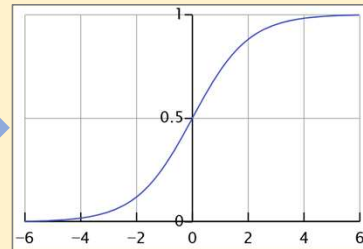
- Large tension-compression asymmetry in moduli at low strains without a slope discontinuity

$$\begin{aligned} A_{vc} &= f(\text{tr } \mathfrak{E}_i) (A_{vi1}) + C_i (1 - f(\text{tr } \mathfrak{E}_i)) A_{vi2} \\ B_{dc} &= f(\text{tr } \mathfrak{E}_i) (B_{di1}) + C_i (1 - f(\text{tr } \mathfrak{E}_i)) B_{di2} \end{aligned}$$

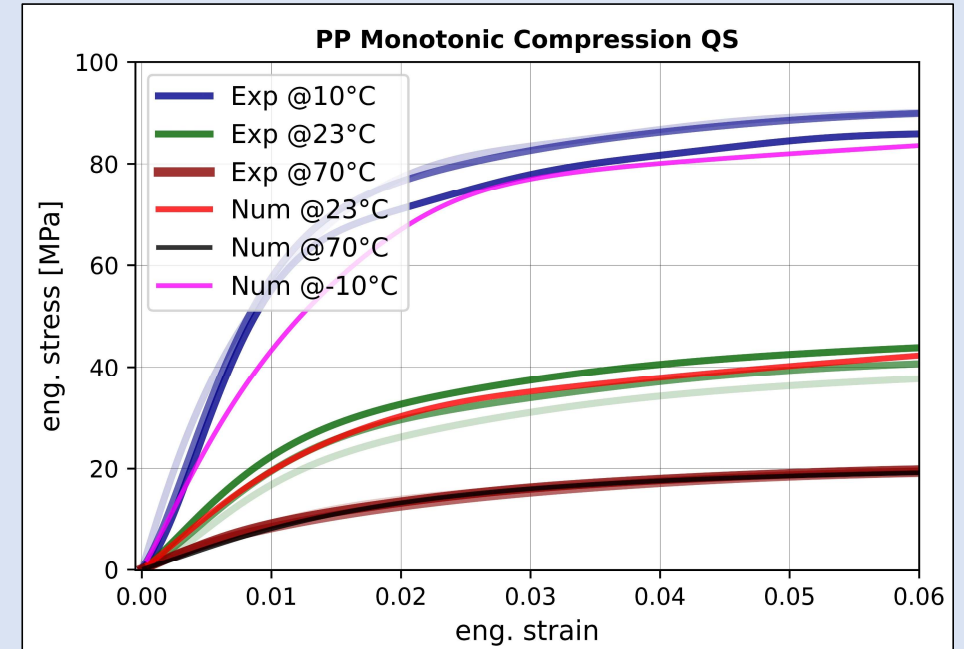
Where, A_{vi1} , B_{di1} activate in tension and A_{vi2} , B_{di2} in compression; C_i is the compression scaler.

- f is the logistic function

$$f = \frac{1}{1 + \exp(-m \text{tr } \mathfrak{E}_i)}$$



Where, m (>100) is a numerical regularisation parameter.



Numerical Setup – QNL TVE + linear exponential isotropic hardening TVP

- $V0$, $V3$, $D0$, $D3 = 0$; linearly decreasing $V1$, $V2$, $D1$, $D2$ with temperature in A_{vi1} , B_{di1} and A_{vi2} , B_{di2}
- Good match with the experimental results

Appendix - Temperature Dependency of QNL TVE

Convolution Integrals in shifted time

- Deviatoric integral shown below

$$\text{dev } \mathfrak{E}_i = \int_{-\infty}^t \exp\left(-\frac{t^* - s^*}{g_i}\right) \frac{d}{ds} \text{dev } \mathbf{E}_e(s) ds$$

where, the WLF shift factor (a_T) is used to evaluate the shifted time-step.

$$\Delta t_n^* = \int_{t_n}^{t_{n+1}} \frac{1}{a_T(\epsilon)} d\epsilon$$

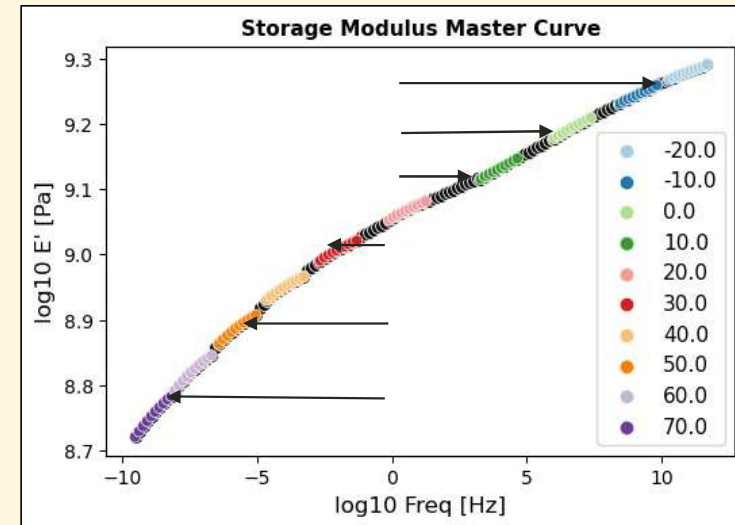
To calibrate: Dynamic moduli and shift factor.

- **Dynamic Mechanical Analyses (DMA)** in tension.

Construction of Tension Master Curve

$$E'(\omega, T) = E'(a_T \omega, T_{\text{ref}})$$

where, T_{ref} is the reference temperature (a bit lower than T_g). The isotherms are rigidly shifted in the log-log plot.



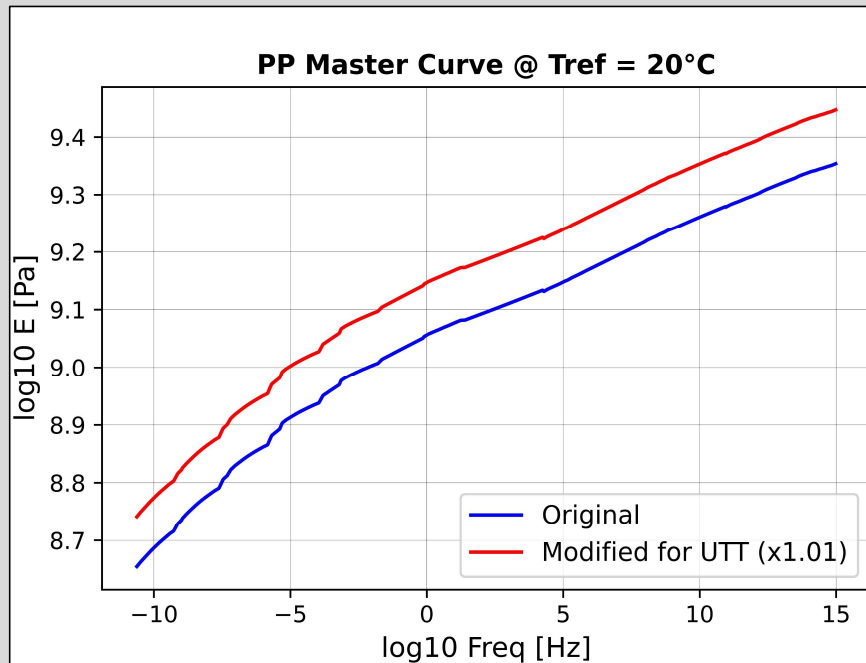
- Rigid shifts give the shift factor:

$$a_T = \exp\left(-\frac{C_1(T - T_{\text{ref}})}{C_2 + T - T_{\text{ref}}}\right)$$

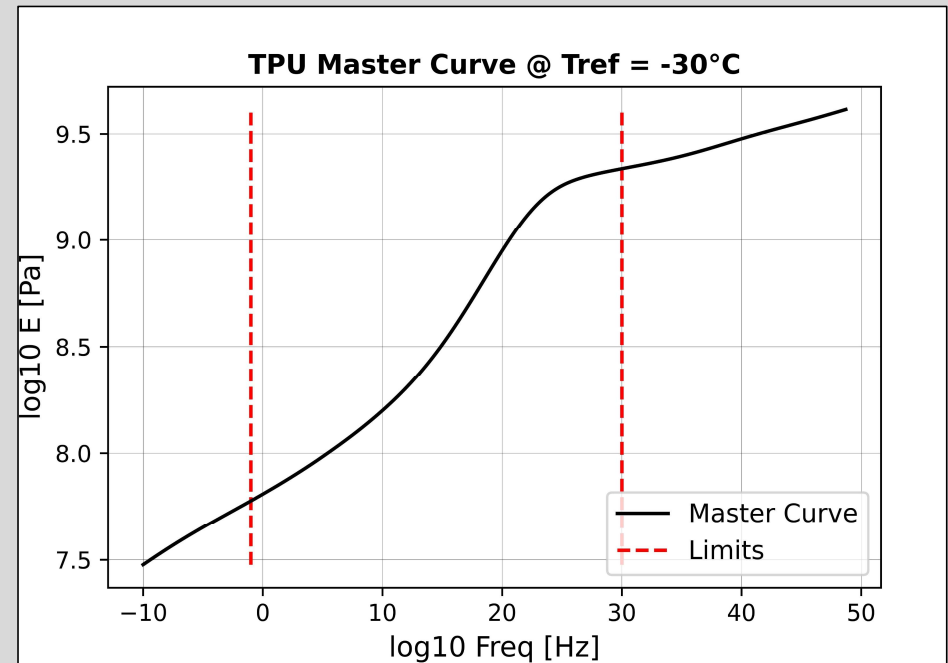
- Curve fitting gives the relaxation spectrum:

$$E(t) = E_{\infty} + \sum_{(i)} E_i \exp\left(-\frac{t}{\tau_i}\right)$$

Appendix: Master Curves



Vertically shifted master curve in -10 to 70°C to match Uniaxial Tensile Test experiments



Master curve obtained for a wide range in -120 to 120°C – limited terms for uniaxial tests at 23°C.

Appendix - Thermo(Visco)Plasticity

Elements

- Extended Drucker-Prager Power Yield Function ($\bar{F}$) - pressure dependency in ϕ_p and a_2, a_1, a_0 coefficients as functions of plastic strain ($\Delta\gamma$) and temperature-dependent tensile and compressive yield strength, Γ is the flow parameter.

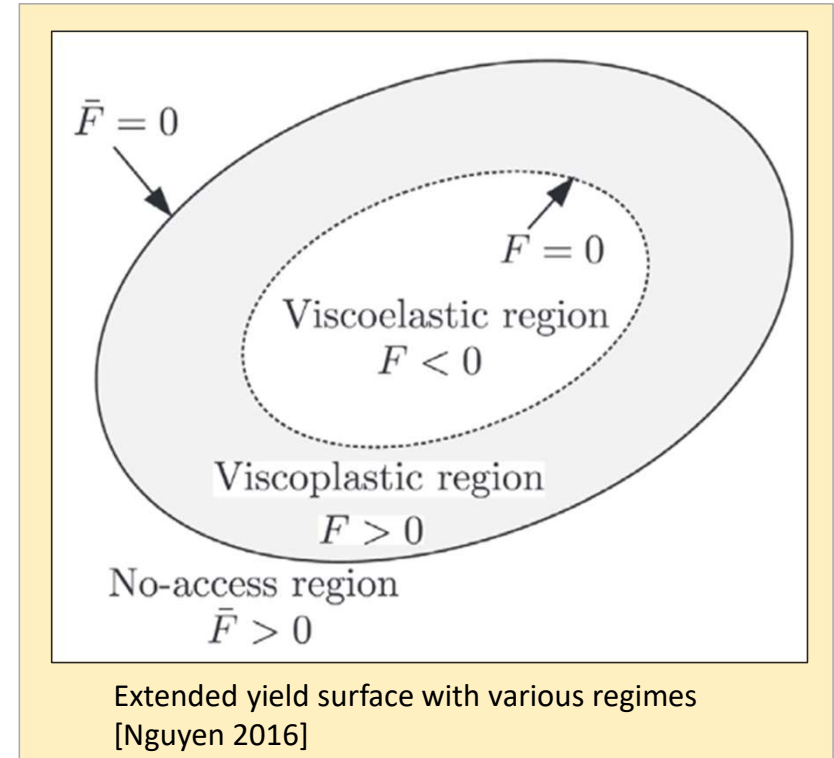
$$\bar{F}(\Gamma, \Delta\gamma, T) = a_2 \phi_e^\alpha - a_1 \phi_p - a_0 - \left(\eta \frac{\Gamma}{\Delta t} \right)^p$$

- Perzyna Flow Rule (non-associative): with temperature-dependent viscosity (η), quadratic plastic potential (P).

$$\mathbf{D}_p = \frac{1}{\eta(T)} \langle \mathbf{F} \rangle^{\frac{1}{p}} \frac{\partial P}{\partial \mathbf{M}_e}$$

- Chaboche NLKH - $\mathbf{B}$ is the backstress and H_b is the kinematic hardening modulus expressed as a function of plastic strain.

$$\dot{\mathbf{B}} = k^2 H_B \mathbf{D}_p + \frac{1}{H_B} \frac{\partial H_B}{\partial \gamma} \dot{\gamma} \mathbf{B} + \frac{1}{H_B} \frac{\partial H_B}{\partial T} \dot{T} \mathbf{B}$$



To calibrate: Yield strengths, hardening moduli, viscosity and power yield parameters
- Uniaxial tensile and compressive tests at different temperatures

Appendix: Thermo(Visco)Plastic Model - Unknowns

Elements

- Extended Drucker-Prager Power Yield Function ($\bar{F}$) - pressure dependency in ϕ_p and a_2, a_1, a_0 coefficients as functions of plastic strain ($\Delta\gamma$) and temperature-dependent tensile and compressive yield strength, Γ is the flow parameter.

$$\bar{F}(\Gamma, \Delta\gamma, T) = a_2 \phi_e^\alpha - a_1 \phi_p - a_0 - \left(\eta \frac{\Gamma}{\Delta t} \right)^p$$

- Perzyna Flow Rule (non-associative): with temperature-dependent viscosity (η), quadratic plastic potential (P)

$$\mathbf{D}_p = \frac{1}{\eta(T)} \langle \mathbf{F} \rangle^{\frac{1}{p}} \frac{\partial P}{\partial \mathbf{M}_e}$$

- Chaboche NLKH - $\mathbf{B}$ is the backstress and H_B is the kinematic hardening modulus expressed as a function of plastic strain

$$\dot{\mathbf{B}} = k^2 H_B \mathbf{D}_p + \frac{1}{H_B} \frac{\partial H_B}{\partial \gamma} \dot{\gamma} \mathbf{B} + \frac{1}{H_B} \frac{\partial H_B}{\partial T} \dot{T} \mathbf{B}$$

TVP Internal Variables:

- Equivalent plastic strain ($\Delta\gamma$): Solved using a rate equation. (k is a material parameter depending on the initial plastic Poisson's ratio)

$$\dot{\gamma} = k \sqrt{\mathbf{D}_p : \mathbf{D}_p}$$

- Flow parameter (Γ): Solved through Newton-Raphson on $\bar{F}$.
- **Two Equations:** Yield function ($\bar{F}=0$) and $\Delta\gamma$ rate equation!

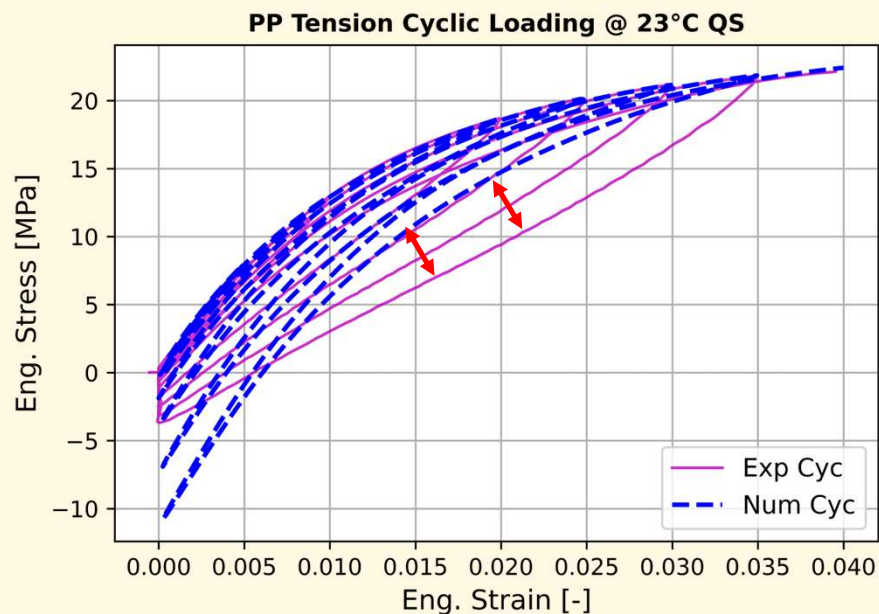
Two unknowns: Γ and $\Delta\gamma$!

Temperature Dependency:

Yield strengths, kinematic hardening modulus (H_B) and viscosity (η) are scaled with temperature dependent negative exponential functions like the WLF shift factor (a_γ). For a parameter, $g = g(\Delta\gamma, T)$, [Krairi, 2019]

$$g(\gamma, T) = g(\gamma) a_g(T)$$

Appendix – Mullin's Effect



Viscoelasto-viscoplastic simulation without Mullin's-like effect

Concept

- Mullin's effect to lower the stress in unloading using a damage variable ($\zeta \rightarrow 1$ to ζ_{min}) functional of maximum deformation energy encountered in load history

$$\zeta = \zeta(\hat{\psi}, \hat{\psi}_{max}) \Rightarrow \tau_e = \zeta \hat{\tau}_e$$

- Linear Mullin's Scaler

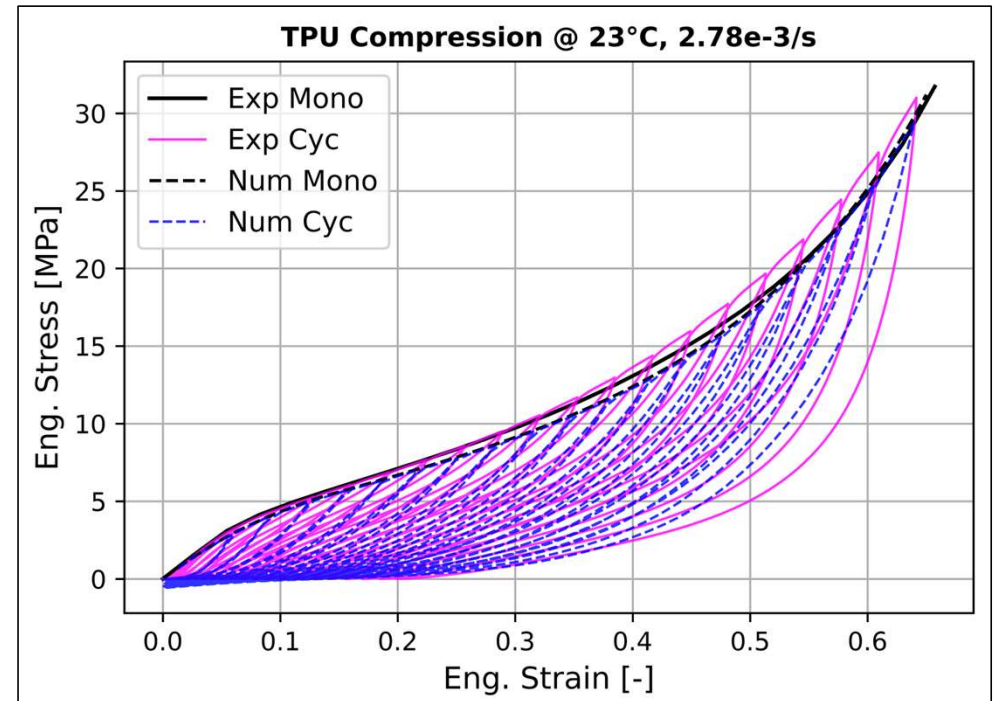
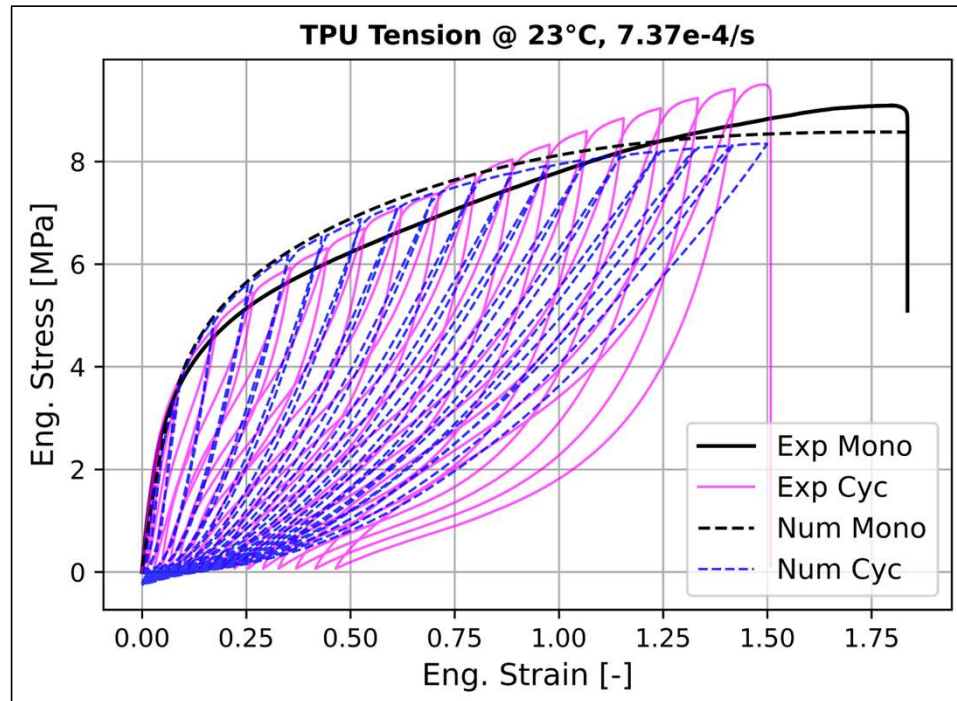
$$\zeta = 1 - z \left(1 - \frac{\hat{\psi}}{\hat{\psi}_{max}} \right)$$

Where, the **material parameter (z)** has the limits $0 \leq z < 1$ for consistency and is temperature dependent.

Assumption: Approximated solution of the viscoelastic deformation energy ($\hat{\psi}_{ve}$) is assumed to be sufficient, viscoplastic energy ($\hat{\psi}_{vp}$) is not considered here.

Appendix - Results for Thermoplastic Polyurethane EOS 1301

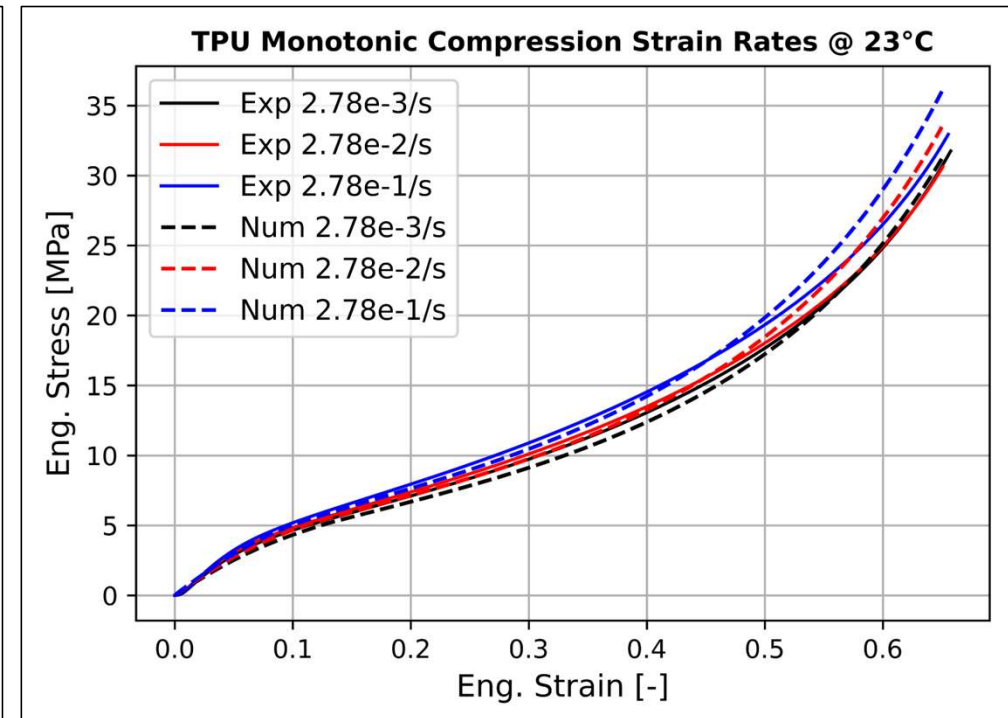
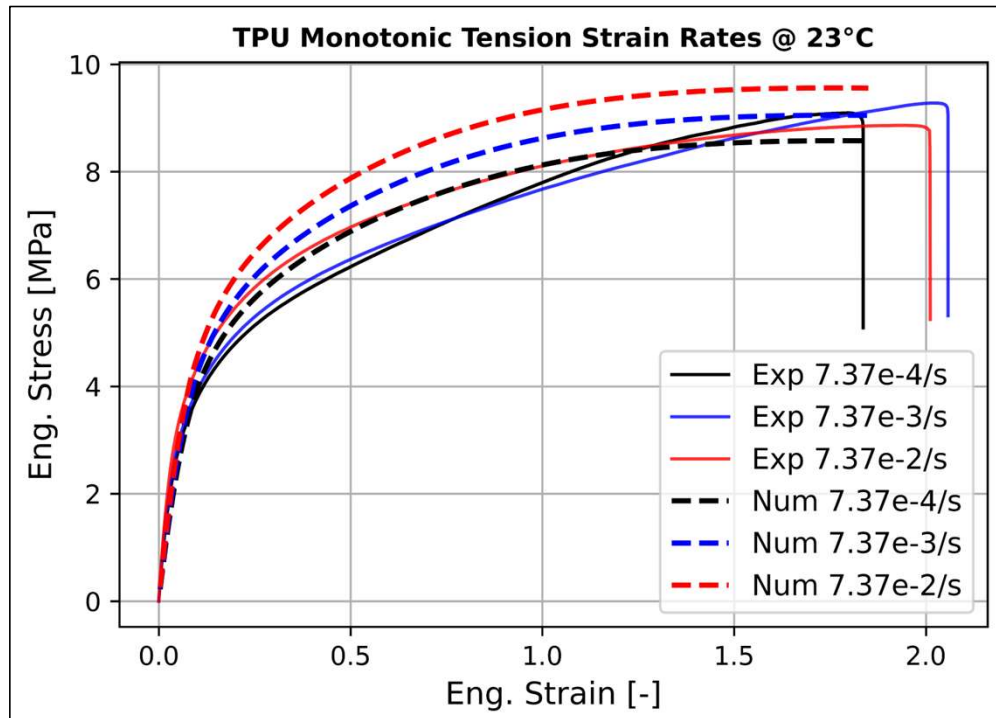
- Monotonic and Cyclic Loading



Numerical Setup - Uniaxial Stress with QNL TVE + linear exponential isotropic hardening + polynomial kinematic hardening TVP + Mullins' effect

- QNL TVE: All TVE branches with equal parameters
- Good agreement with experimental results in compression, mismatch in tension attributed to less viscoplasticity

Appendix - Results for Thermoplastic Polyurethane EOS 1301 - Variable Strain Rate

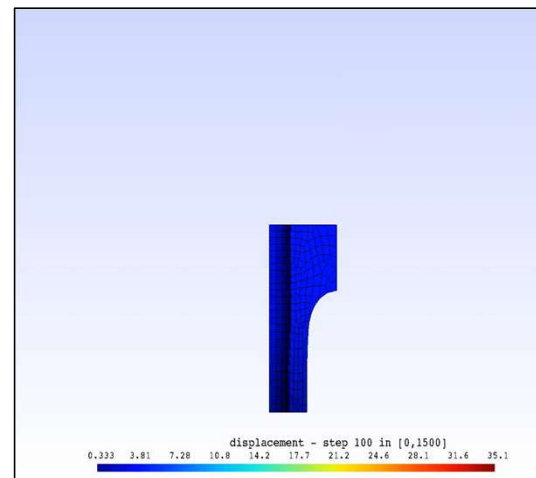
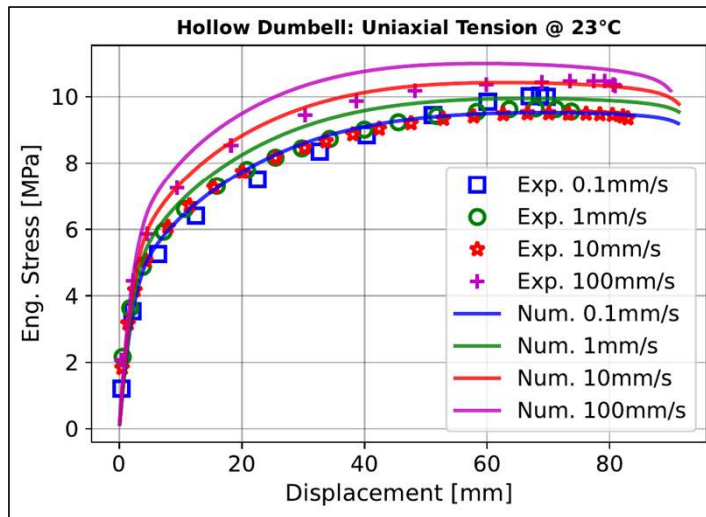
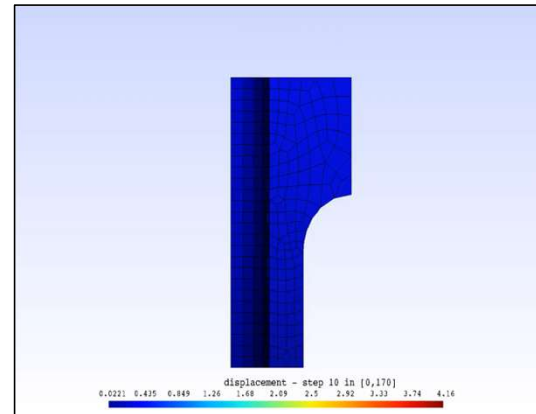
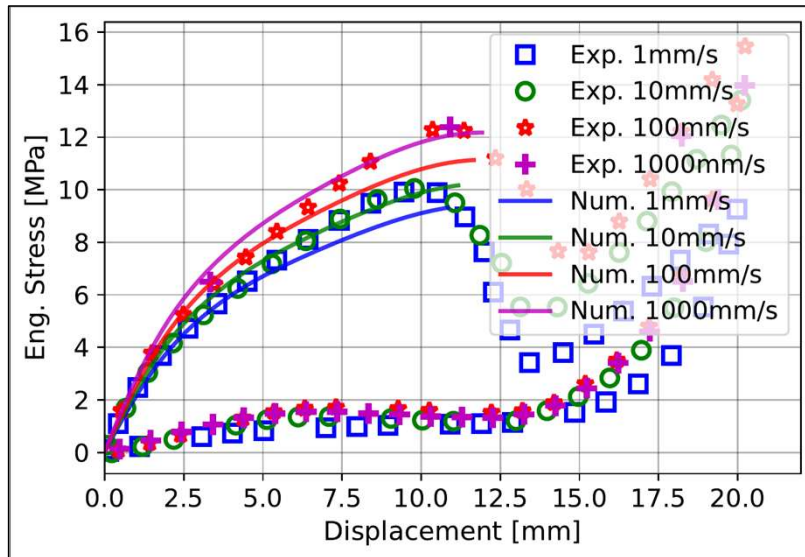


Numerical Setup - Uniaxial Stress with QNL TVE + linear exponential isotropic + polynomial kinematic hardening TVP

- QNL TVE: All TVE branches with equal parameters

Takeaway: Sensitivity to strain rates is overpredicted by the model

Appendix - TPU EOS 1301 – Axisymmetric Dumbbell in Tension and Compression



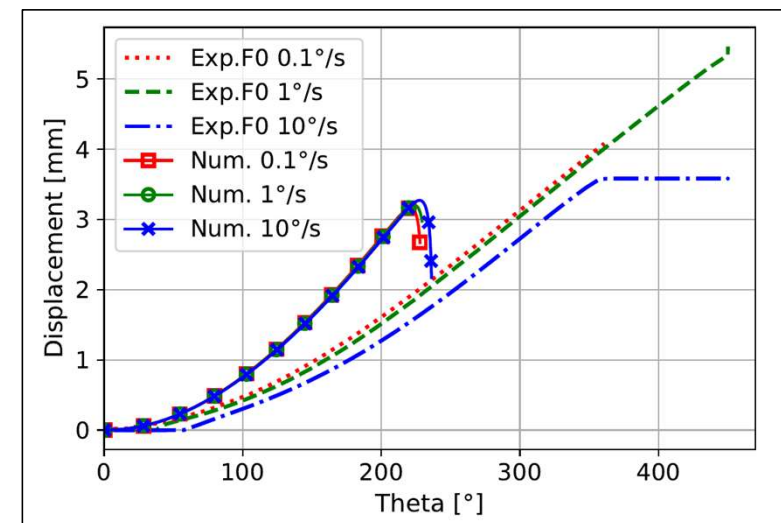
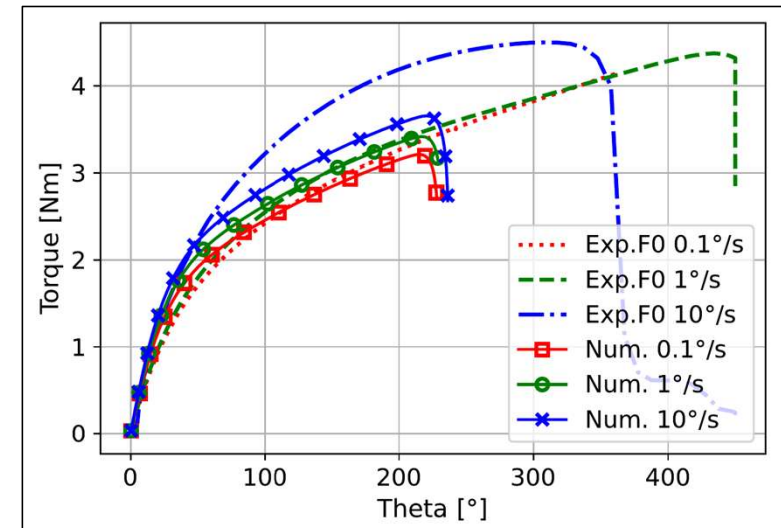
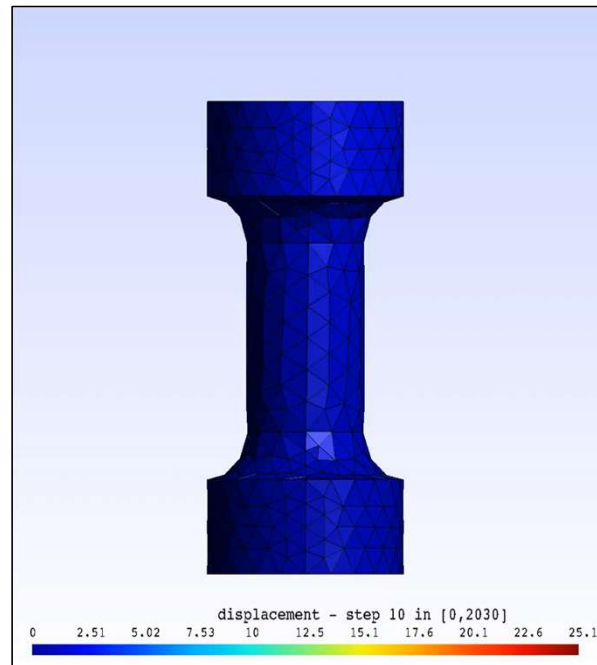
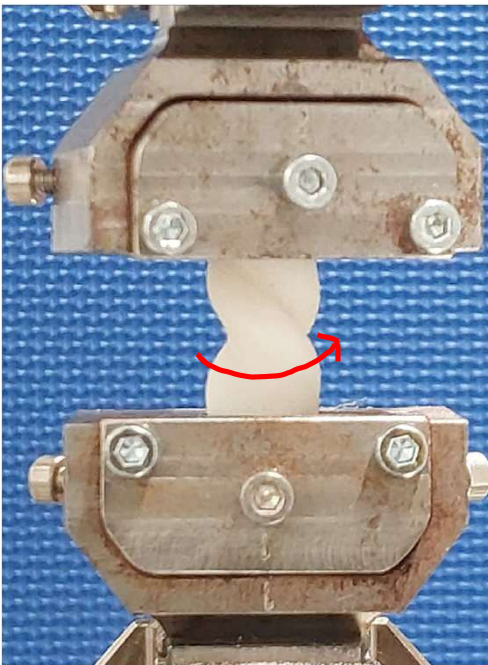
Takeaways: Captured strain rate effect and buckling shape in compression.

Appendix - TPU EOS 1301

- Dumbbell in Torsion

Setup: Bottom cylindrical surface fixed, top cylindrical surface is twisted and top surface free to move.

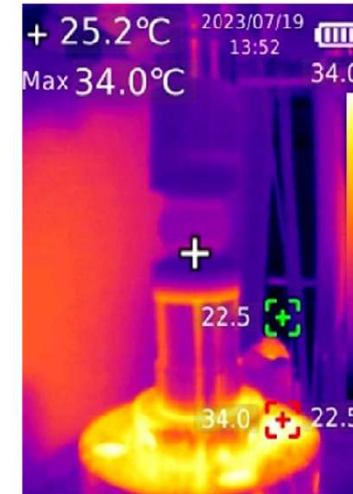
Takeaway: Torsional buckling encountered at lower angles of twist in simulations. Poynting effect is overestimated.



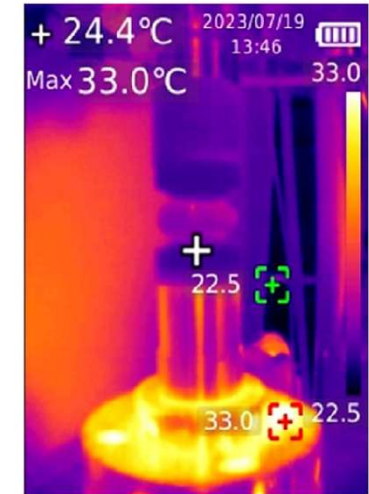
Appendix - Self-heating

Experimental Setup: Dumbbell Compression at low and high strain rates in DIC.

Takeaway: Simulated $\sim 2^\circ\text{C}$ rise in temperature.



Low strain rate



High strain rate

Mechanical Source: Heat source from viscoplasticity and Mullins effect.

$$W_M = \underbrace{\zeta}_{\text{Scaled by Mullin's Effect}} \left(\underbrace{-C_p \dot{T}}_{\text{Plastic Power}} + \underbrace{\phi : \mathbf{D}_p}_{\text{Dissipation due to isotropic hardening}} - \underbrace{(R \dot{\gamma})}_{\text{Mullins' Dissipation}} \right) - \frac{\partial \psi}{\partial \hat{\psi}_{\max}} \dot{\hat{\psi}}_{\max}$$

Scaled by Mullin's Effect

Plastic Power

Dissipation due to isotropic hardening

Mullins' Dissipation

