SAND2017-4991PE

Characterizing the Viscoelastic Behavior of PDMS/PDPS Copolymers

In Partial Fulfillment of the Requirements for the Degree:

Master of Science in Mechanical Engineering

Mark E. Small, B.S.

10 May 2017

UNM | Mechanical Engineering

Thesis Committee

- Professor Yu-Lin Shen Ph.D
  - Committee Chair, ME faculty
- Professor Walter Gerstle Ph.D
  - Outside-Dept. Committee member, CE faculty
- Ryan Jamison Ph.D
  - Outside-Dept. Committee member, Sandia National Laboratories

Thesis

- Determine the viscoelastic behavior of polydimethylsiloxane-polydiphenylsiloxane (PDMS/PDPS) copolymer

Step1: Experimentally determine properties DMA, TMA, Pressure Dilatometry

↓

Step2: Calibrate data to populate Simplified Potential Energy Clock Model (SPEC)

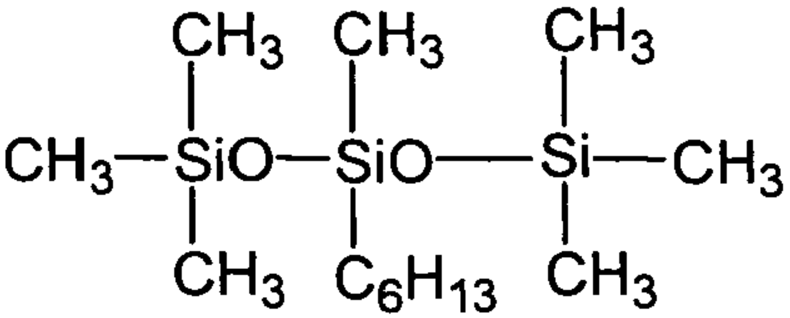
↓

Step3: Validate Material Model

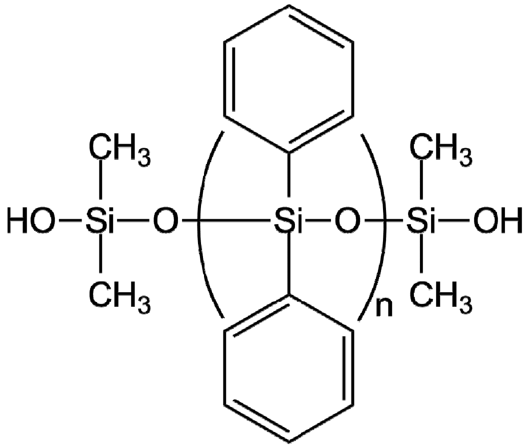
Contribution to Scientific Community

- Objective is to calibrate a linear thermo-viscoelastic model for PDMS/PDPS
- A model for PDMS/PDPS has yet to be determined
  - The siloxane polymer of interest consists of dimethyl (DMS), diphenyl (DPS), and methyl vinyl (MVS) siloxane monomer units.
  - The composition is approximately 90.7 wt% DMS, 9.0 wt% DPS, between 0.1 and 0.5% MVS, and 6.8 wt% ethoxy- endblock siloxane processing aid.

polydimethylsiloxane



polydiphenylsiloxane



Tri-block (ABA)

Todd M. Alam. Quantitative analysis of microstructure in polysiloxanes using high resolution si29 nmr spectroscopy

"Silicon in Polymer Synthesis." *H.R. Kricheldorf | Springer*. Springer-Verlag Berlin Heidelberg, n.d. Web. 09 May 2017.

UNM Mechanical Engineering

Contribution to Scientific Community

- PDMS/PDPS copolymers are used in a wide range of applications due to their favorable thermal and mechanical properties:
    - Earplugs, gaskets, computer disks, medical diagnosis, vibration abatement, tire performance, sports
- PDMS/PDPS will behave differently than already built models for PDMS due to its heavily cross-linked structure
- One may deliberately use of the viscoelasticity of PDMS/PDPS in design process to achieve desired goal i.e. shock enviroment
    - An accurate material model will give the ability to predict the behavior in a shock environment and allow for better design and engineering for its application

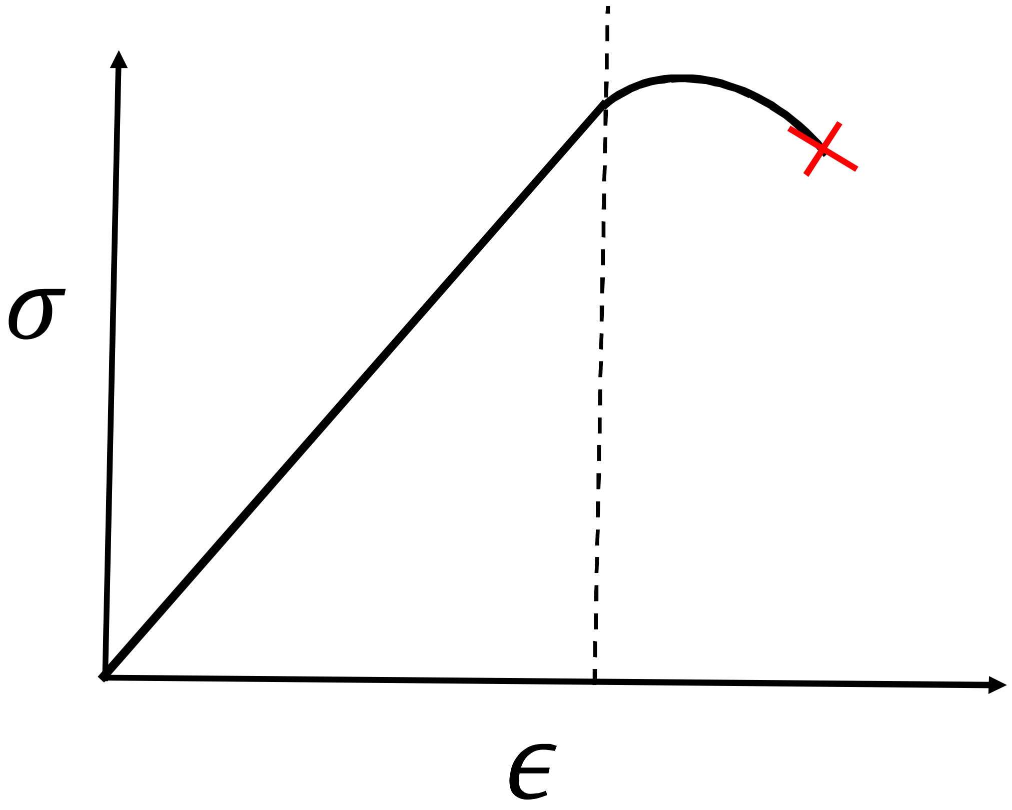
Outline

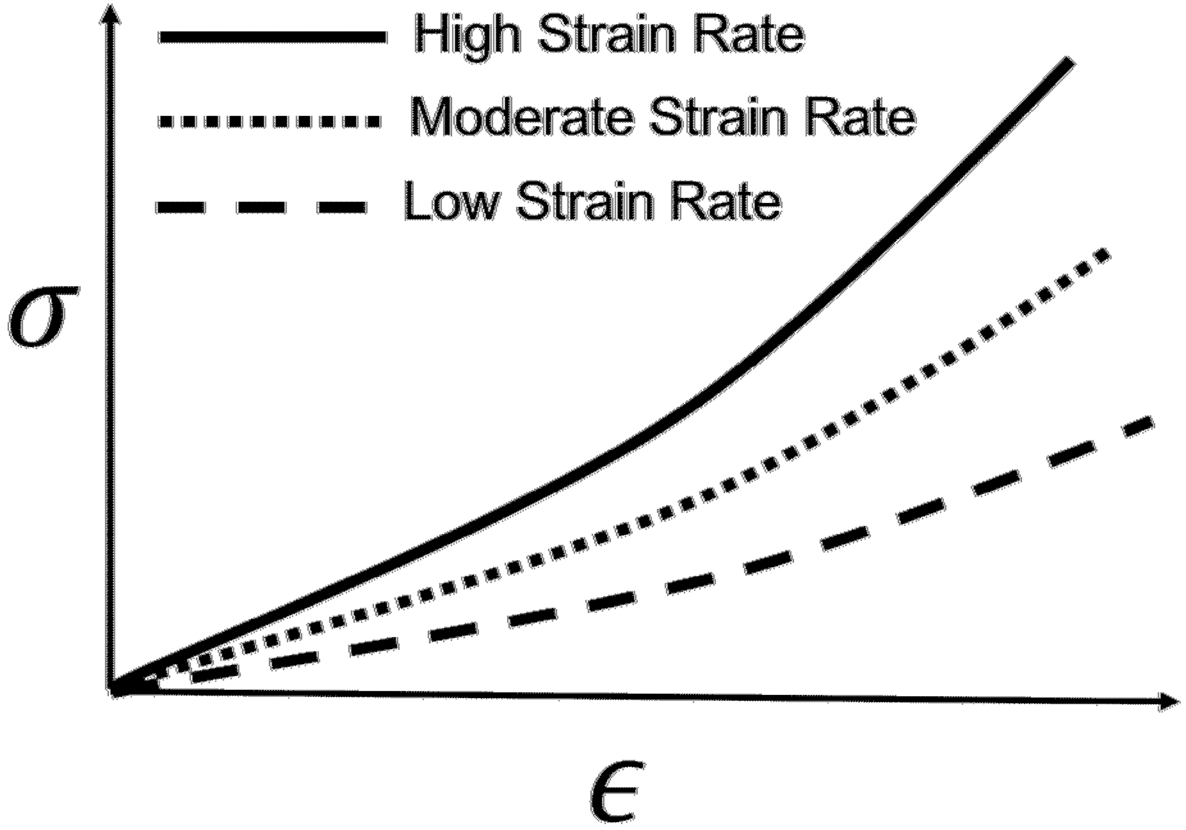
- Linear Viscoelasticity Theory
  - Developing Constitutive Equations
- Experiments
  - Dynamic Mechanical Analysis
  - Thermal Mechanical Analysis
  - Pressure Dilitometry
  - Flexural/Axial Storage Modulus
- Calibrate Experimental Data
- Model Validation
- Conclusions
- Future work

UNM | Mechanical Engineering

What is Viscoelasticity?

- Viscoelasticity is the property of materials that exhibit both viscous and elastic characteristics when undergoing deformation.



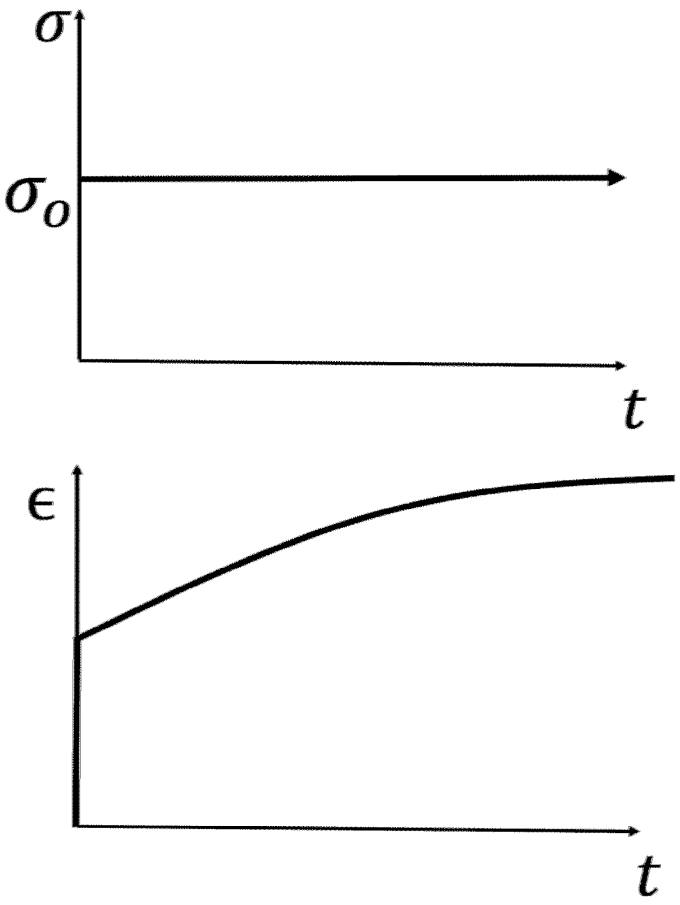


UNM | Mechanical Engineering

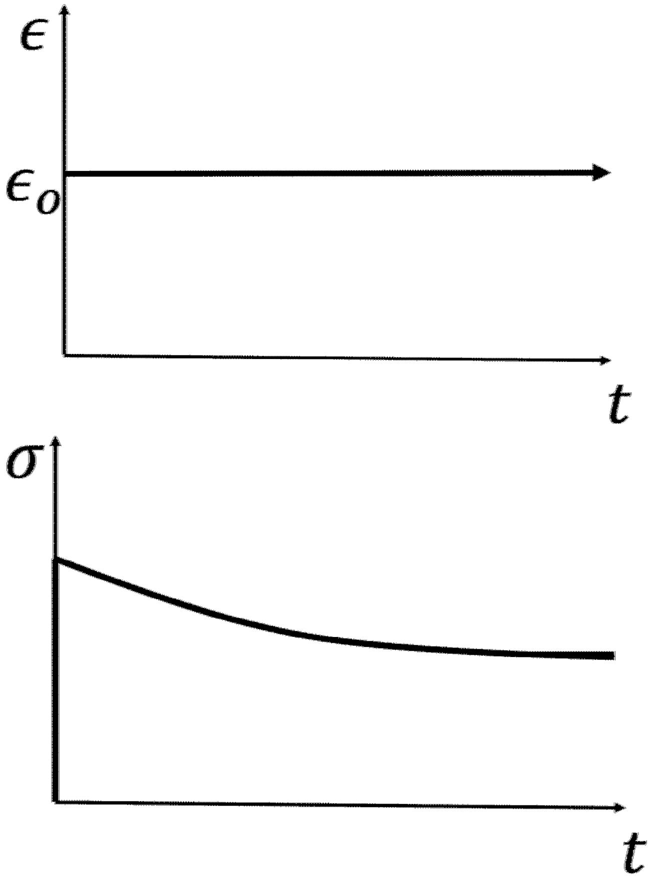
What is Viscoelasticity?

- Viscoelastic materials mechanical properties are time dependent

Creep



Stress Relaxation

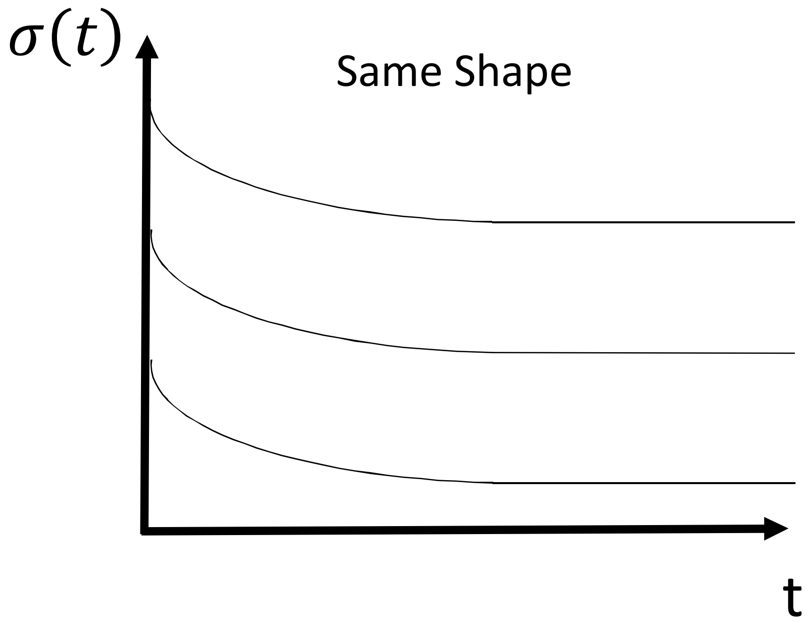


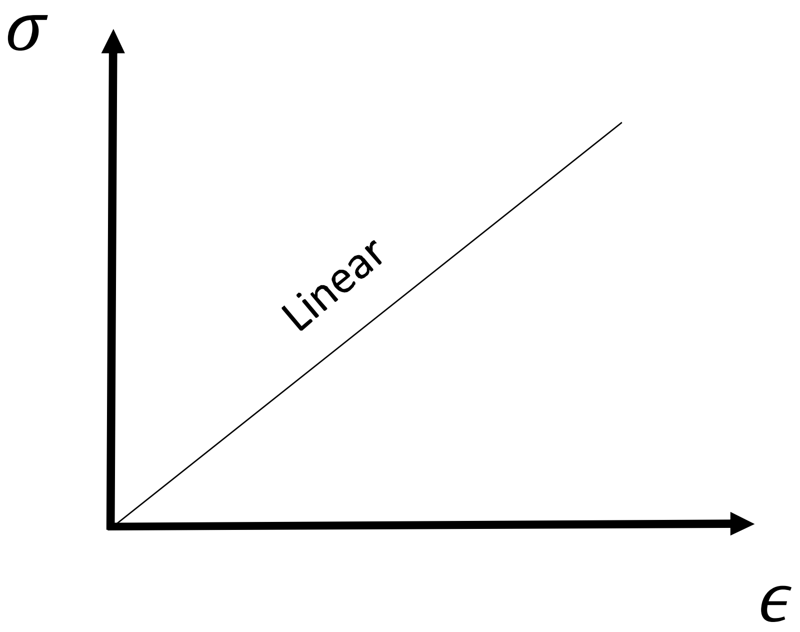
Linear Viscoelasticity

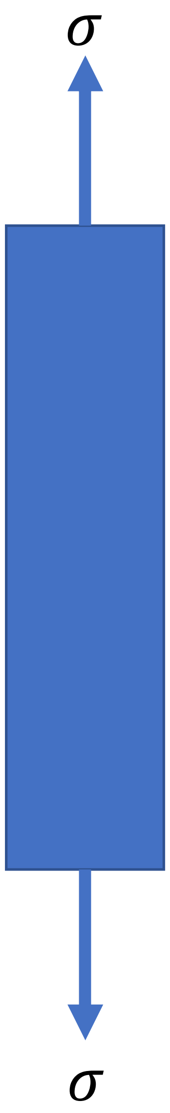
Two Assumptions for Linear Viscoelasticity:

1. The relaxation modulus is independent of the applied strain level

2. The relationship of stress vs. strain is linear







Transient Behavior

Hook’s Law:

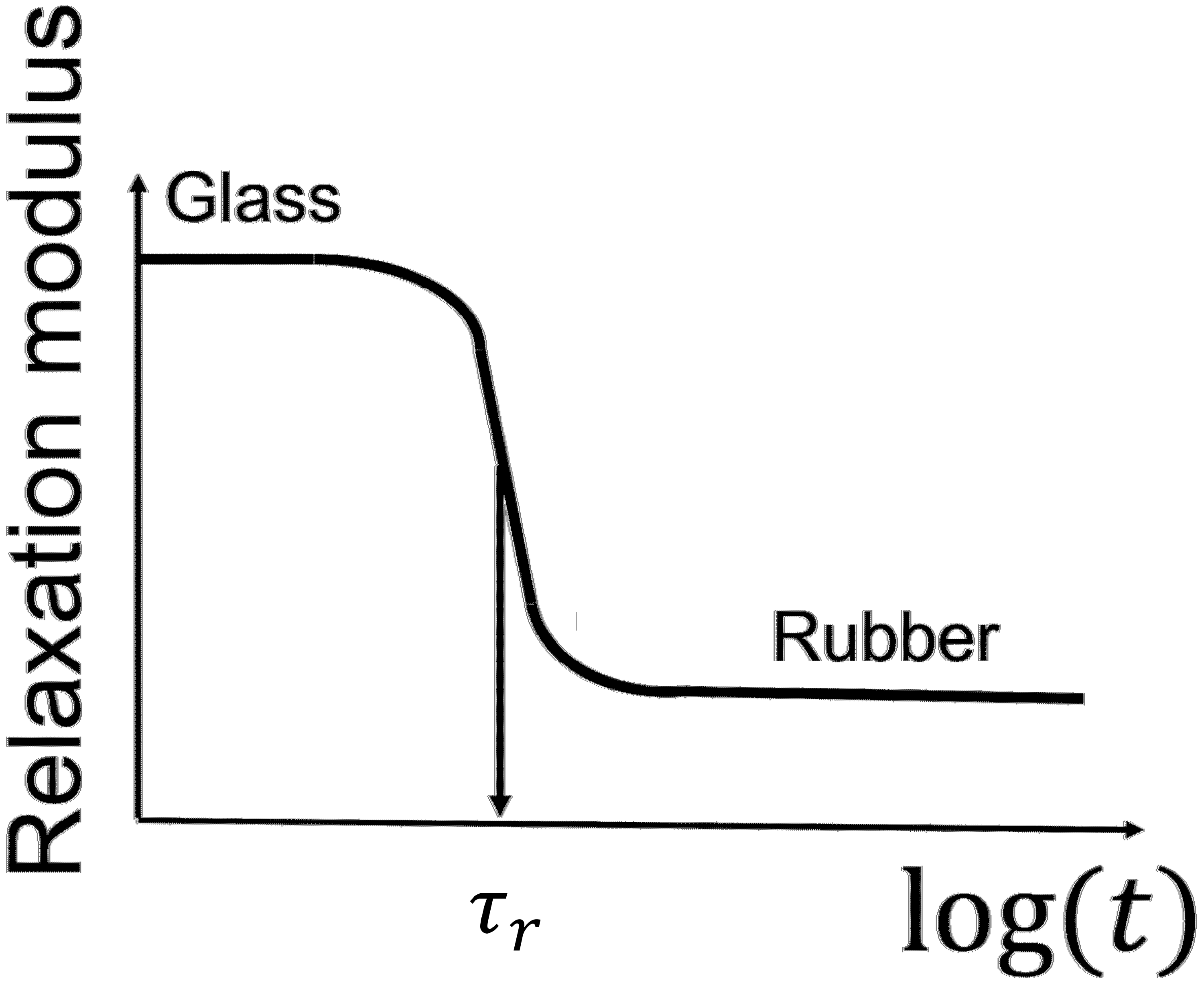
Young’s Modulus: resistance to deformation

(1) $\sigma = E\epsilon$

Relaxation Modulus: How stiffness changes with time

(2) $\sigma(t) = E(t)\epsilon_o$

Relaxation Modulus

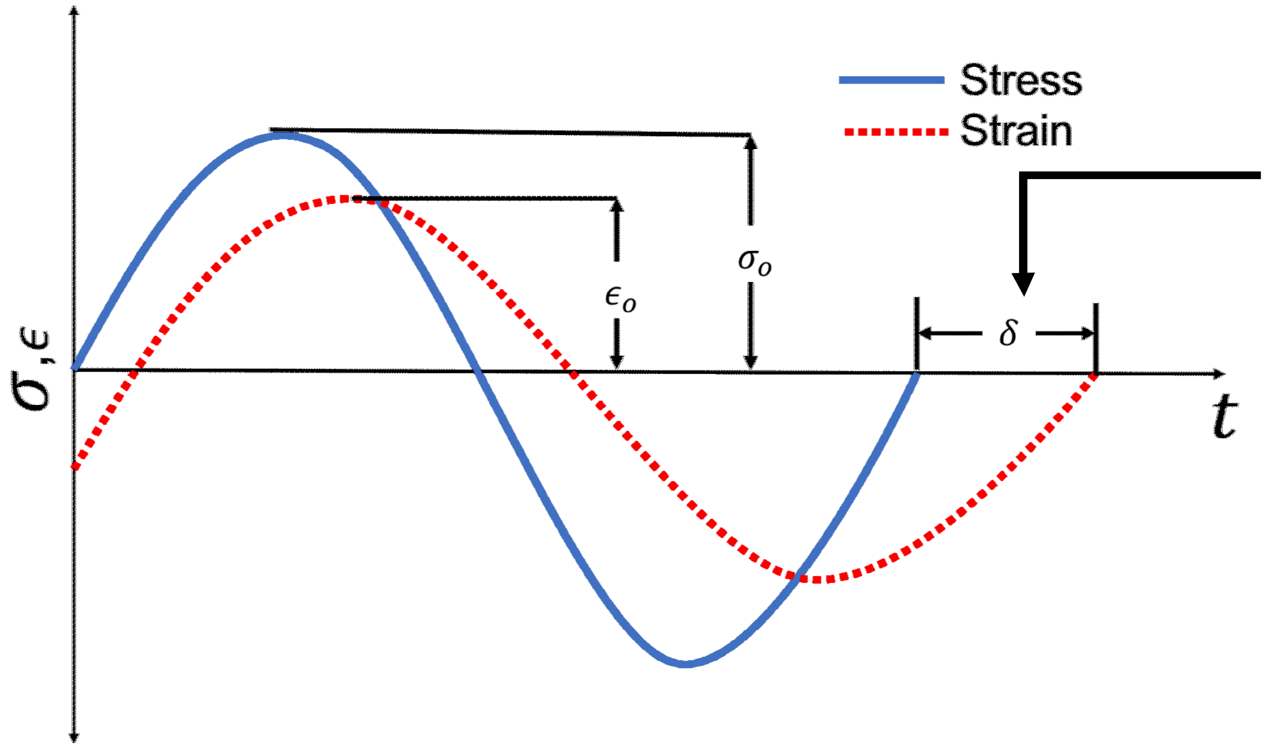


$\frac{-t}{\tau_r}$

Dynamic Loading

Now suppose the stress $\sigma(t)$ varies sinusoidally with respect to time:

$$\sigma(t) = \sigma_o \sin(2\pi\nu t)$$



Phase lag between stress and strain phase angle: δ

$$\epsilon(t) = \epsilon_o \sin(2\pi\nu t - \delta)$$

Dynamic Stiffness

- Dynamic stiffness can be expressed as a complex number:

Real

$$E' = |E^*|\cos(\delta)$$

Imaginary

$$E'' = |E^*|\,sin(\delta)$$

Loss Tangent

$$\tan(\delta)$$

$$|E^*| = \sqrt{(E')^2 + (E'')^2}$$

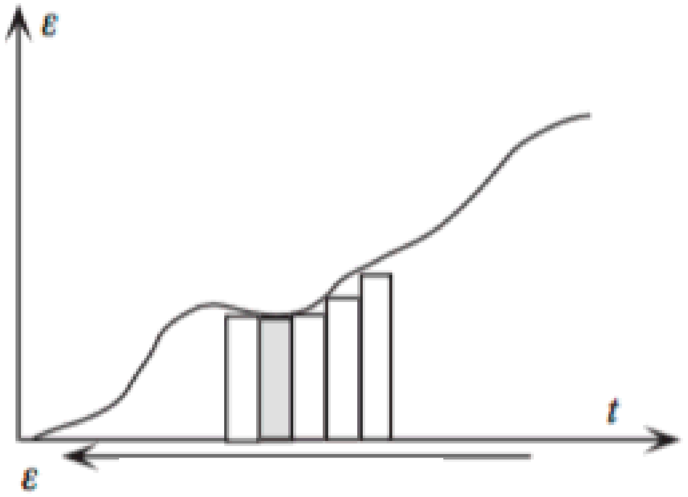
$$\frac{\sigma}{\epsilon_o} = E^* = E' + iE''$$

Proportional to the Energy stored per cycle (E')

Proportional to the Energy lost per cycle (E'')

Constitutive Equations

Consider an arbitrary loading history



1. $\epsilon(t) = \epsilon_o H(t)$

$$H(t) = \begin{cases} 0 & t < 0 \\ \frac{1}{2} & t = 0 \\ 1 & t > 0 \end{cases}$$

- A series of step increases are used:

2. $\epsilon(t) = \sum_{i=1}^{r} \Delta\epsilon_i \, H(t-\tau)$

- Boltzmann Superposition Principle
  - The compound cause is the sum of the individual causes

$$\epsilon(t) = \sum_{i=1}^{r} \Delta\epsilon_i \, H(t-\tau) \quad \rightarrow \quad \sigma(t) = E(t)\epsilon_o$$

3. $\sigma(t) = \sum_{i=1}^{r} E(t-\tau_i)H(t-\tau_i)$

- Converges to a hereditary integral:

3. $\sigma(t) = \int_0^t E(t-\tau)H(t-\tau)d\epsilon(\tau)$

- Constitutive equation for a linear viscoelastic material with differentiable strain history:

4. $\sigma(t) = \int_0^t E(t-\tau)\frac{d\epsilon(\tau)}{d\tau}d\tau$

Prony Series

- Cannot solve hereditary integral directly so use Prony series
  - Approximate relaxation modulus using Prony series:

1. $\sigma(t) = \int_0^t E(t-\tau)\frac{d\epsilon(\tau)}{d\tau}d\tau \quad \rightarrow \quad E(t) = \sum_{i=1}^{N} E_i e^{\frac{-t}{\tau_r}} + \mathrm{E}_\infty$

- Now the stress can be expressed as:

2. $\sigma(t) = \int_0^t [\sum_{i=1}^{t} E_i e^{-\left(\frac{t-\tau}{\tau_i}\right)} + E_\infty]\frac{d\epsilon(\tau)}{d\tau}d\tau$

- The incremental formulation for linear viscoelasticity:

3. $\sigma_{n+1} = \sum_{i=1}^{N} E_i \left[e^{-\left(\frac{\Delta t_n}{\tau_i}\right)} + \frac{1-e^{-\left(\frac{\Delta t_n}{\tau_i}\right)}}{\frac{\Delta t_n}{\tau_i}} \right] + E_\infty \epsilon_{n+1}$

Material Model

- Models to choose from: Viscoelastic Swanson Model, HyperYeohDamage Model, Specific Potential Energy Clock Model (SPEC)
- SPEC model is the flexible and most production hardened model available viscoelastic material at moderate to small deformations
- These models have been proven to accurately predict viscoelastic behavior of glassy and semi-crystalline polymers
- SPEC model is a thermodynamically consistent fully nonlinear viscoelastic constitutive model

$$\underline{\underline{\sigma}} = \left[\Delta K \int_0^t ds\, f_v(t^* - s^*) \frac{dI_1}{ds}(s) - \Delta(K\beta) \int_0^t ds\, f_v(t^* - s^*) \frac{dT}{ds}(s)\right]\underline{\underline{I}} + 2\Delta G \int_0^t ds f_s(t^* - s^*) \frac{d\underline{\underline{\epsilon_{dev}}}}{ds}(s)$$

$$+\left[K_\infty I_1 - K_\infty \beta_\infty \Delta T\right]\underline{\underline{I}} + 2G_\infty \underline{\underline{\epsilon_{dev}}}$$

Pressure/Volume terms

Shear terms

D.B. Adolf. Modeling the response of monofilament nylon cords with the non- linear viscoelastic, simplified potential energy clock model. Polymer(1), April 2010.
Robert S. Chambers Adolf, Douglas B. and Matthew A. Neidigk. A simplified potential energy clock model for glassy polymers. Polymer(1), April 2009.

Simplified Potential Energy Clock Model

- Model is driven by a material clock
  - Hereditary integrals over the difference in material time
  - Increment in material time, dt', and laboratory time, dt, are related through shift factor:

$$t^* - s^* = \int_s^t \frac{dw}{a(w)} \qquad \log(a) = -C_1\left(\frac{N}{C_2 + N}\right)$$

$$N = \left\{[T(t) - T_{ref}] - \int_0^t ds f_v(t^* - s^*)\frac{dT}{ds}(s)\right\} + C_3\left\{I_1(t) - \int_0^t ds f_v(t^* - s^*)\frac{dI_1}{ds}(s)\right\} + C_4\left\{\int_0^t ds f_s(t^* - s^*)\frac{\epsilon_{dev}(s)}{ds}\right\}$$

- Volumetric and shear relaxation functions:

$$f_v(t) = \sum_K A_k e^{-\frac{t}{\tau_k}} \qquad f_s(t) = \sum_K w_k e^{-\frac{t}{\tau_k}}$$

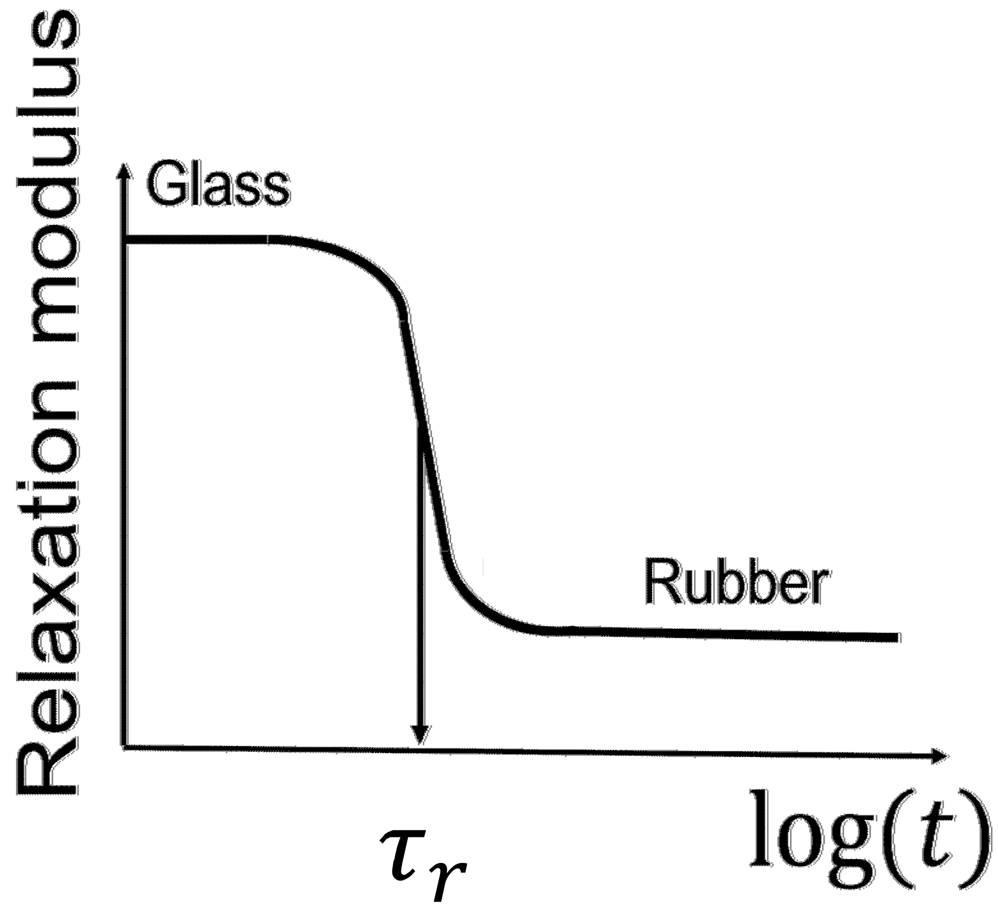
UNM | Mechanical Engineering

Parameters for SPEC

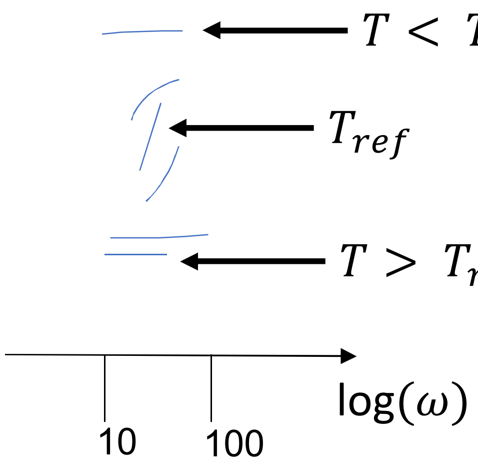
Symbol	Definition
T_{ref}	Reference temperature
K_∞	Rubbery bulk modulus
$\frac{dK_\infty}{dT}$	Derivative of K_∞ with respect to temperature
K_g	Glassy bulk modulus
$\frac{dK_g}{dT}$	Derivative of K_g with respect to temperature
α_∞	Rubbery coefficient of thermal expansion
$\frac{d\alpha_\infty}{dT}$	Derivative of α_∞ with respect to Temperature
α_g	Glassy coefficient of thermal expansion
$\frac{d\alpha_g}{dT}$	Derivative of α_g with respect to temperature
G_∞	Rubbery shear modulus
$\frac{dG_\infty}{dT}$	Derivative of G_∞ with respect to temperature
G_g	Glassy shear modulus
$\frac{dG_g}{dT}$	Derivative of G_g with respect to temperature
C_1	First Williams-Landel-Ferry (WLF) coefficient
C_2	Second WLF coefficient
~~C_3~~	~~Determined by the pressure dependence of T_g~~
~~C_4~~	~~Parameter accelerating relaxations by applied deformations~~
f_v	Volumetric relaxation spectrum
f_s	Shear relaxation spectrum

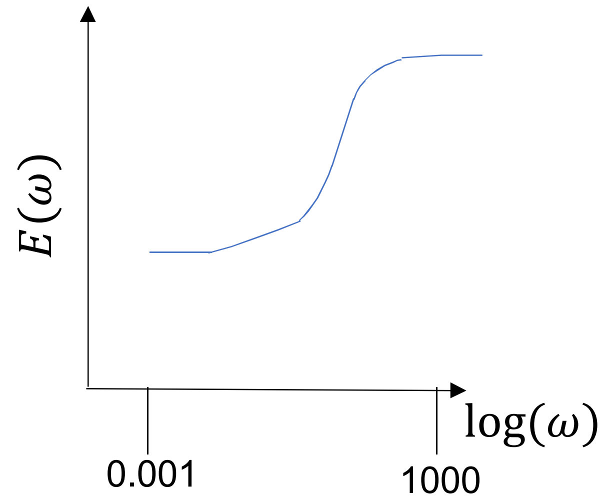
Mechanical Engineering

Time Temperature Superposition (TTS)



$$\sigma(\omega)e^{-i\omega t} = E(\omega)\epsilon(\omega)e^{-i\omega t}$$





WLF Equation:

$$\log(a_T) = -C1\left(\frac{T - T_g}{C_2 + T - T_g}\right)$$

J.D. Ferry. Viscoelastic Properties of Polymers. Willey, New York, 1980.

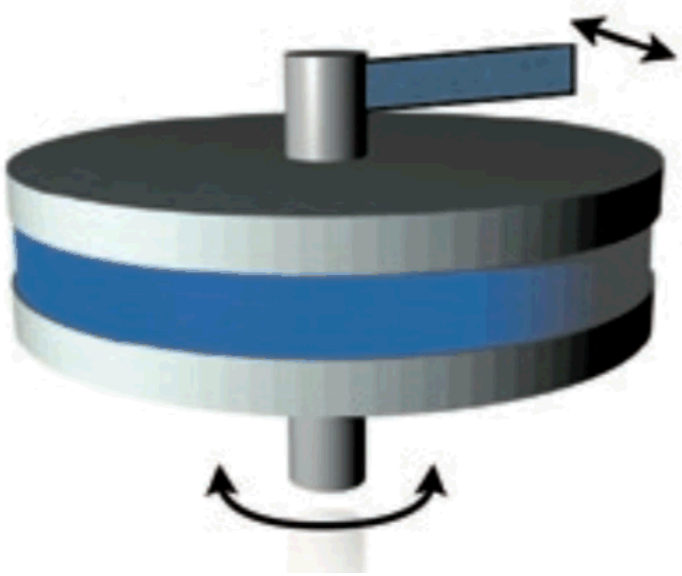
UNM | Mechanical Engineering

Dynamic Mechanical Analysis (DMA)

- Shear relaxation and two WLF coefficients can be determined by commercial rheometers

ARES-G2

- Frequency Range: 1-15 Hz
- Temperature Range: -100^o C – 50^o C

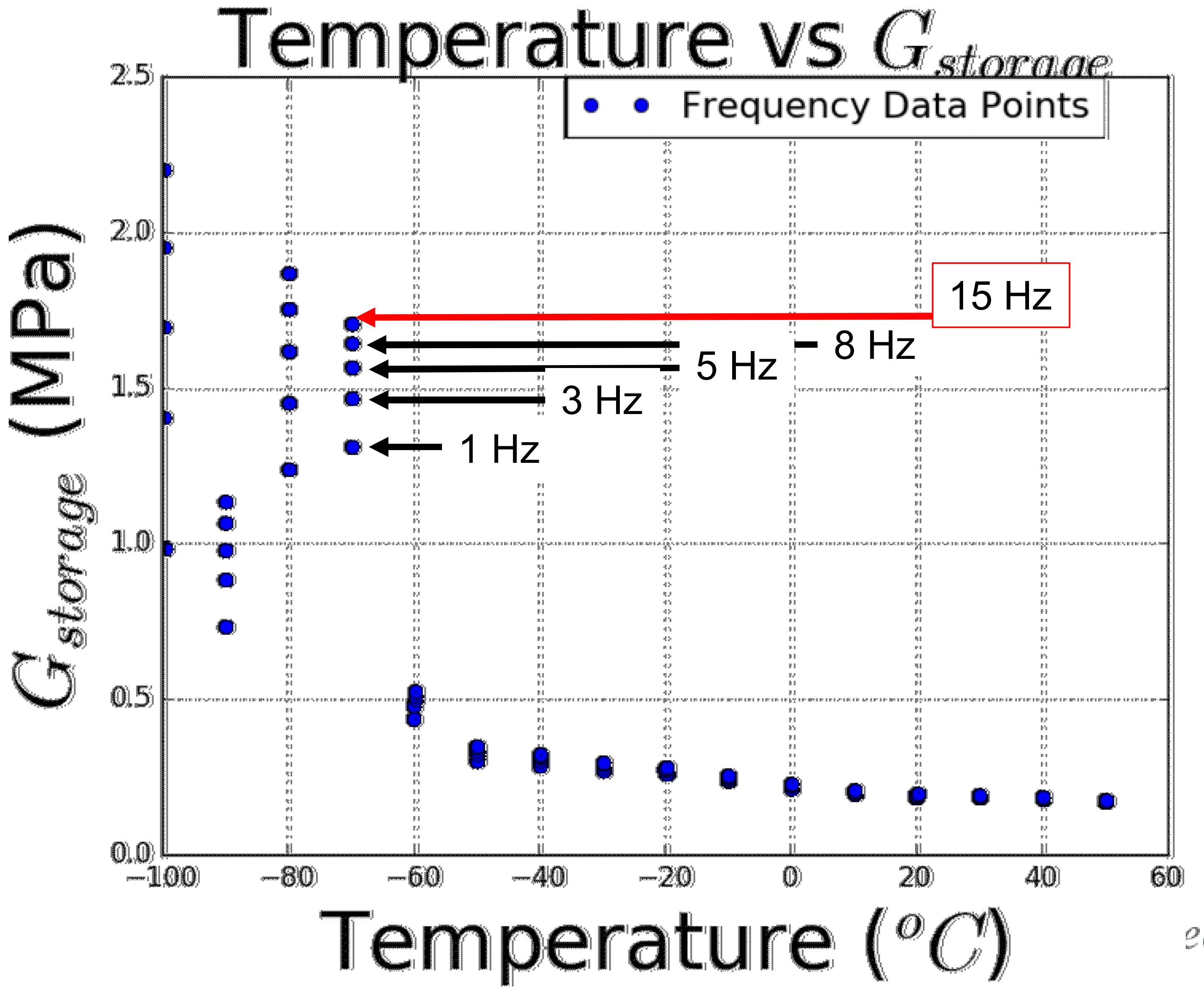


- A small normal force is applied to hold the specimen in place

UNM | Mechanical Engineering

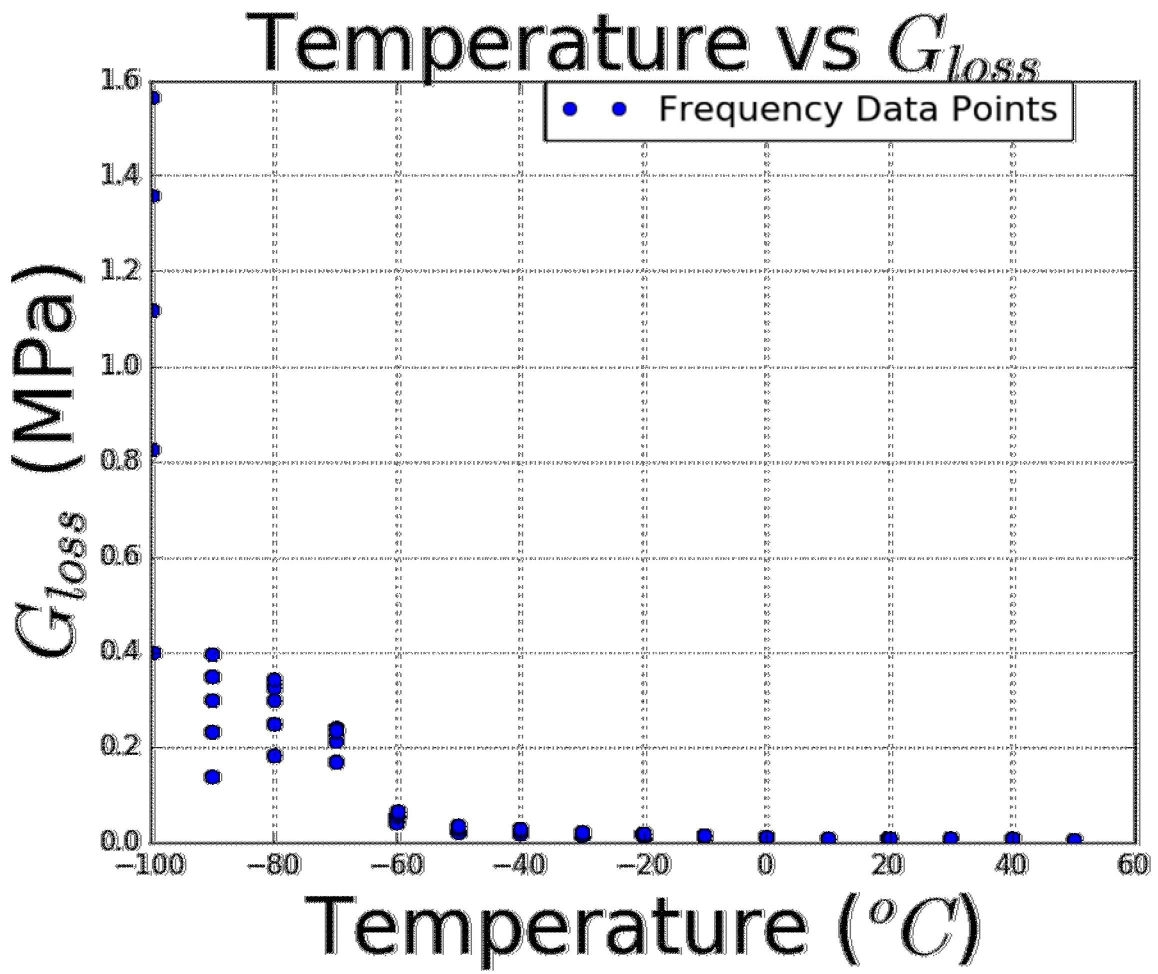
Data from DMA

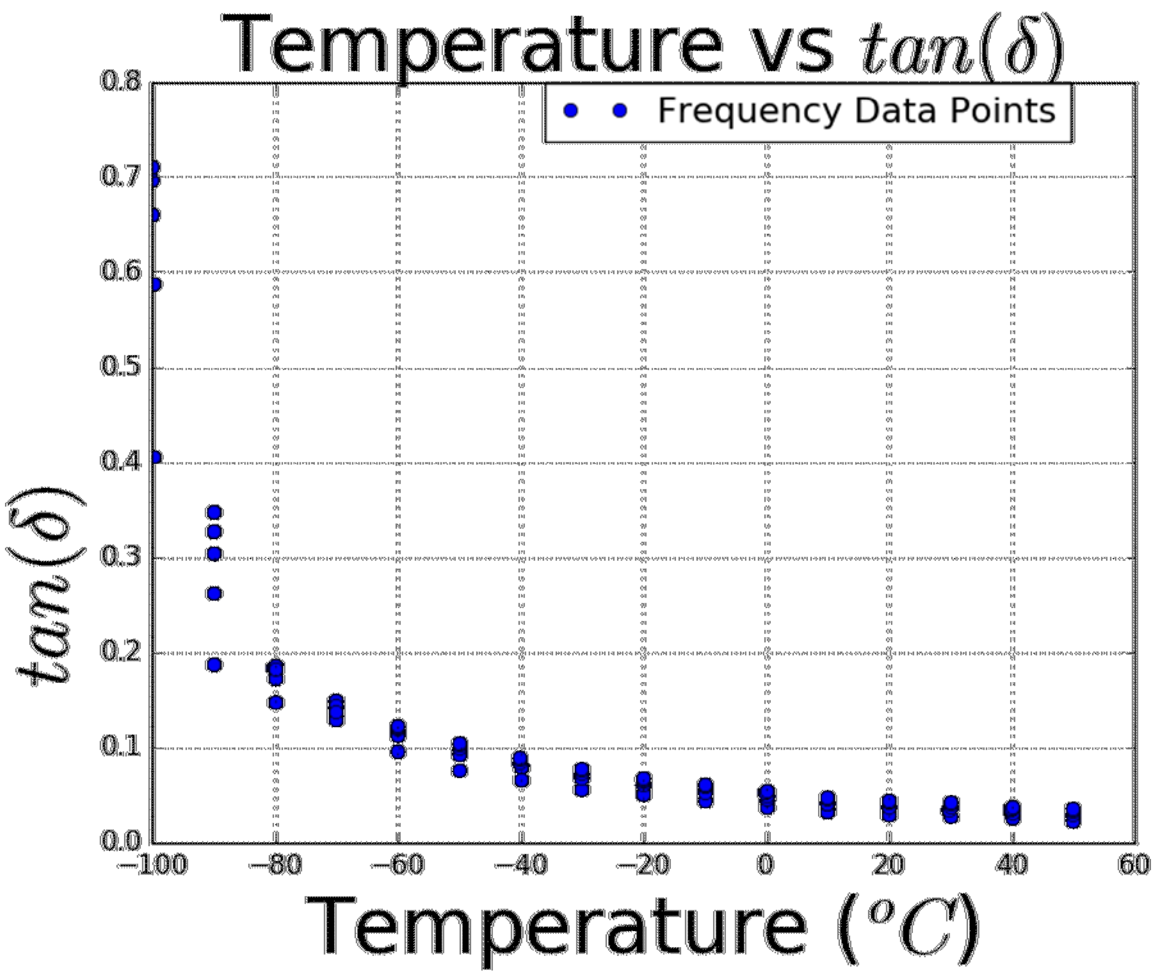
To avoid inertial effects the data was clipped at 15 Hz



echanical Engineering

Data from DMA



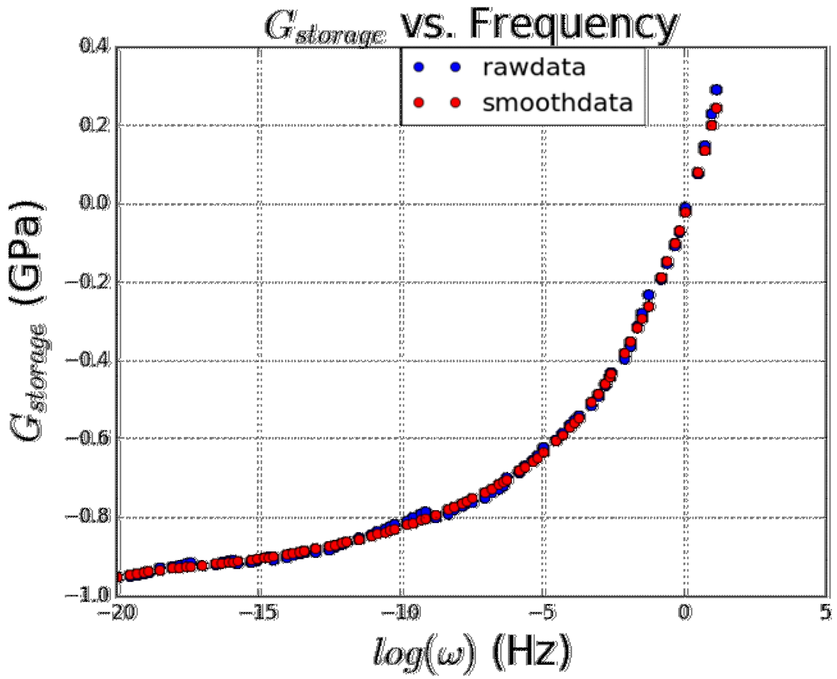


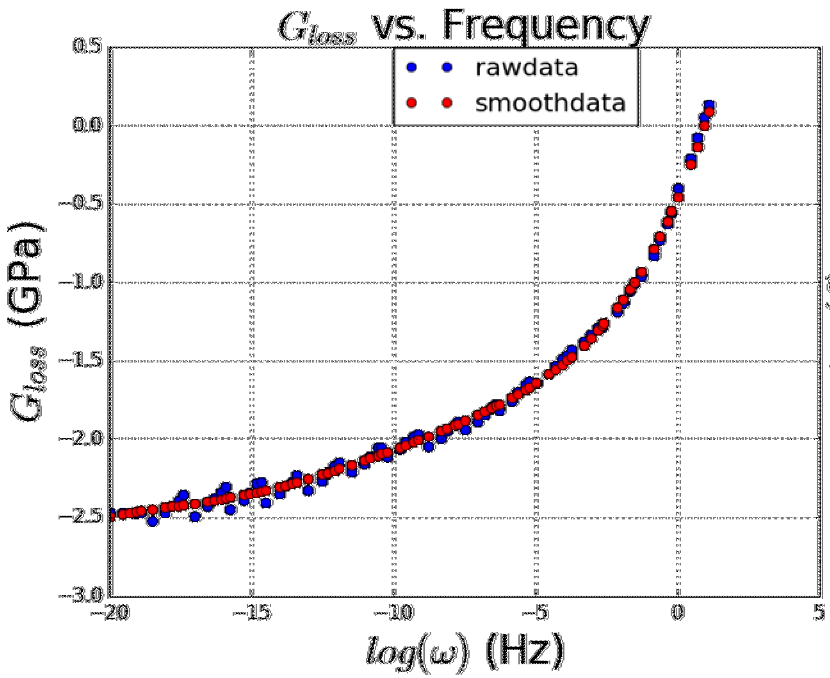
UNM Mechanical Engineering

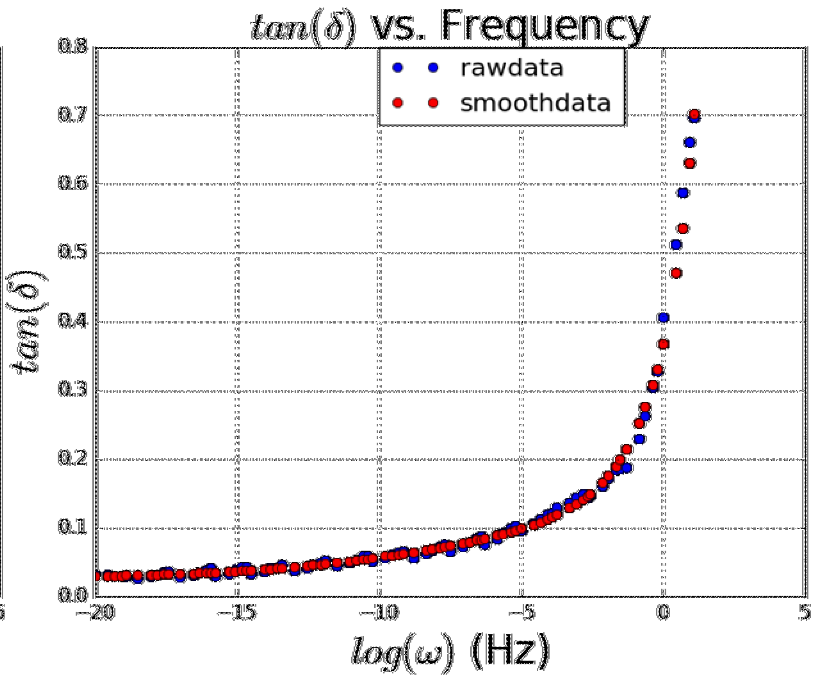
Shear Master Curve

- Recall TTS
- Must be smooth and monotonically decreasing
- Still have some inertial effects, but they can be ignored

$T_{ref} = -100$ ºC

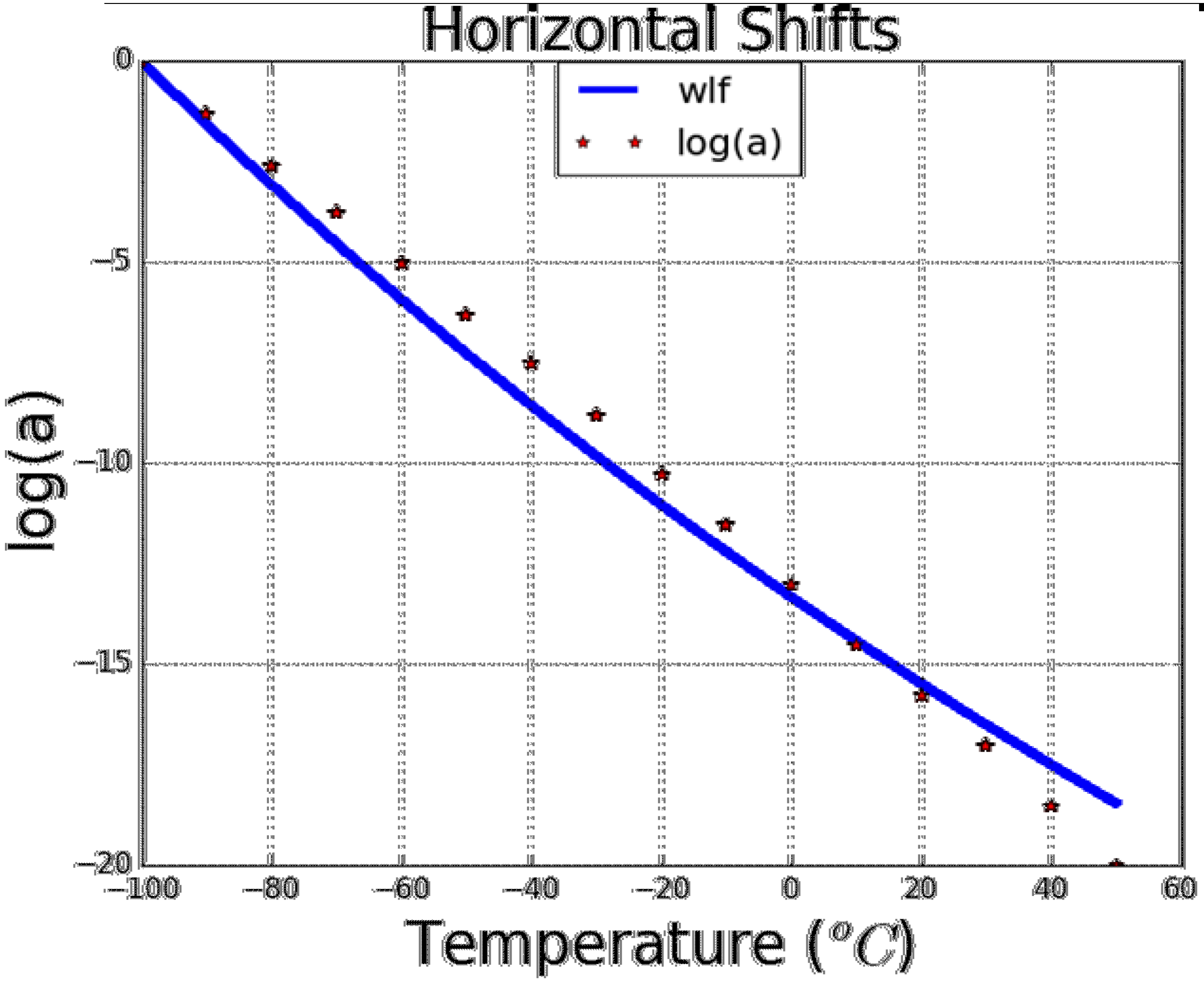






UNM | Mechanical Engineering

WLF Values for Shifted Data

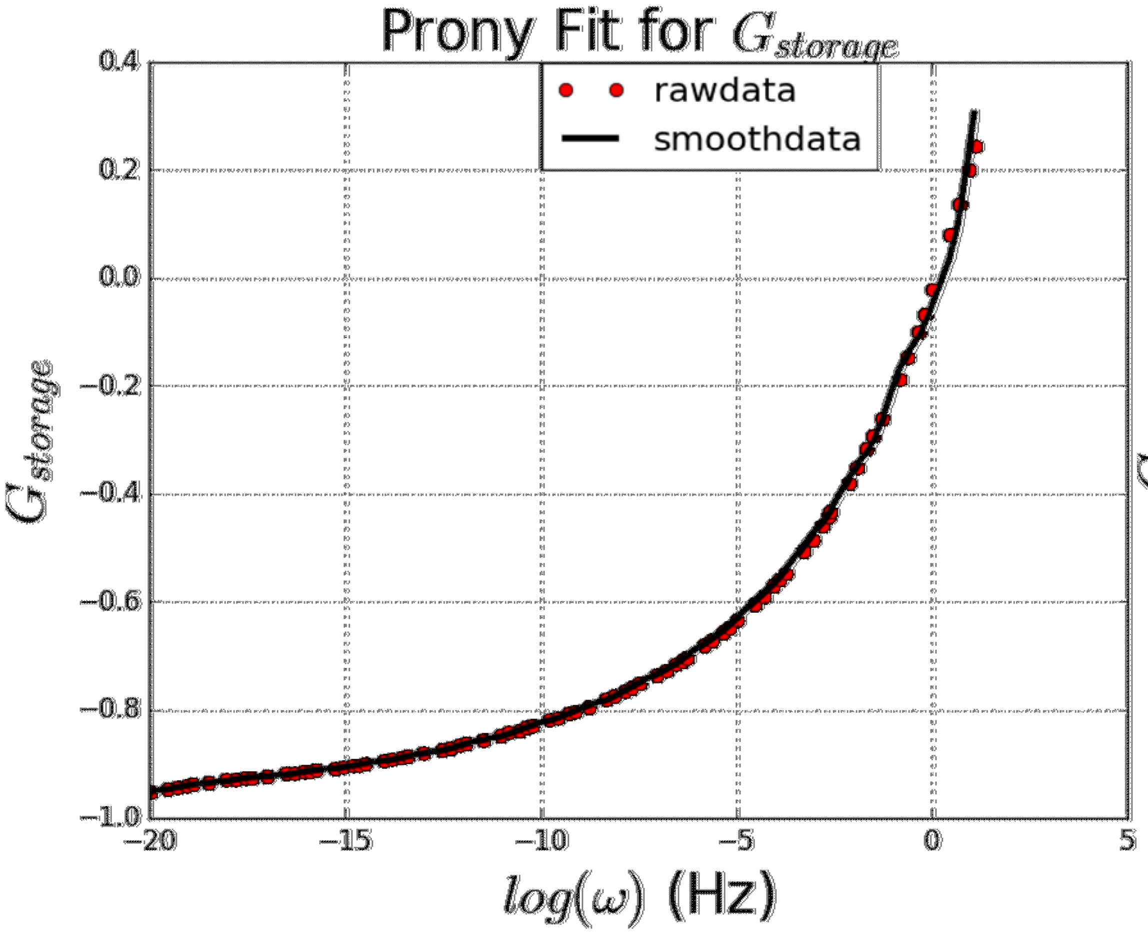


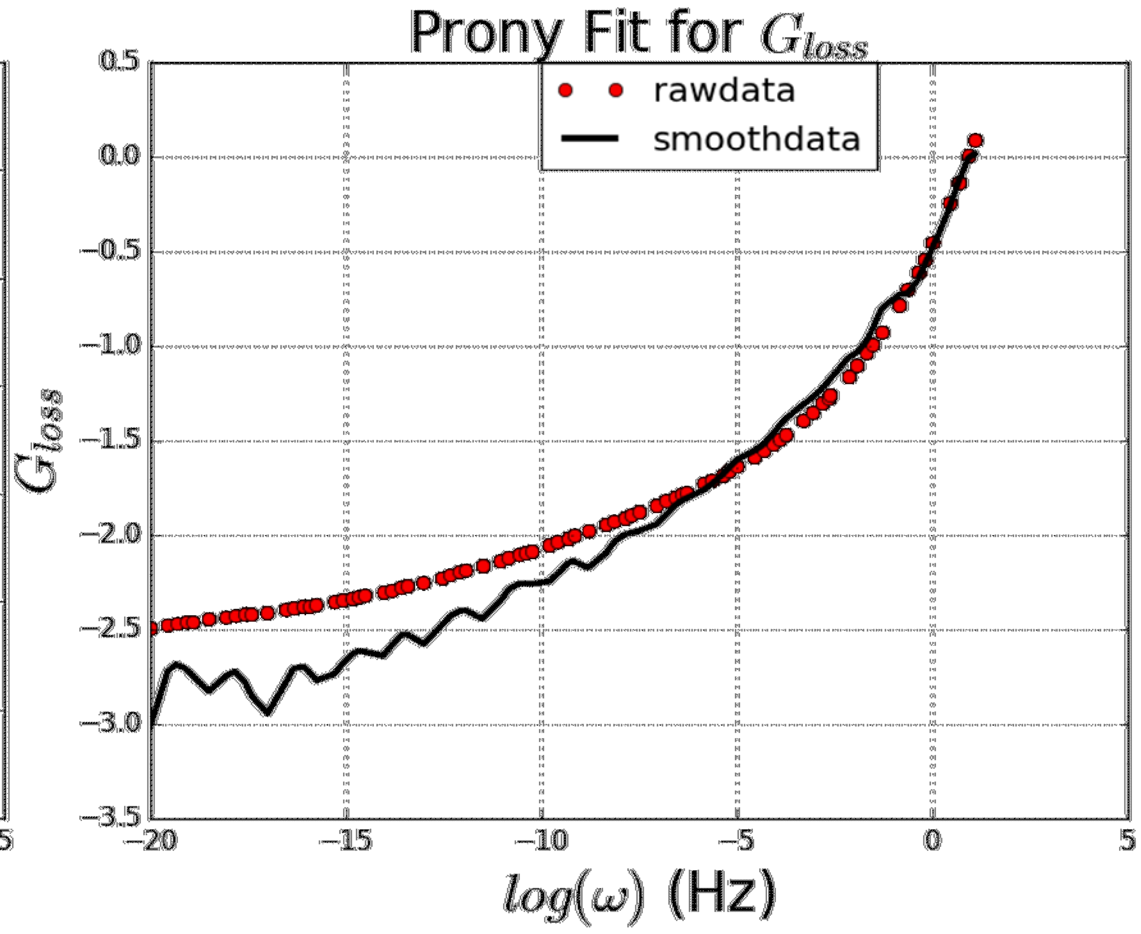
Coefficient	Value
C_1	80
C_2	500

UNM Mechanical Engineering

Calibrated Shear Function

- Recall: $f_s(t) = \sum_K w_k e^{-\frac{t}{\tau_k}}$

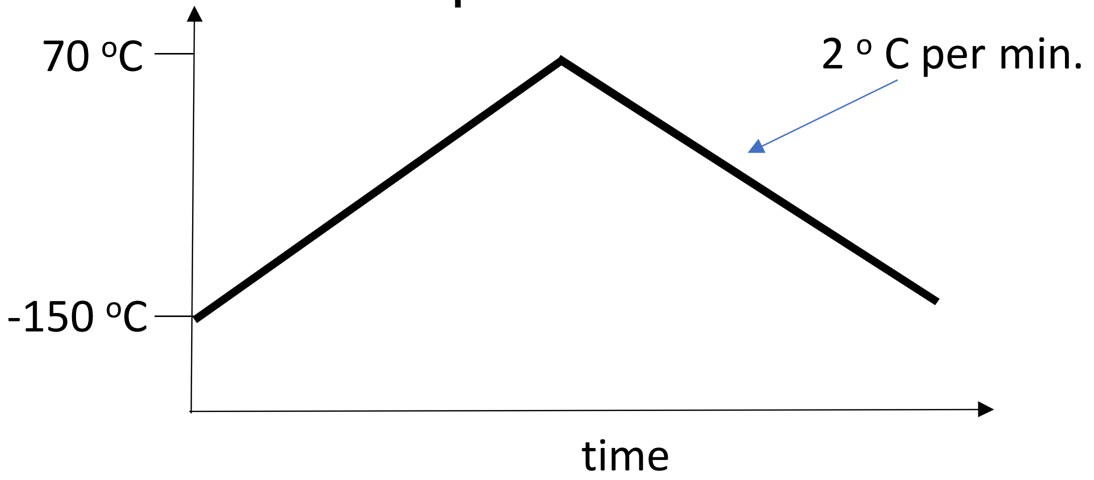


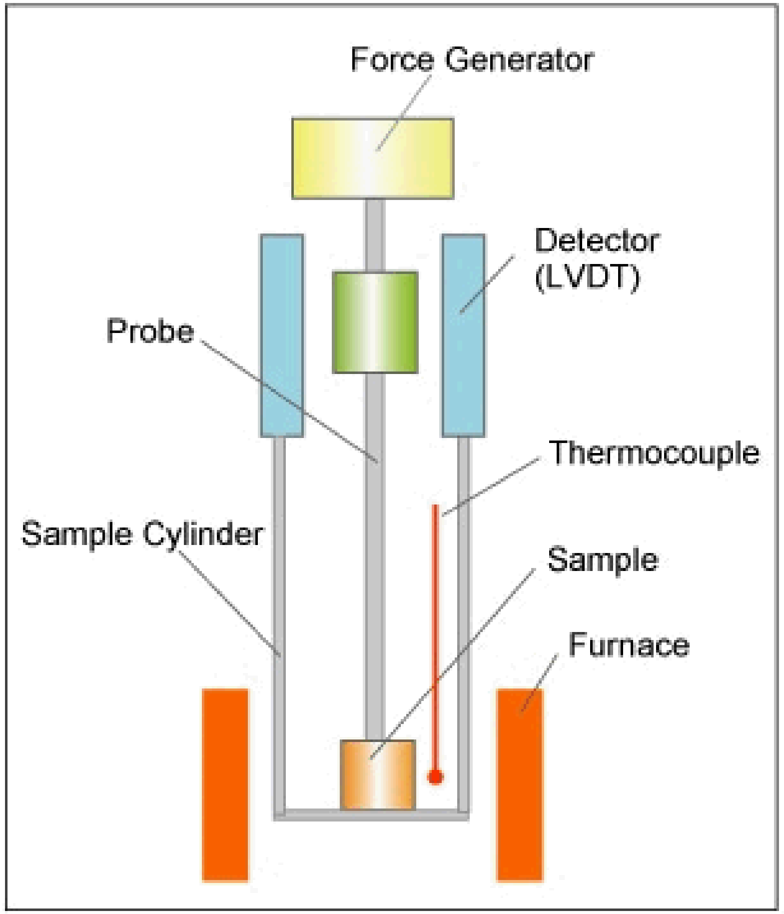


UNM | Mechanical Engineering

Thermal Mechanical Analysis (TMA)

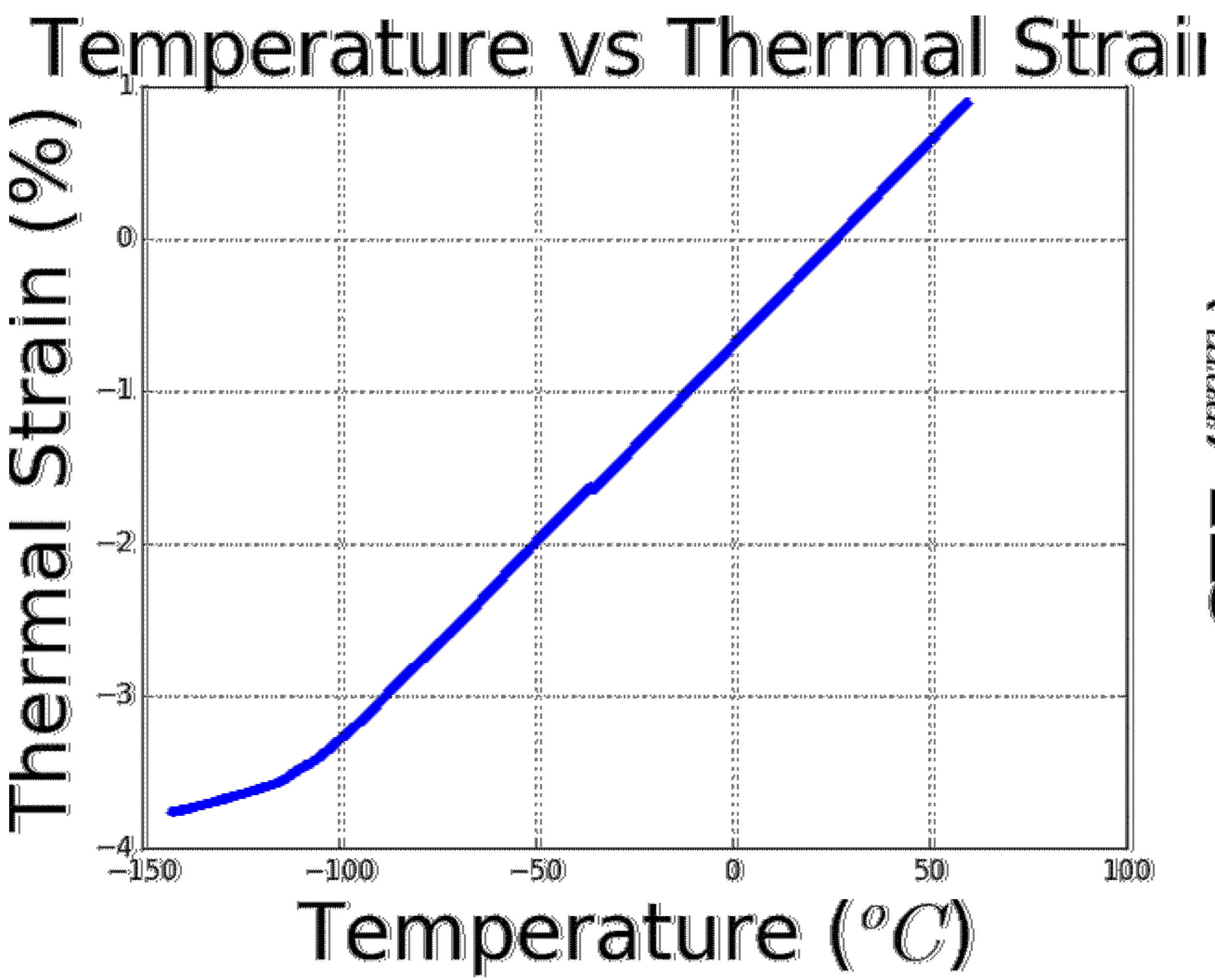
Temperature B.C.

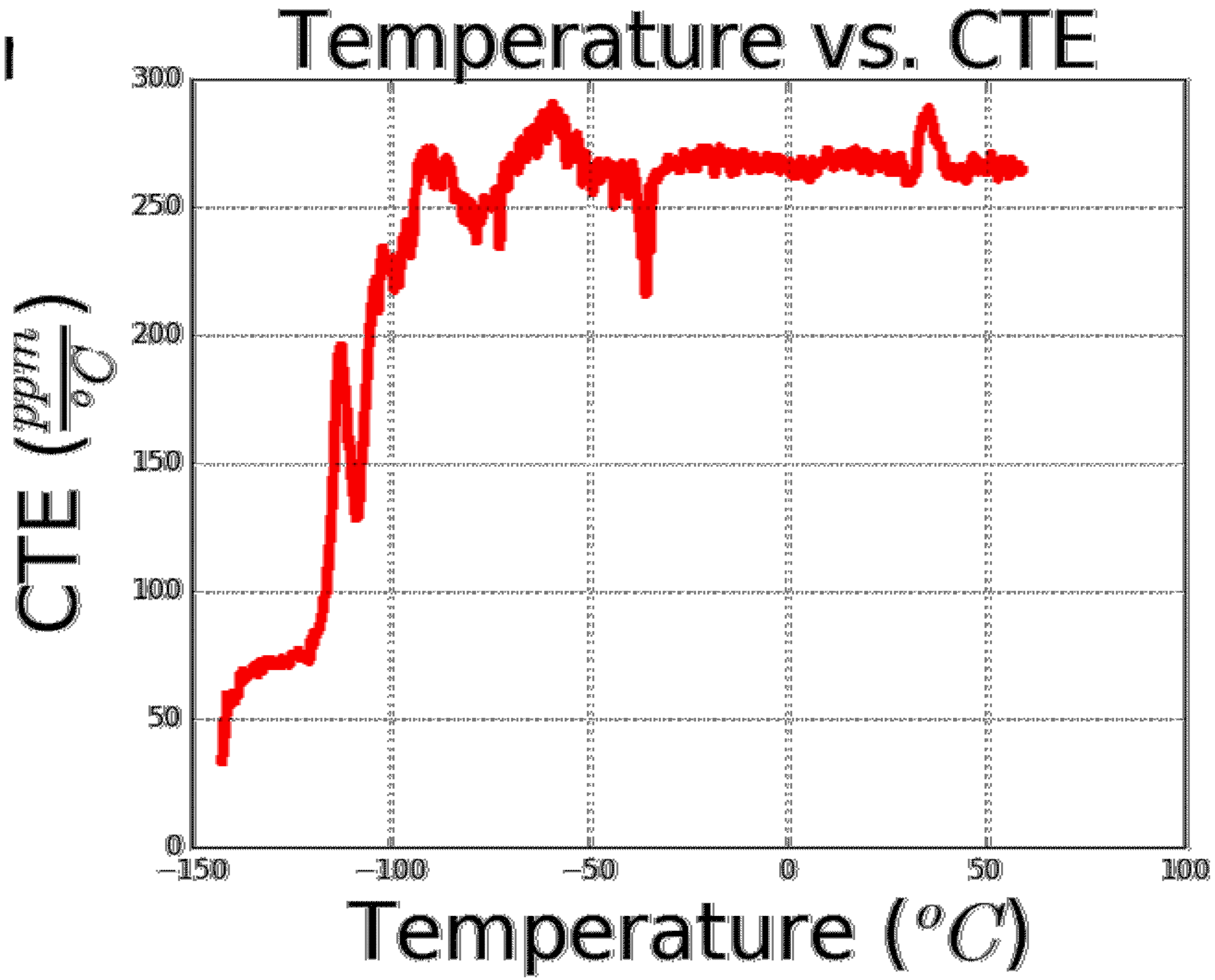




UNM Mechanical Engineering

Data from TMA

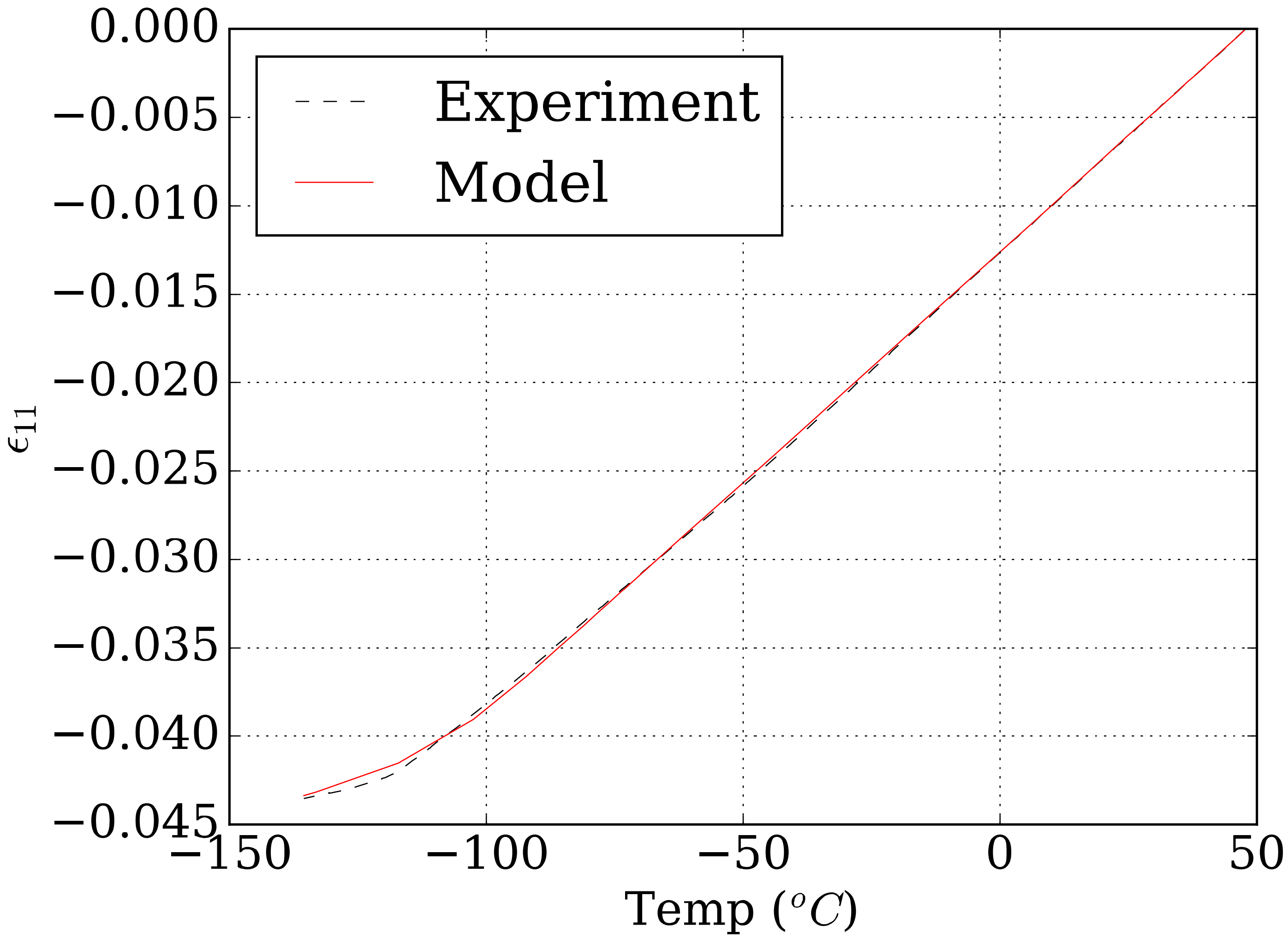




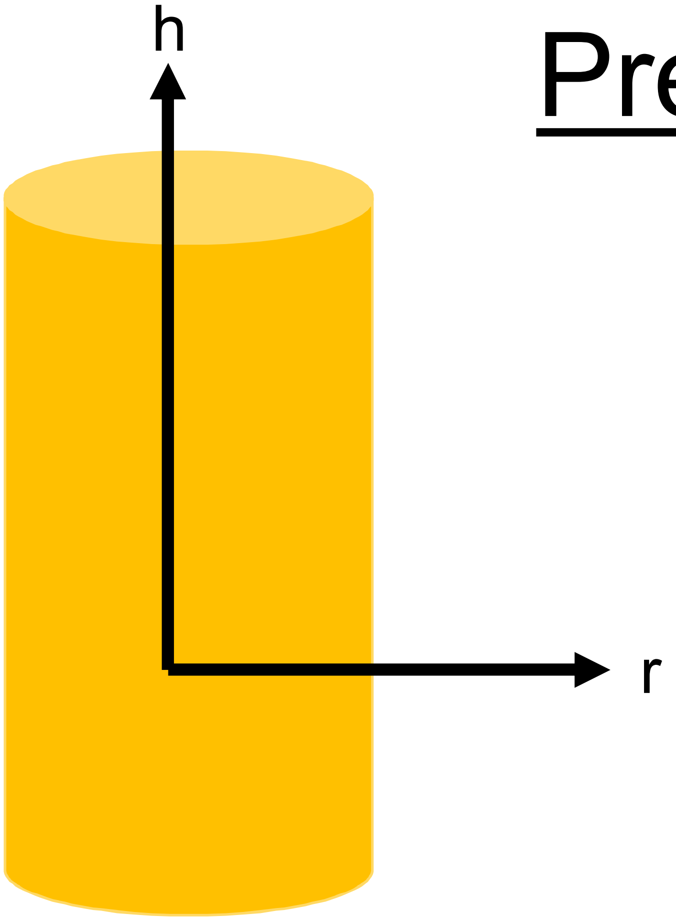
UNM | Mechanical Engineering

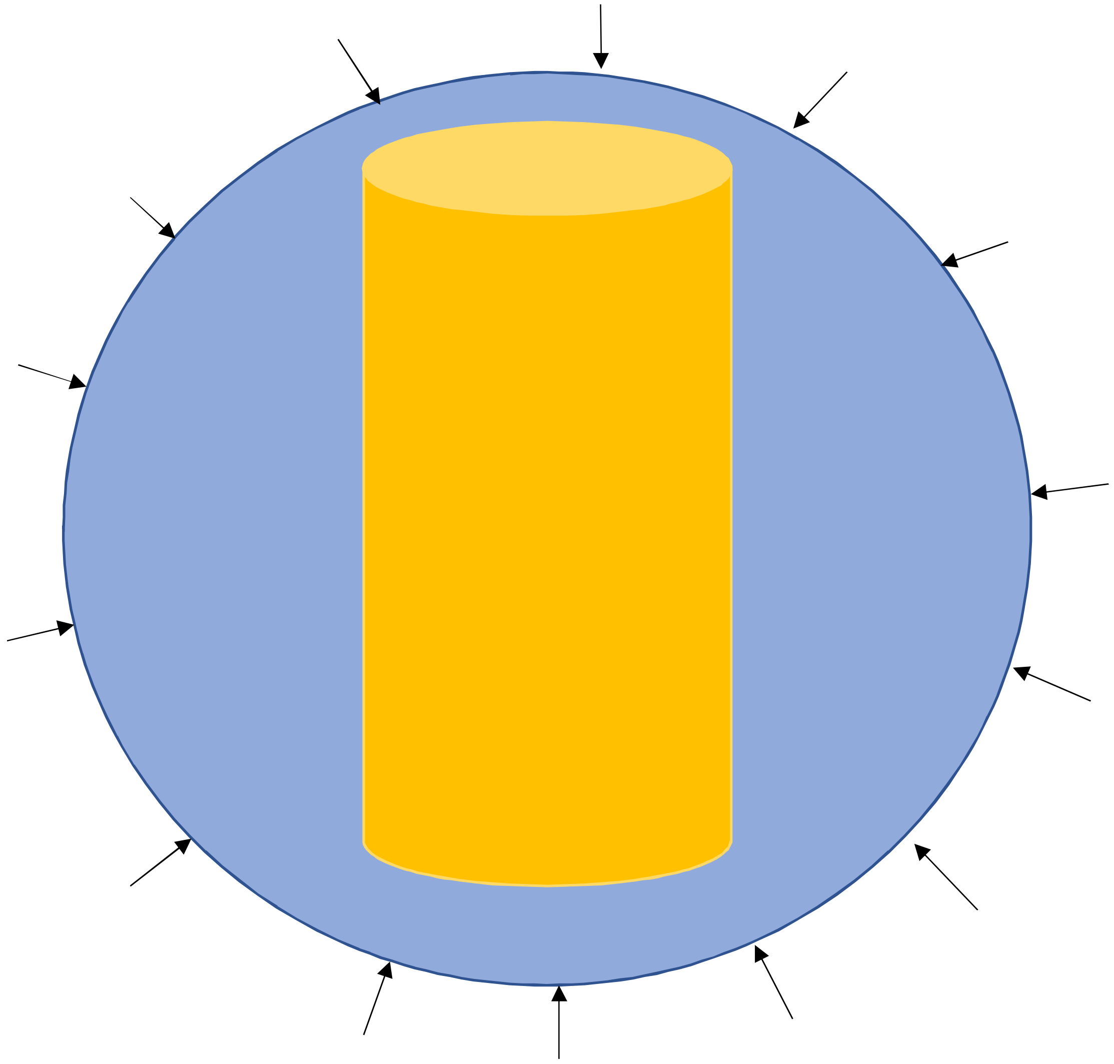
Calibrating CTE Data

- Recall: $f_v(t) = \sum_K A_k e^{-\frac{t}{\tau_k}}$
- Single uniform-gradient finite element subjected to the same BC as the TMA



Pressure Dilatometry

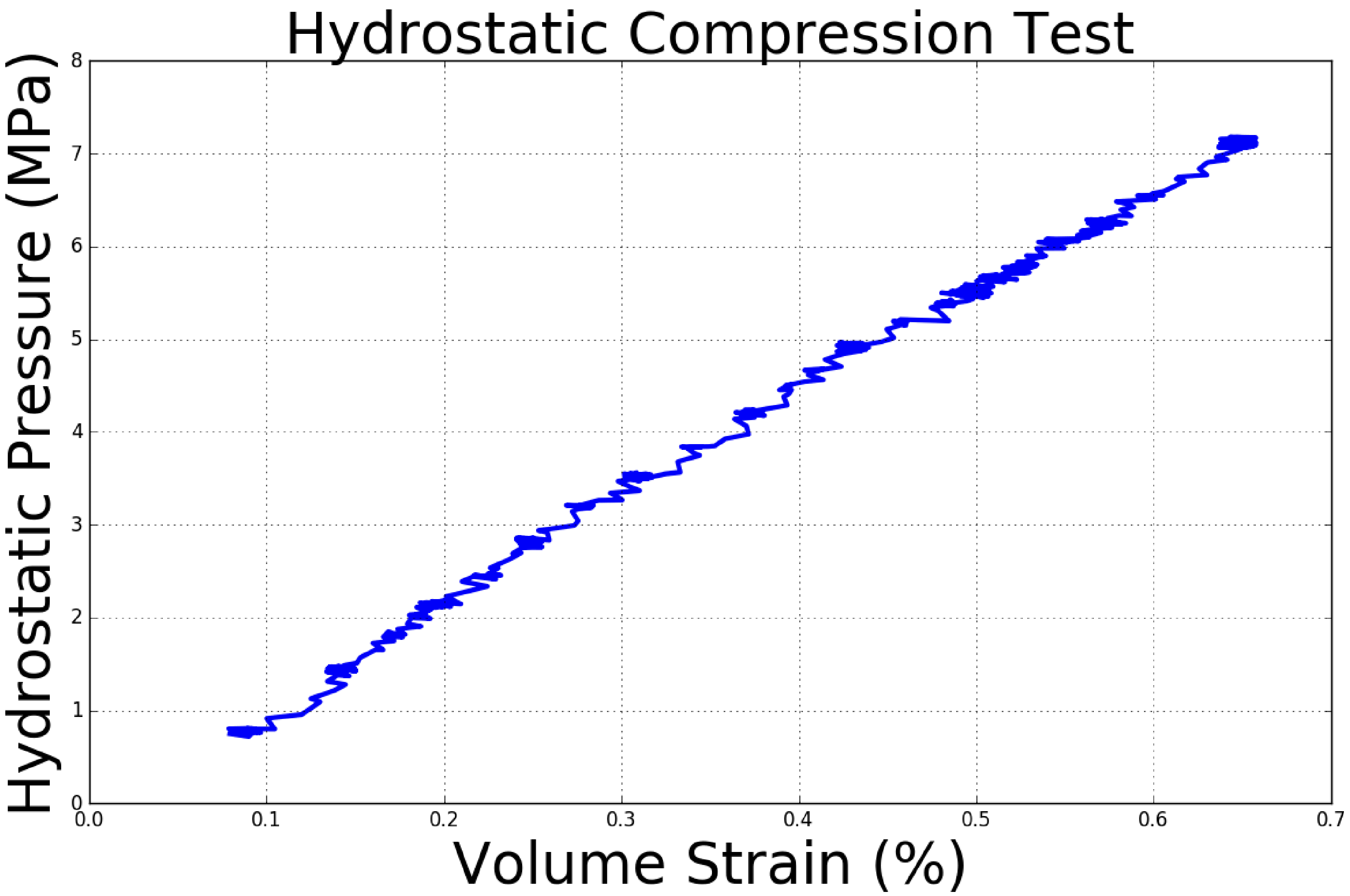




- h = 28.956 mm
- r = 6.25 mm

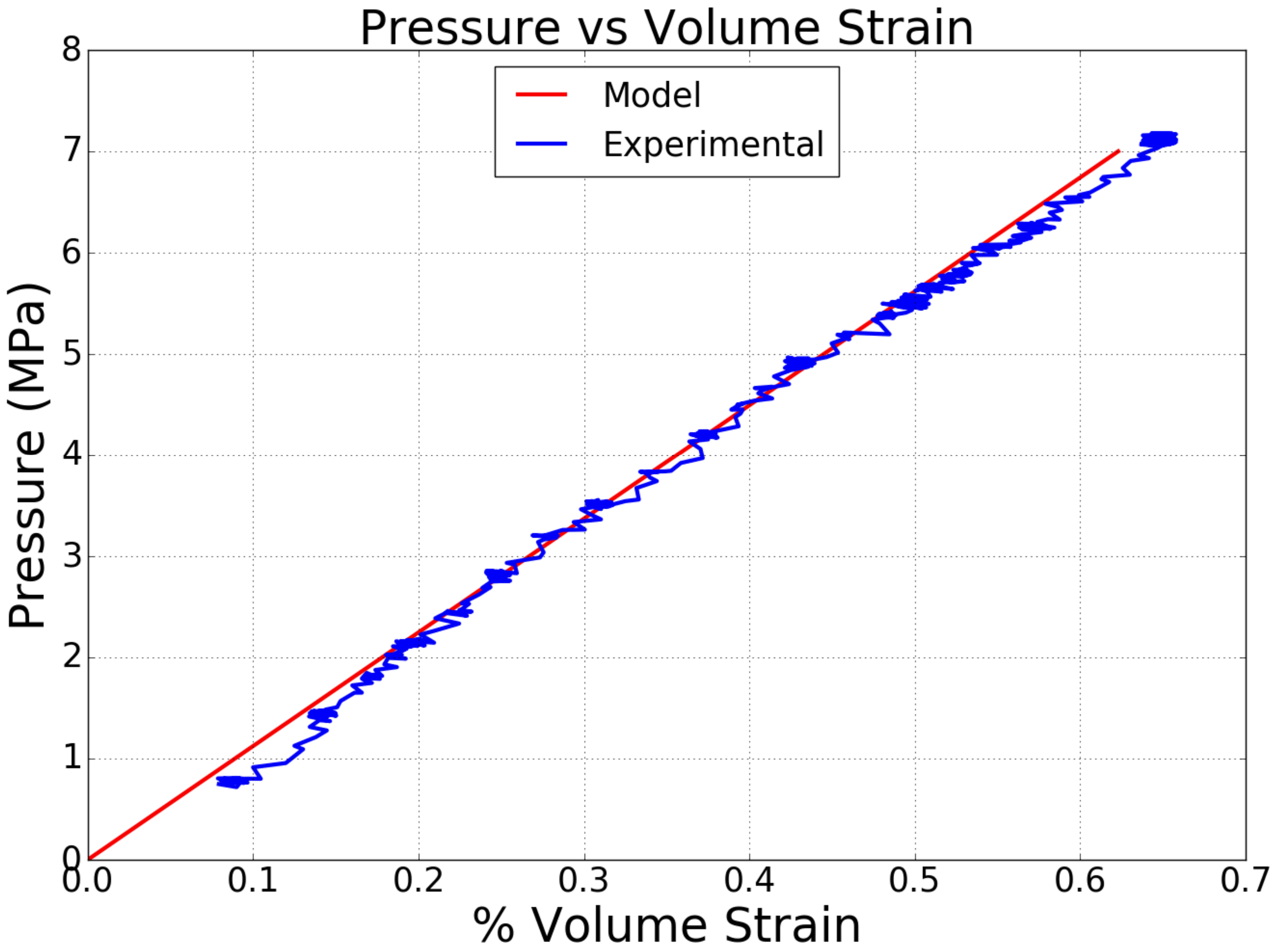
UNM | Mechanical Engineering

Pressure Dilatometry Data



UNM | Mechanical Engineering

Calibrating Bulk Data



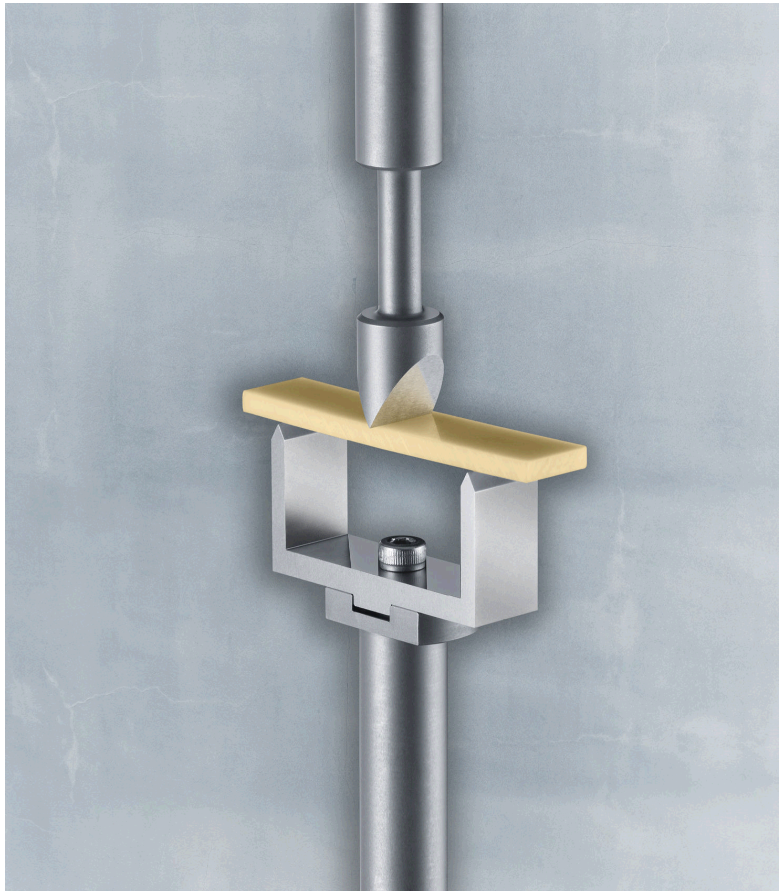
Engineering

SPEC Parameters

Symbol	Definition	Units
T_{ref}	-100.0	^oC
K_∞	1.100	GPa
$\frac{dK_\infty}{dT}$	0	$\frac{Pa}{^oC}$
K_g	7.250	GPa
$\frac{dK_g}{dT}$	0.000	$\frac{Pa}{^oC}$
α_∞	8.070	-
$\frac{d\alpha_\infty}{dT}$	-0.001E-4	-
α_g	2.100E-04	-
$\frac{d\alpha_g}{dT}$	0	-
G_∞	0.112	MPa
$\frac{dG_\infty}{dT}$	0	$\frac{Pa}{^oC}$
G_g	3.00	GPa
$\frac{dG_g}{dT}$	0	$\frac{Pa}{^oC}$
C_1	80	-
C_2	500	-
f_s	See Appendix	-
f_v	See Appendix	-

Flexural and Storage Modulus

Three point Bend



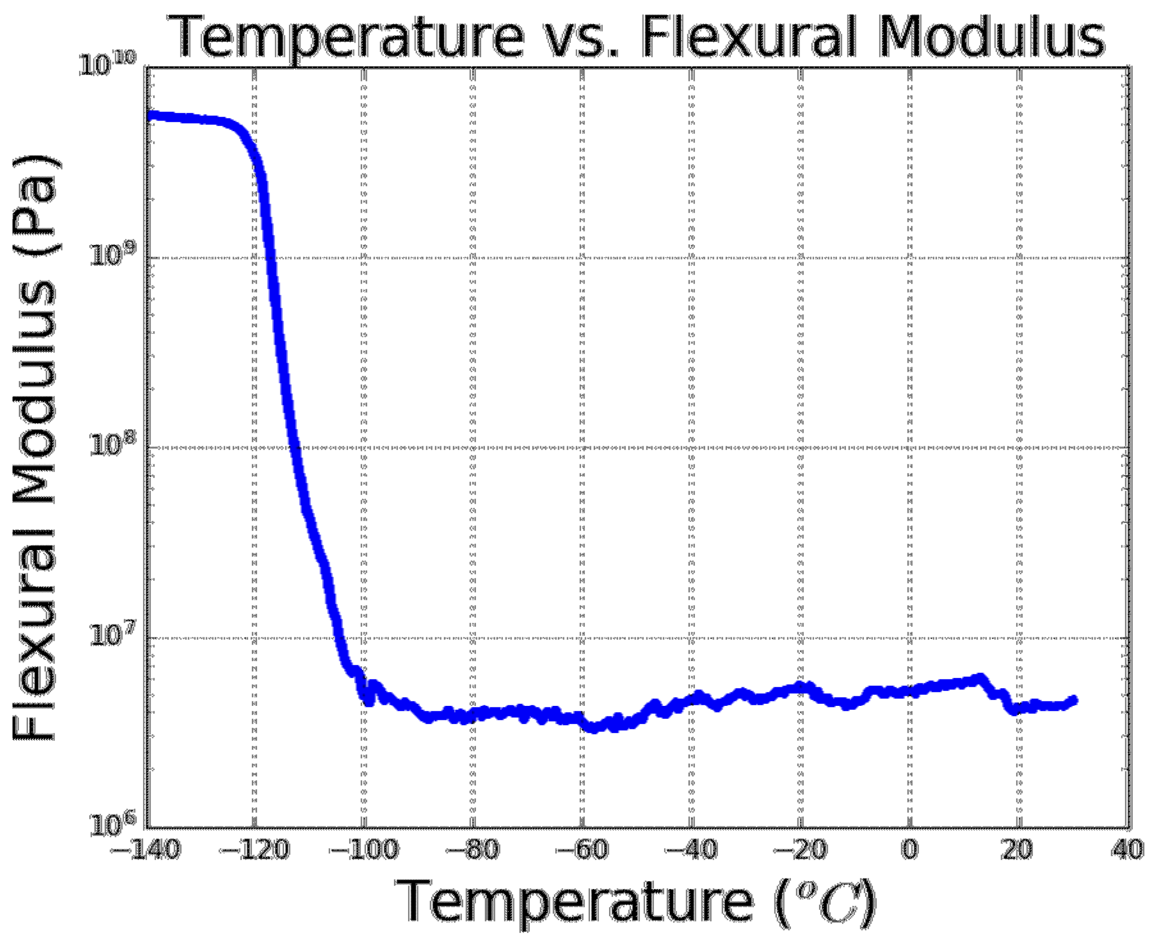
Uniaxial

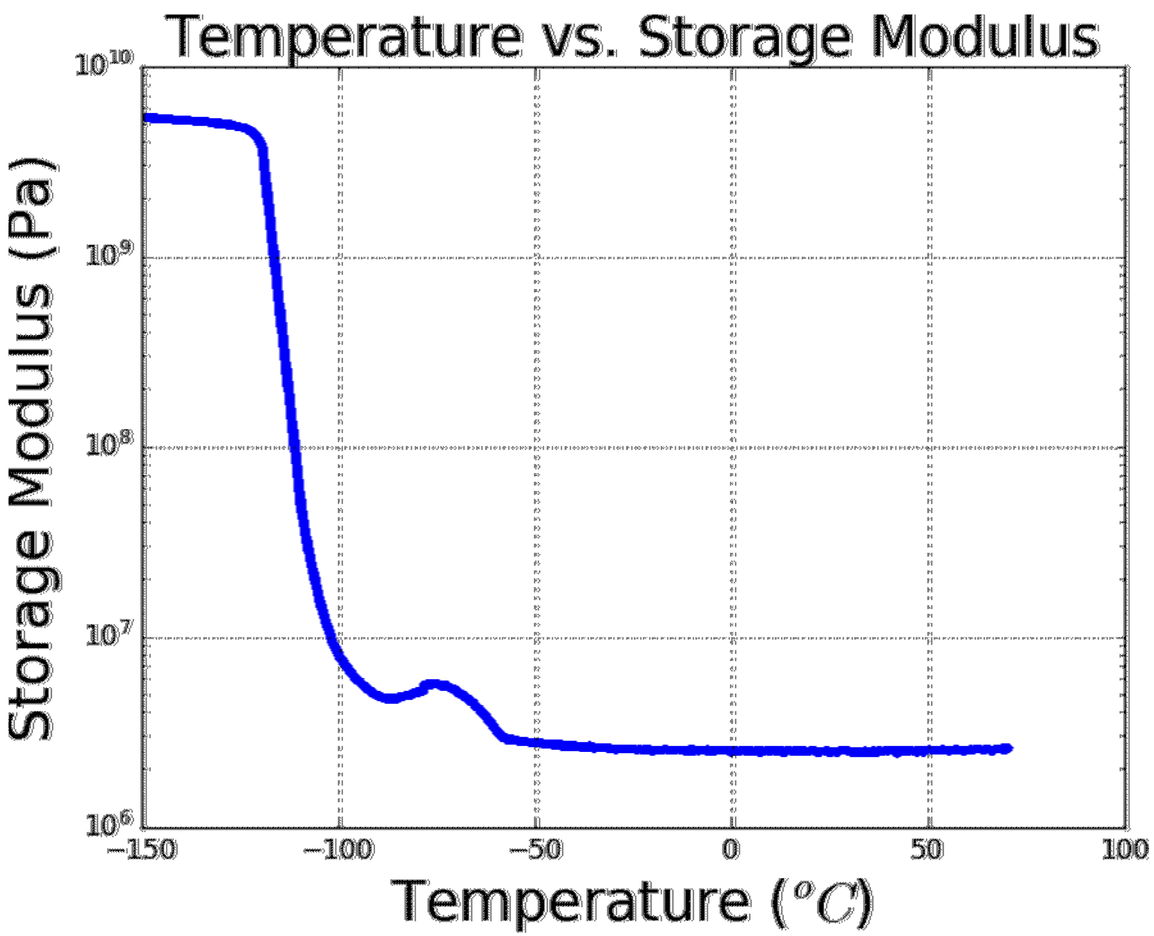
Temperature B.C. -140 º C → 30 º C

$$\omega = 1\ Hz$$

UNM | Mechanical Engineering

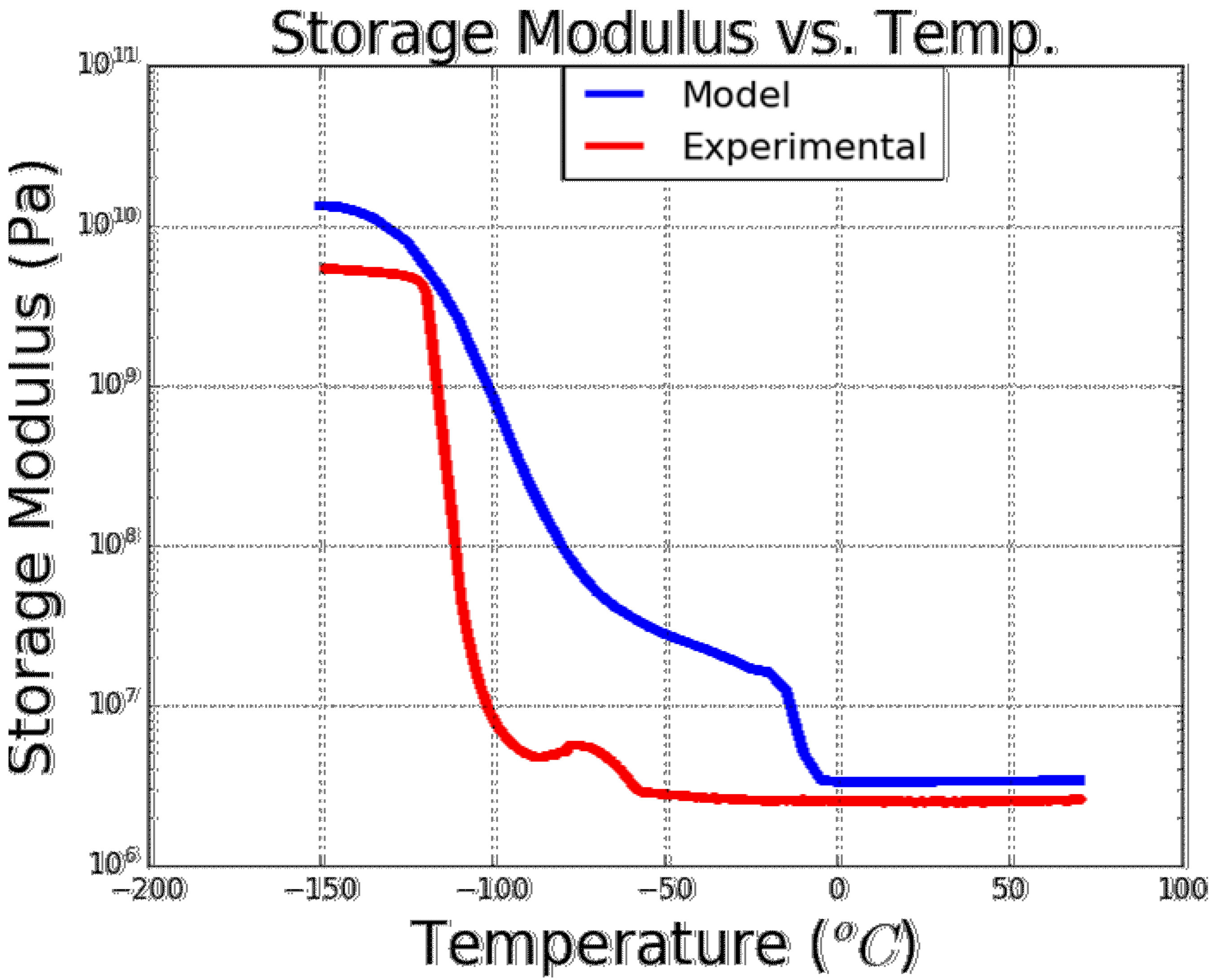
Flexural/Storage Modulus Data





UNM | Mechanical Engineering

Predicting of Calibrated SPEC Model



UNM Mechanical Engineering

Conclusions

- Calibrated SPEC model was determined for PDMS/PDPS copolymer
  - ✓ Shear response was determined with DMA
  - ✓ Thermal response was determined with TMA
  - ✓ Volumetric response was determined with pressure dilatometry
- Validation of SPEC model was conducted with uniaxial simulation
- SPEC applications:
  - Thermal Environments
  - Shock Environments
  - Stress/Yield/Enthalpy Relaxation

Conclusions

- Things to note:
  - The DMA data did not reach temperatures below T_g
    - Model only valid for frequency of constructed master curve
  - Pressure dilatometry measure measurements did not reach sub-ambient
    - The glassy response was assumed to be similar to Sylgard 184

Future Work

- Fit the model to the uniaxial data
- Shift to a different ref Temp.
- Conduct DMA with sample geometry that will go sub-ambient

References

1.[1] D.B. Adolf. Modeling the response of monofilament nylon cords with the non- linear viscoelastic, simplified potential energy clock model. Polymer(1), April 2010.
2.[2] Robert S. Chambers Adolf, Douglas B. and Matthew A. Neidigk. A simplified potential energy clock model for glassy polymers. Polymer(1), April 2009.
3.[3] Todd M. Alam. Quantitative analysis of microstructure in polysiloxanes using high resolution si29 nmr spectroscopy: Investigation of lot variability in the lvm97 and hvm97 pdms/pdps copolymers. Polymer, April 2002.
4.[4] Douglas B. Adolf Robert S. Chambers Caruthers, James M. and Prashant Shrikhande. A thermodynamically consistent, nonlinear viscoelastic approach for modeling glassy polymers. Polymer(1), April 2004.
5.[5] Douglas B. Adolf Robert S. Chambers Caruthers, James M. and Prashant Shrikhande. A thermodynamically consistent, nonlinear viscoelastic approach for modeling glassy polymers. Polymer(1), April 2004.
6.[6] J.D. Ferry. Viscoelastic Properties of Polymers. Willey, New York, 1980.
1.[7] Roderic S. Lakes. Viscoelastic Materials. Cambridge, New York: Cambridge,
7.2014.

1. W. Pyckhout-Hintzen Lorenz, B. and B.n.j. Persson. The temperature depen- dence of relaxation mechanisms in amorphous polymers and other glass-forming liquids. Polymer(1), April 1955.

2.[9] OBERTF.LANDEALNDJOHN D.FERR MALCOLLM.WILLIAMSR. Master curve of viscoelastic solid: Using causality to determine the optimal shifting procedure, and to test the accuracy of measured data. Polymer(1), April 2014.

51

Bibliography

10.[10] H. Markovitz. Boltzmann and the beginnings of linear viscoelasticity. 1(1), April 1977.

11.[11] S.w. Park and R.a. Schapery. Methods of interconversion between linear vis- coelastic material functions. part i a numerical method based on prony series. 36(11), April 1999.

12.[12] Donna Dykeman Pearl Lee-Sullivan*. Guidelines for performing storage modulus measurements using the ta instruments dma 2980 three-point bend mode i. amplitude effects. Polymer(1), April 1998.

13.[13] Kevin Levi. Troyer. Viscoelastic Characterization and Modeling of Musculoskele- tal Soft Tissues. Doctoral dissertation, Colorado State University, Colorado, USA, April 2012.

14.[14] Julian Vincent. Structural Biomaterials. Princeton University Press., New Jer- sey: Princeton, 2012.

15.[15] Prof. Hans Wyss Dr. Weitz, David and Ryan Larsen. Measuring the viscoelastic behaviour of soft materials. n., April 2007.