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Calibration of a nonlinear viscoelastic model to predict physical aging

Ken Cundiff, Kevin Long, Jamie Kropka, Shianne Carroll, Catherine Groves

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The 12th International Conference on the Mechanics of Time-Dependent Materials

SAND2022-XXXX P

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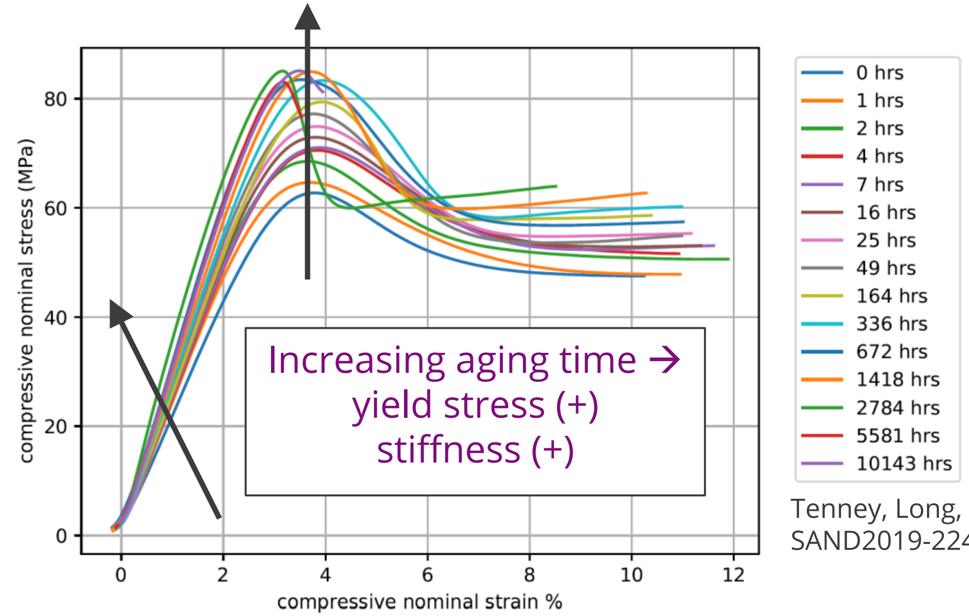
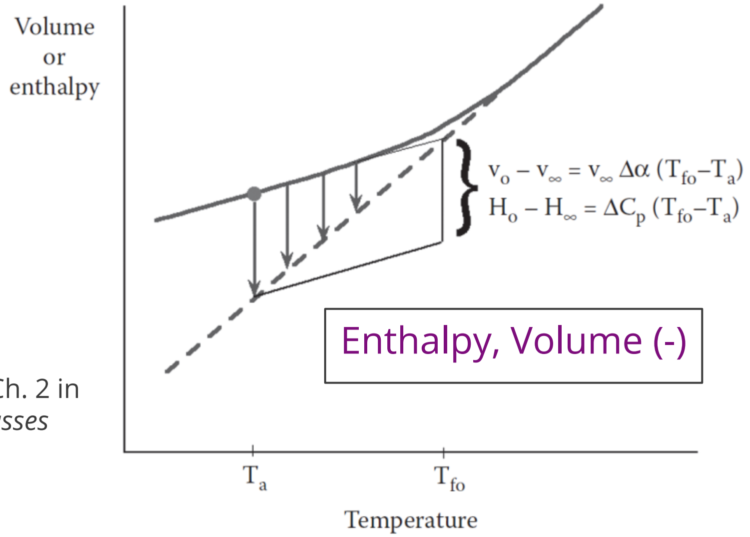
Physical Aging

Physical aging – material evolution in the glassy state (T<Tg) as thermodynamic state variables evolve towards equilibrium (*usually very slowly!*)

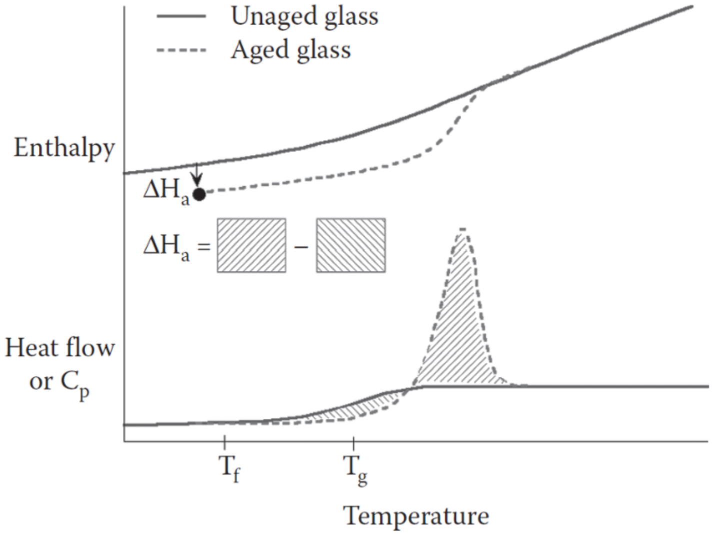
- Increases residual stress
- Could cause cracking/delamination

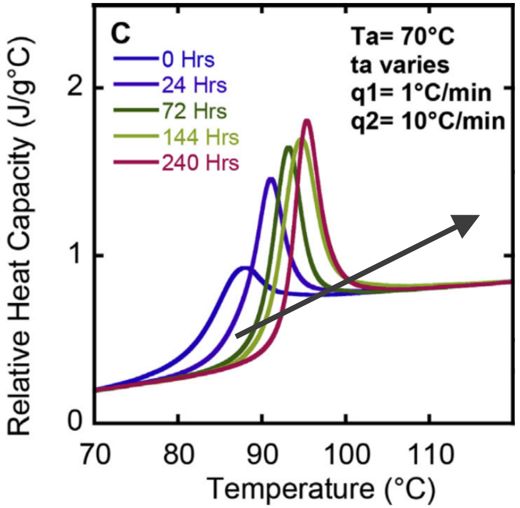


Tenney, Long, Kropka, SAND2019-2248R



Simon and McKenna, Ch. 2 in *Polymer Glasses*





Clarkson, McCoy, Kropka, *Polymer*, 2016

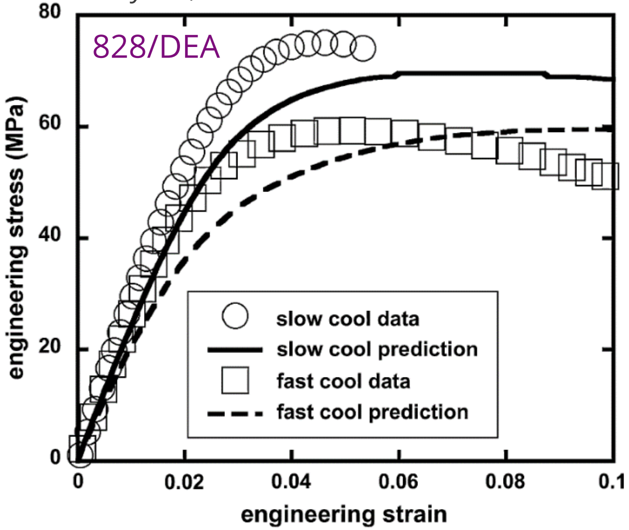
Increasing Aging time →
Heat capacity overshoot (+)
CTE overshoot (+)

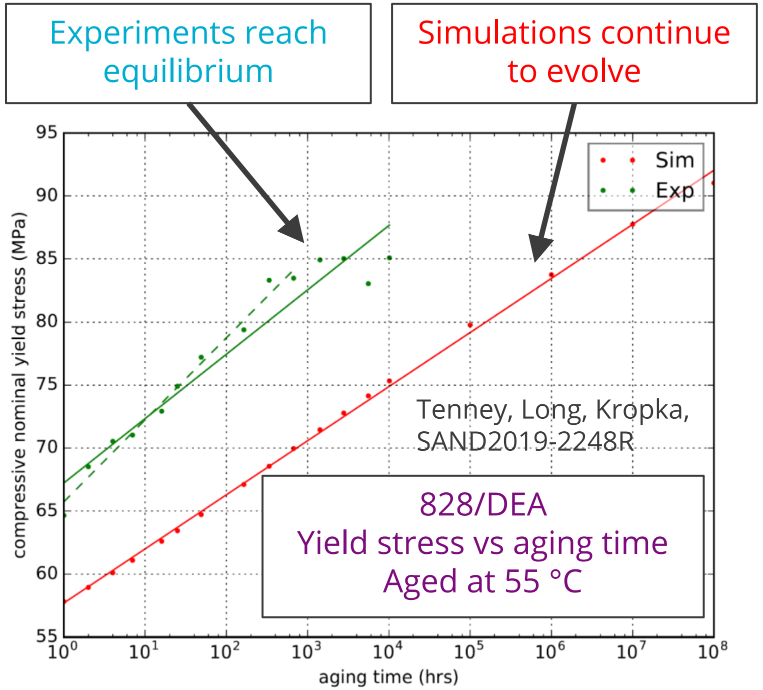
For high-reliability designs that need to perform over decades, the need for accurate models of physical aging are clear

Previous attempts at modeling physical aging

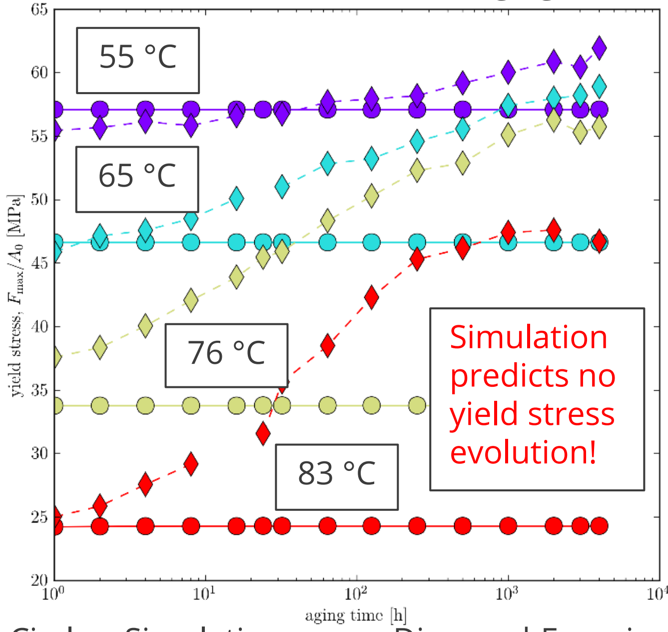
- Nonlinear viscoelastic constitutive model
- Simplified Potential Energy Clock (SPEC) model [1-5]

Adolf *et al.*,
Polymer, 2004





828/T403 – Yield stress vs aging time



Circle – Simulation   Diamond-Experiment

- Although SPEC can ***qualitatively*** predict physical aging, but quantitative predictions are very sensitive to model parameterization.

- *Objective: Evaluate ability of SPEC to predict multiple measures of material evolution using a single set of parameters*
  - Search for a robust calibration procedure
  - Identify issues preventing accurate predictions
- 828/T403 (Tg ~ 90C)
- 828/DEA (Tg ~ 75C)

[1] Caruthers *et al.*, *Polymer*, 2004
[2] Adolf *et al.*, *Polymer*, 2004
[3] Adolf *et al.*, *Polymer*, 2009
[4] Talamini *et al.* SAND2021-9851CTF
[5] Cundiff *et al.* SAND2021-11193

The SPEC(tacular) Model

Volume Strain Contributions

Shear Strain Contributions

$$\Psi(t) = \Psi_\infty(\boldsymbol{H},\theta) + \frac{1}{2}K_D(\theta)\int_0^t\int_0^t f_1(t^*-s^*,t^*-u^*)\frac{dI_1}{ds}\frac{dI_1}{du}\,dsdu + G_D(\theta)\int_0^t\int_0^t f_2(t^*-s^*,t^*-u^*)\frac{d\boldsymbol{H}^{\text{dev}}}{ds}:\frac{d\boldsymbol{H}^{\text{dev}}}{du}\,dsdu$$

$$-L_D(\theta)\int_0^t\int_0^t f_3(t^*-s^*,t^*-u^*)\frac{d\theta}{ds}\frac{dI_1}{du}\,dsdu - \frac{C_D(\theta)}{2\theta_{\text{ref}}}\int_0^t\int_0^t f_4(t^*-s^*,t^*-u^*)\frac{d\theta}{ds}\frac{d\theta}{du}\,dsdu$$

Thermal-Strain Contributions

Thermal Contributions

Coleman-Noll →

$$\frac{\partial\Psi}{\partial\boldsymbol{H}} = \boldsymbol{\sigma}(t)$$

$$\frac{\partial\Psi}{\partial\theta} = \eta(t)$$

All relaxation functions monotonically decrease from 1 to 0

Strain

- H – Hencky strain
- $I_1 = \text{tr}(\boldsymbol{H})$ – Volume strain
- $\boldsymbol{H}^{\text{dev}}$, deviatoric strain

Integral Prefactors

- "D" –difference between glassy and rubbery
    - $X_D(\theta) = X_g(\theta) - X_\infty(\theta)$
- K – bulk modulus
- G – shear modulus
- $L = K\alpha$ – Thermal expansion pressure
- C – Constant-strain heat capacity

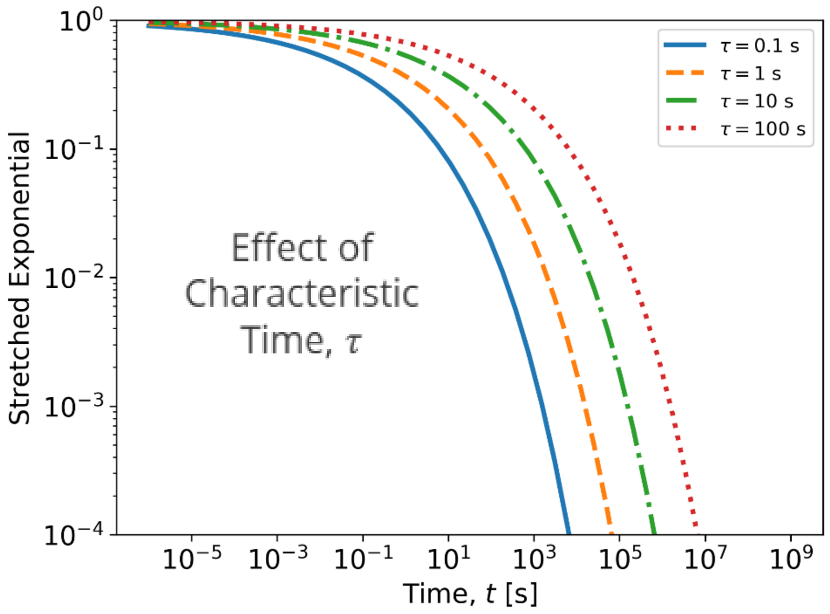
Material time related to laboratory time by WLF-like shift factor

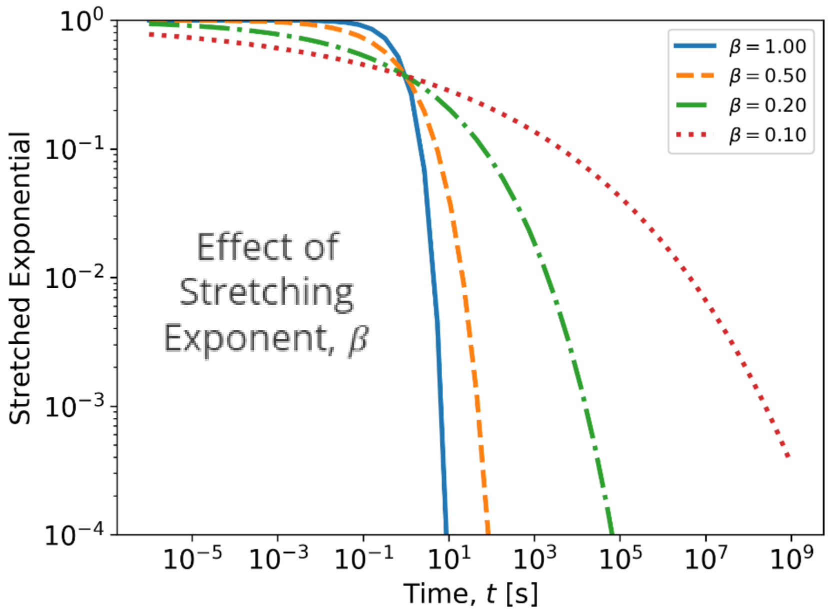
$$a\,dt^* = dt, \qquad t^*-s^* = \int_s^t \frac{du}{a(u)}, \qquad \log a = -\frac{C_1 N(t)}{C_2 + N(t)}$$

Stress and Relaxation Functions

$$\boldsymbol{\sigma}(t) = K_D \mathbf{1} \int_0^t f_1(t^* - s^*) \frac{\mathrm{d}I_1}{\mathrm{d}s} \mathrm{d}s - L_D \mathbf{1} \int_0^t f_3(t^* - s^*) \frac{\mathrm{d}\theta}{\mathrm{d}s} \mathrm{d}s + 2G_D \int_0^t f_2(t^* - s^*) \frac{\mathrm{d}\boldsymbol{H}^{\mathrm{dev}}}{\mathrm{d}s} \mathrm{d}s + [K_\infty I_1 - L_\infty(\theta - \theta_{\mathrm{sf}})]\mathbf{1} + 2G_\infty \boldsymbol{H}^{\mathrm{dev}}$$

- All relaxation functions monotonically decrease from 1 to 0
- Typically parameterized using stretched exponentials
  - $f_i(t) = \exp\left[-\left(\frac{t}{\tau_i}\right)^{\beta_i}\right]$
  - Characteristic time, τ_i
  - Breadth, β_i





Material Clock Definition

Material time related to laboratory time by WLF-like shift factor

$$a\,dt^* = dt, \qquad t^* - s^* = \int_s^t \frac{du}{a(u)}, \qquad \log a = -\frac{C_1 N(t)}{C_2 + N(t)}$$

High shift factor → slow clock → Glassy
Low shift factor → fast clock → Rubbery

$$N(t) = \theta - \theta_{\mathrm{ref}} - \int_0^t f_3(t^* - s^*)\frac{\mathrm{d}\theta}{\mathrm{d}s}\mathrm{d}s$$

Thermal Contribution

Hotter → faster clock

$$+C_3\left(I_1 - I_{1,\mathrm{ref}} - \int_0^t f_1(t^* - s^*)\frac{\mathrm{d}I_1}{\mathrm{d}s}\mathrm{d}s\right)$$

Volume Contribution

Less dense → faster clock

$$+C_4\int_0^t\int_0^t f_2(t^* - s^*, t^* - u^*)\frac{\mathrm{d}\boldsymbol{H}^{\mathrm{dev}}}{\mathrm{d}s} : \frac{\mathrm{d}\boldsymbol{H}^{\mathrm{dev}}}{\mathrm{d}u}\mathrm{d}s\mathrm{d}u$$

Shear Contribution

Shear strain → faster clock

How does SPEC predict physical aging?

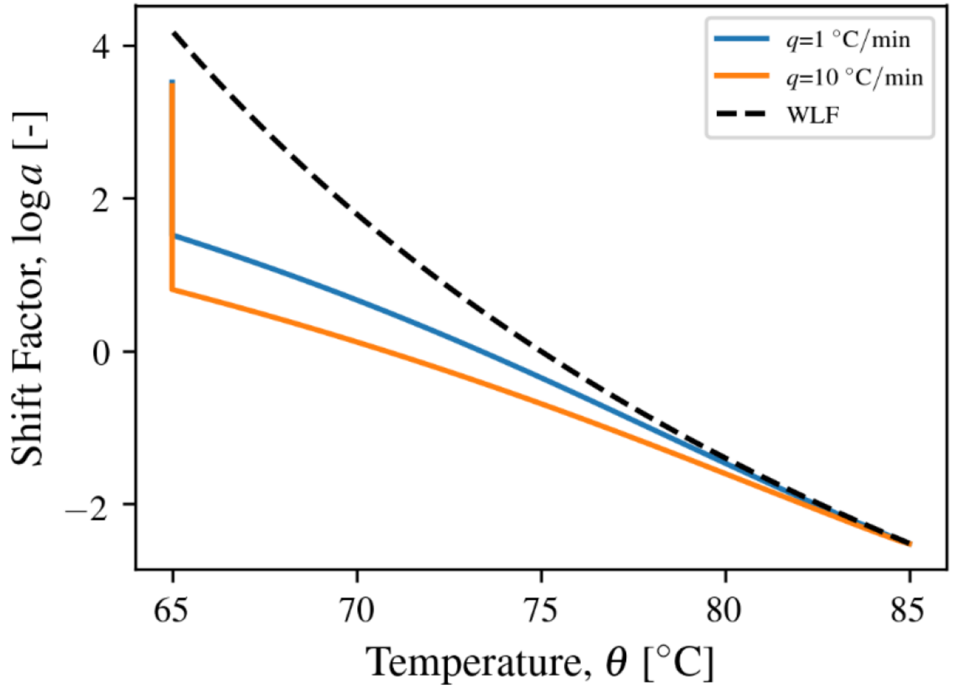
- Memory of thermal history causes shift factor to lag behind WLF.
- As the memory is forgotten, the shift factor increases, slowing relaxation processes in the model

The key to physical aging predictions!

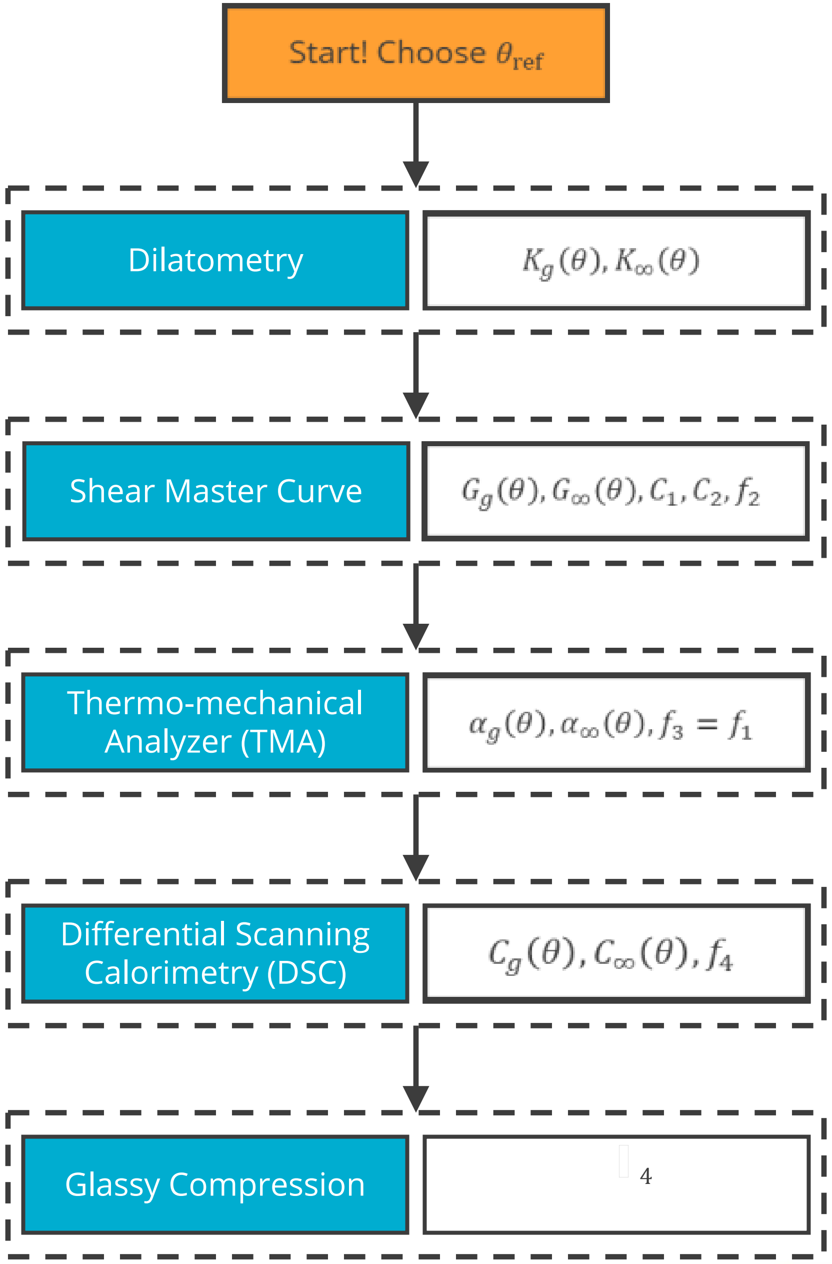
$$N(t) = \theta - \theta_{\mathrm{ref}} - \int_0^t f_3(t^* - s^*)\frac{\mathrm{d}\theta}{\mathrm{d}s}\mathrm{d}s$$

$$+C_3\left(I_1 - I_{1,\mathrm{ref}} - \int_0^t f_1(t^* - s^*)\frac{\mathrm{d}I_1}{\mathrm{d}s}\mathrm{d}s\right)$$

$$+C_4\int_0^t\int_0^t f_2(t^* - s^*, t^* - u^*)\frac{\mathrm{d}\boldsymbol{H}^{\mathrm{dev}}}{\mathrm{d}s}:\frac{\mathrm{d}\boldsymbol{H}^{\mathrm{dev}}}{\mathrm{d}u}\mathrm{d}s\mathrm{d}u$$



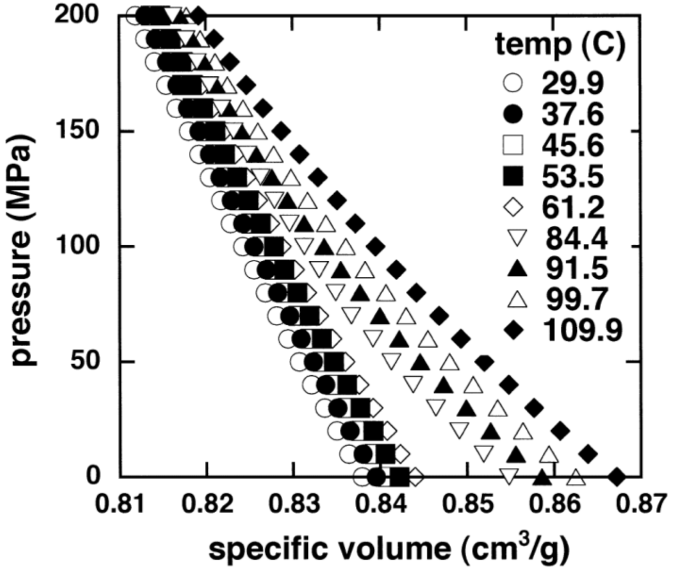
Standard Calibration Approach

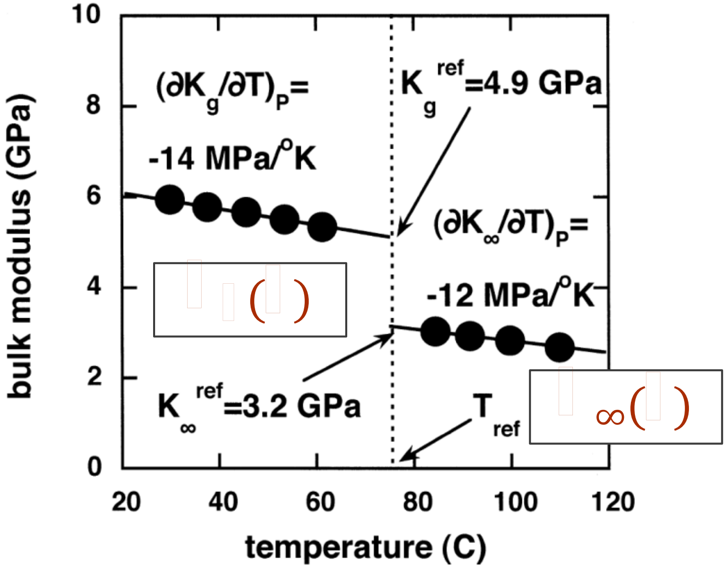


Parameters: 29

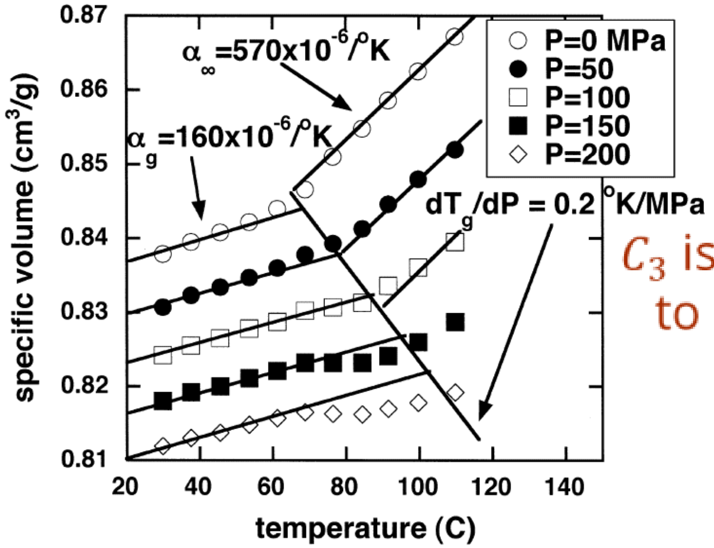
- Reference Temperature θ_{ref}: 1
- Integral prefactor terms: 16
  - K, G, α, C
  - Rubbery and glassy for each
  - Linear temperature dependence for each
    - $K_g(\theta) = K_g^{\mathrm{ref}} + K_g'(\theta - \theta_{\mathrm{ref}})$
- Relaxation functions: 8
  - Four relaxation functions f_i
  - Two parameters per function
    - $f_i(t) = \exp\left[-\left(\frac{t}{\tau_i}\right)^{\beta_i}\right]$
- Clock Parameters: 4

Standard Calibration Approach

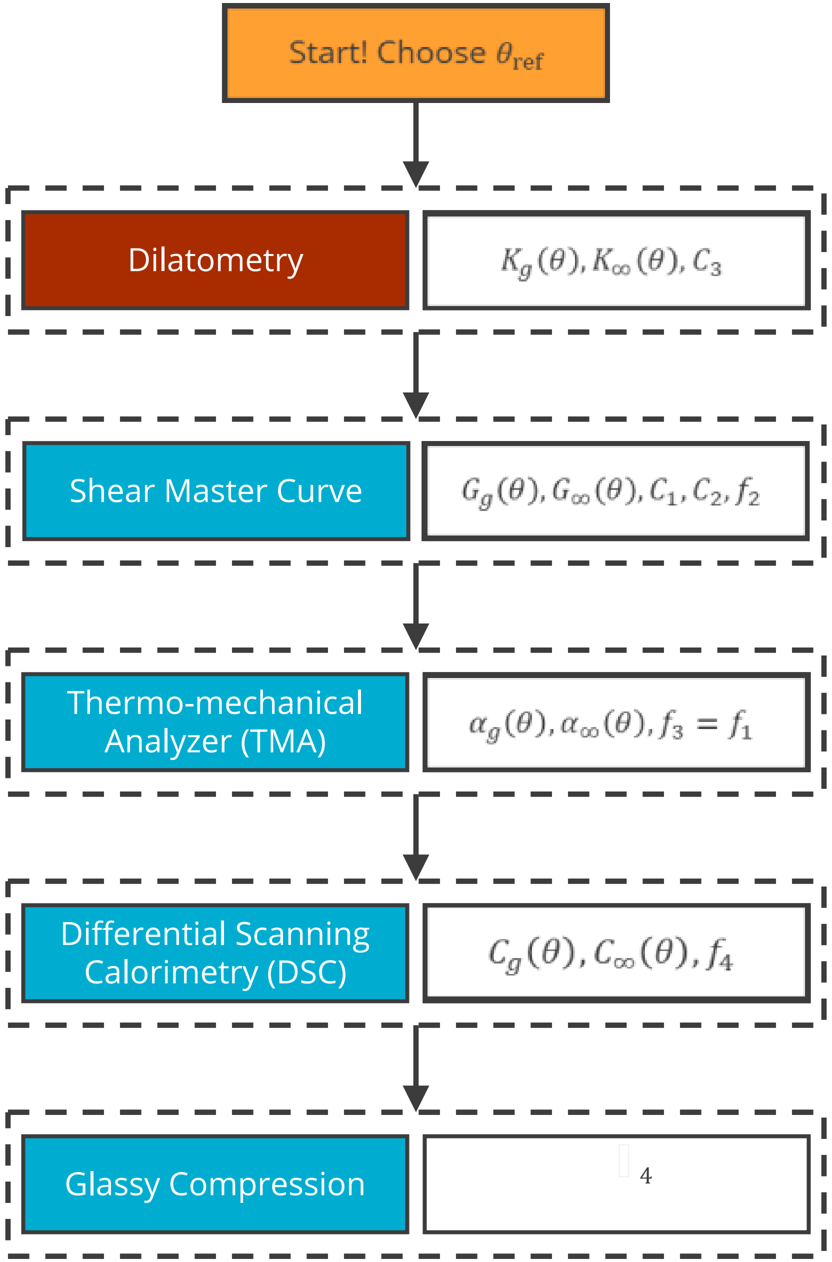




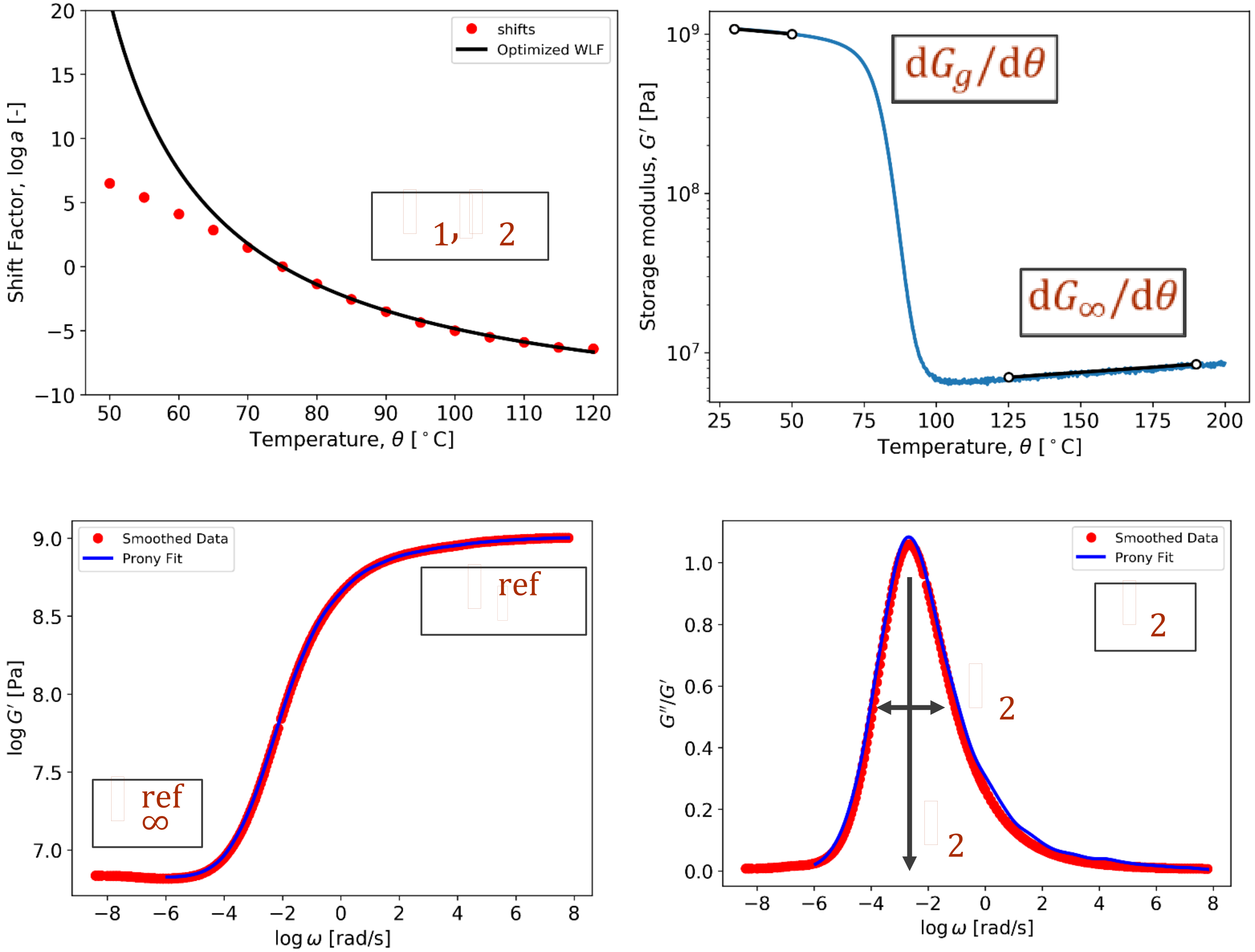
Adolf *et al.*, *Polymer*, 2004



C_3 is related to $d\theta_g/dp$



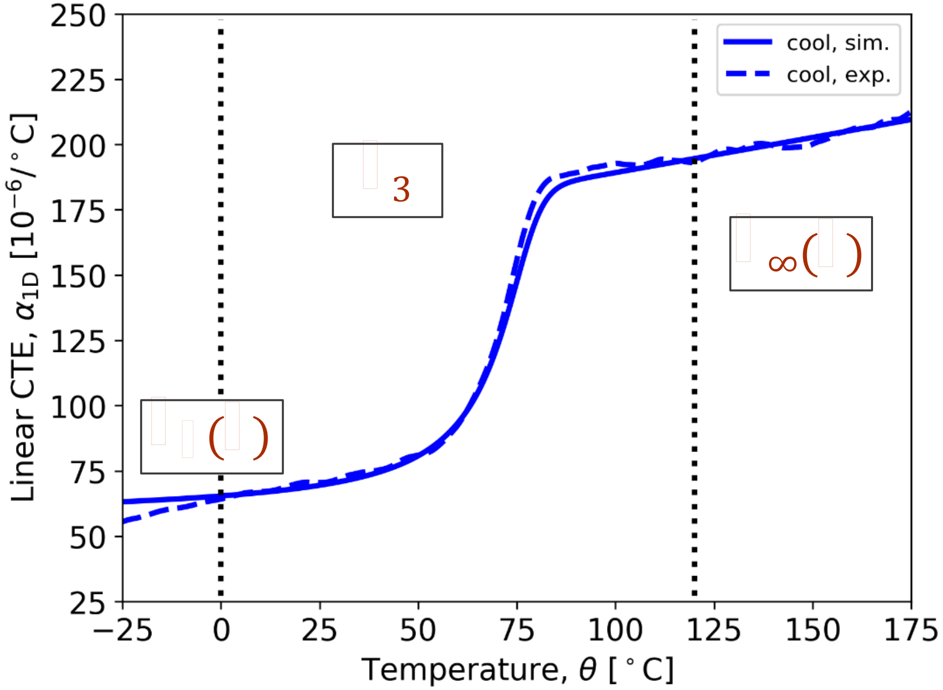
Standard Calibration Approach

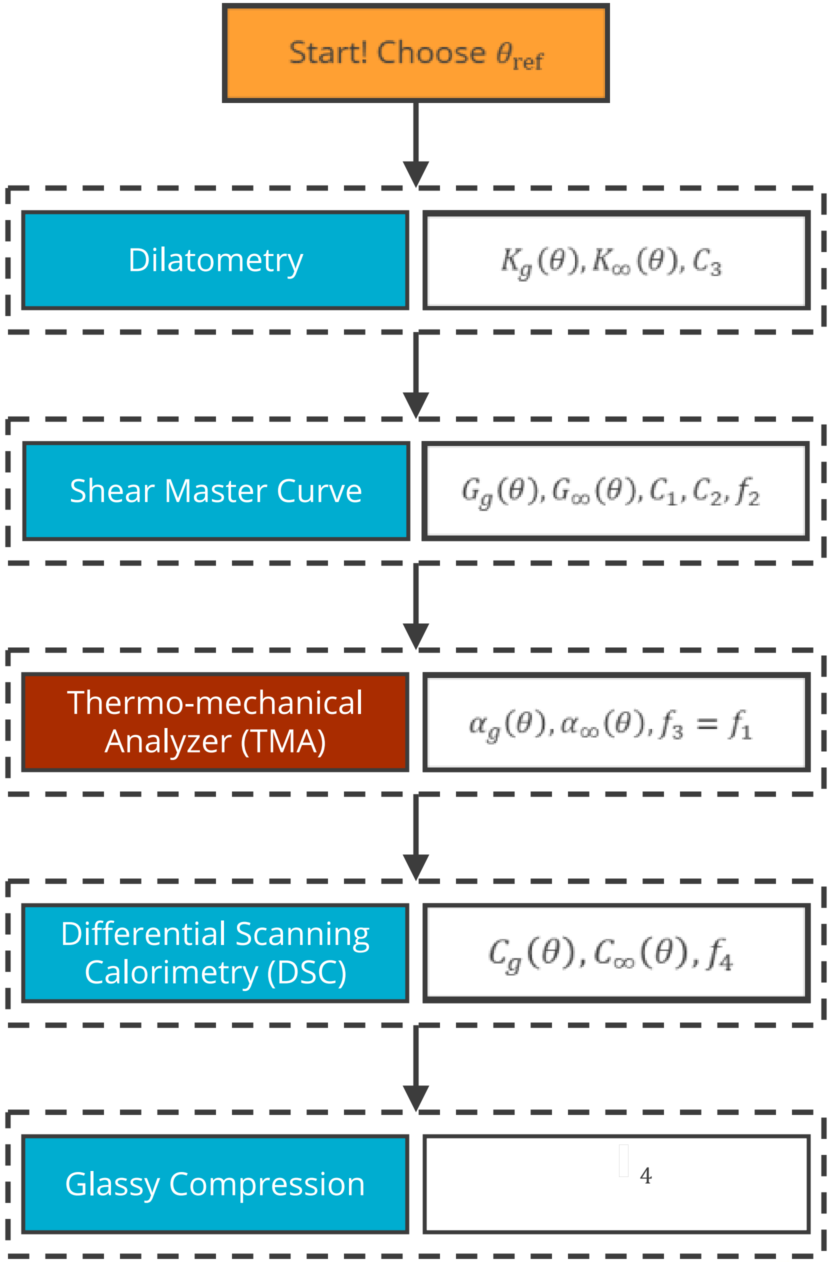


Start! Choose θ_{ref}

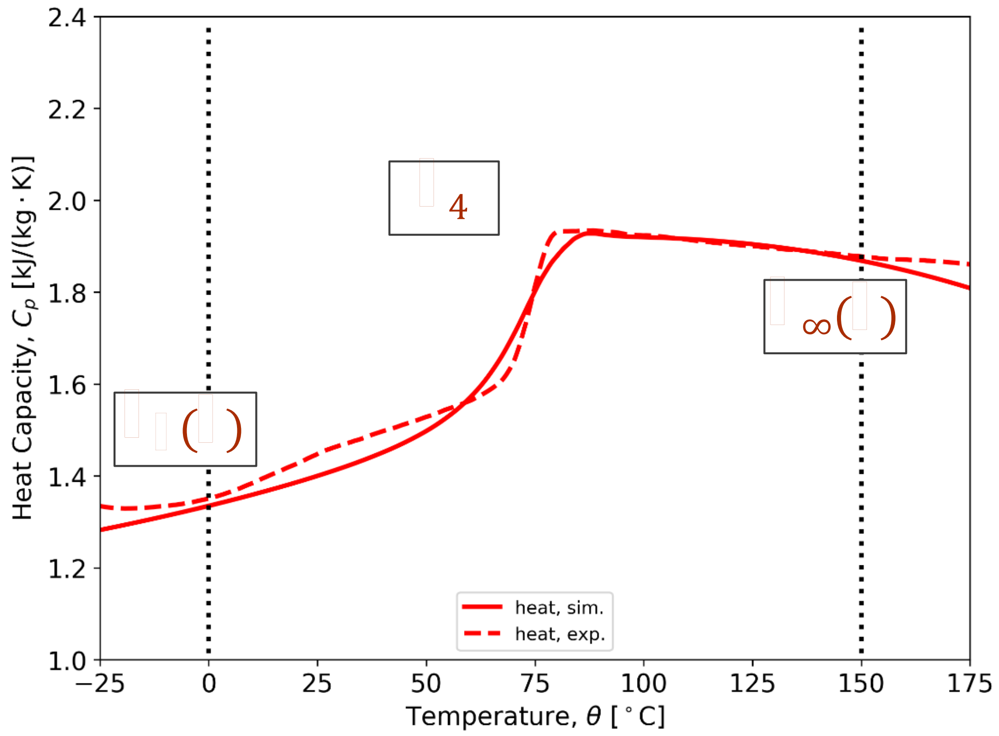
Experiment	Parameters
Dilatometry	$K_g(\theta), K_\infty(\theta), C_3$
Shear Master Curve	$G_g(\theta), G_\infty(\theta), C_1, C_2, f_2$
Thermo-mechanical Analyzer (TMA)	$\alpha_g(\theta), \alpha_\infty(\theta), f_3 = f_1$
Differential Scanning Calorimetry (DSC)	$C_g(\theta), C_\infty(\theta), f_4$
Glassy Compression	4

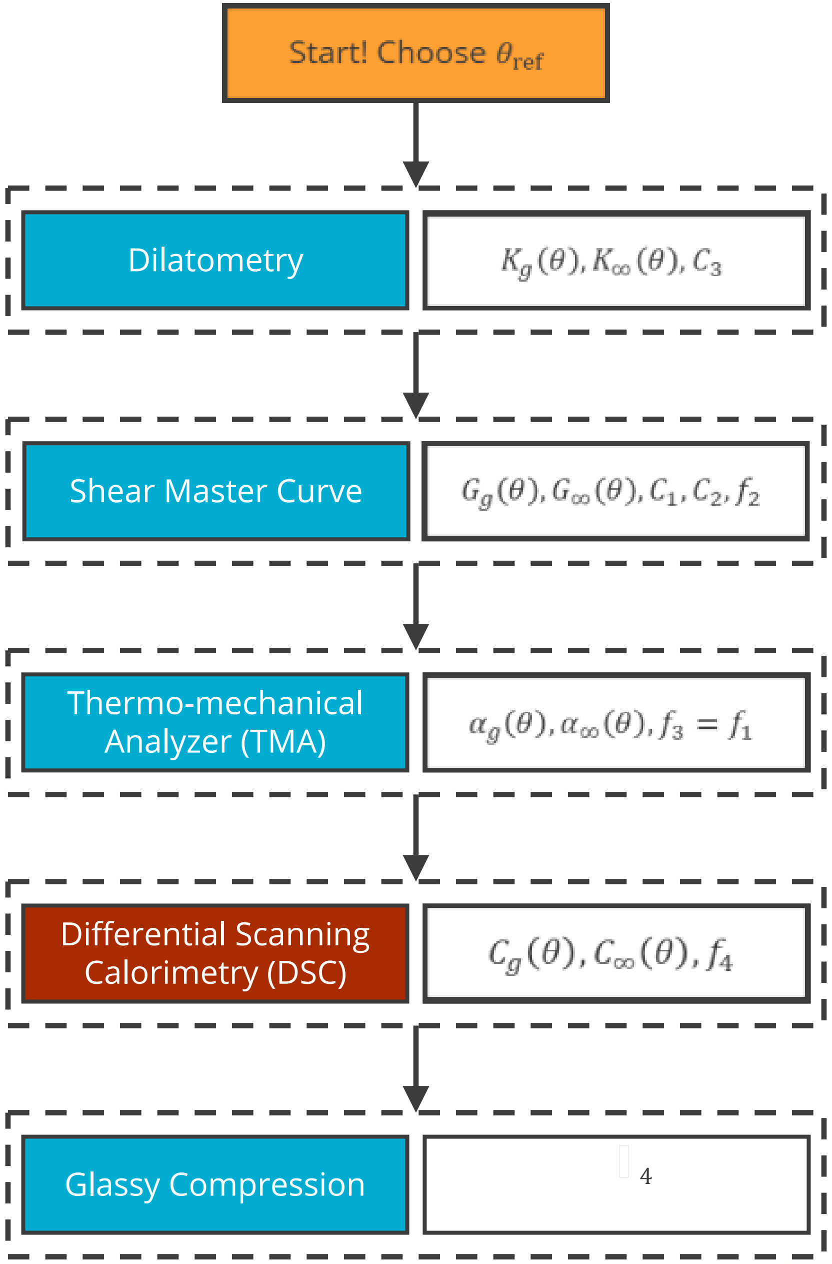
Standard Calibration Approach



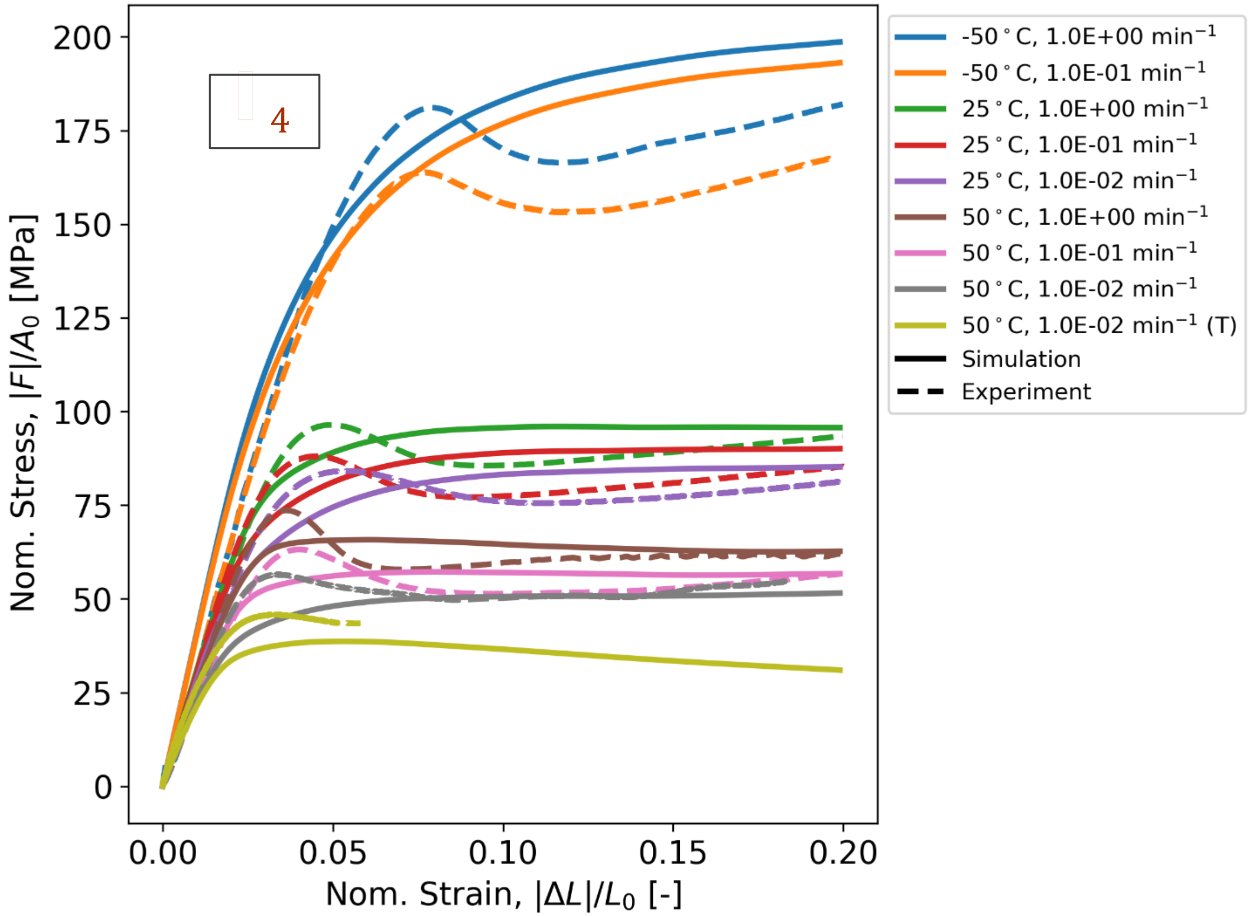


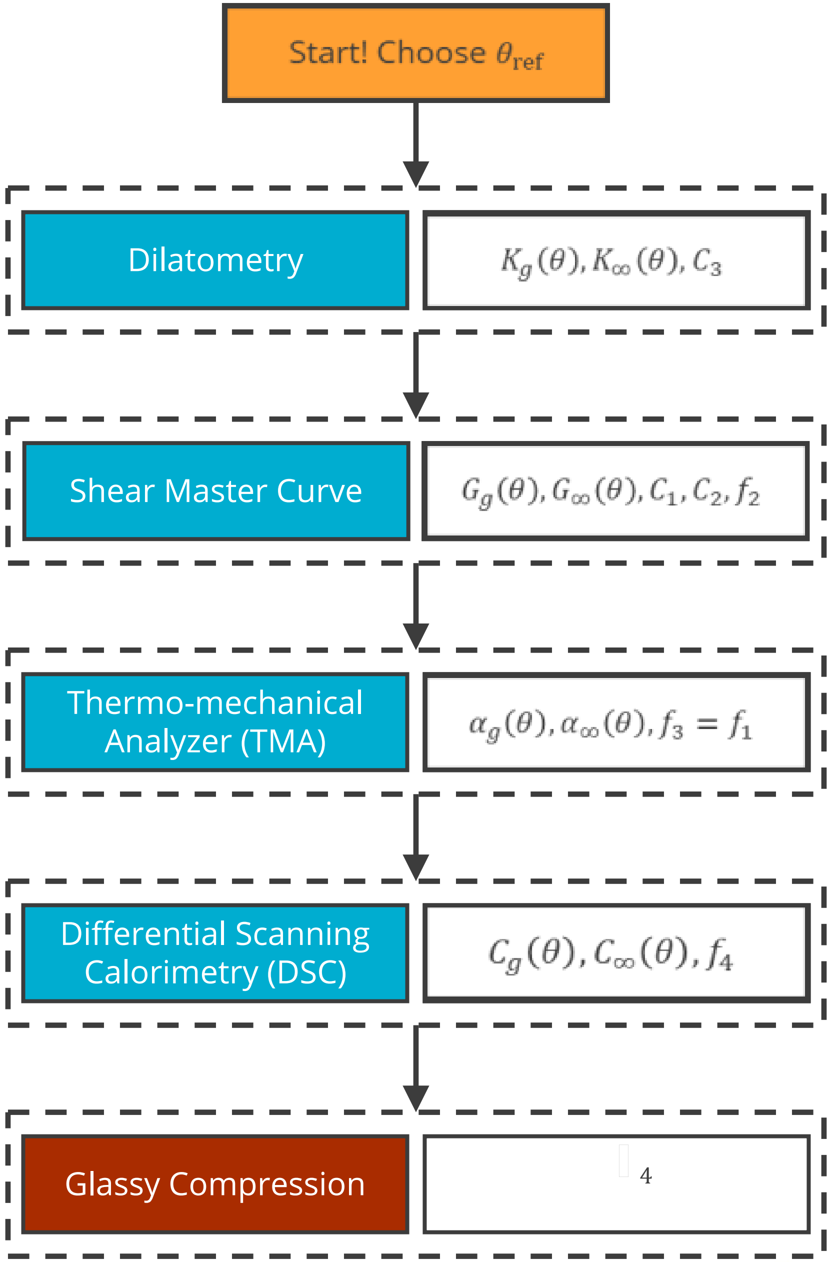
Standard Calibration Approach





Standard Calibration Approach

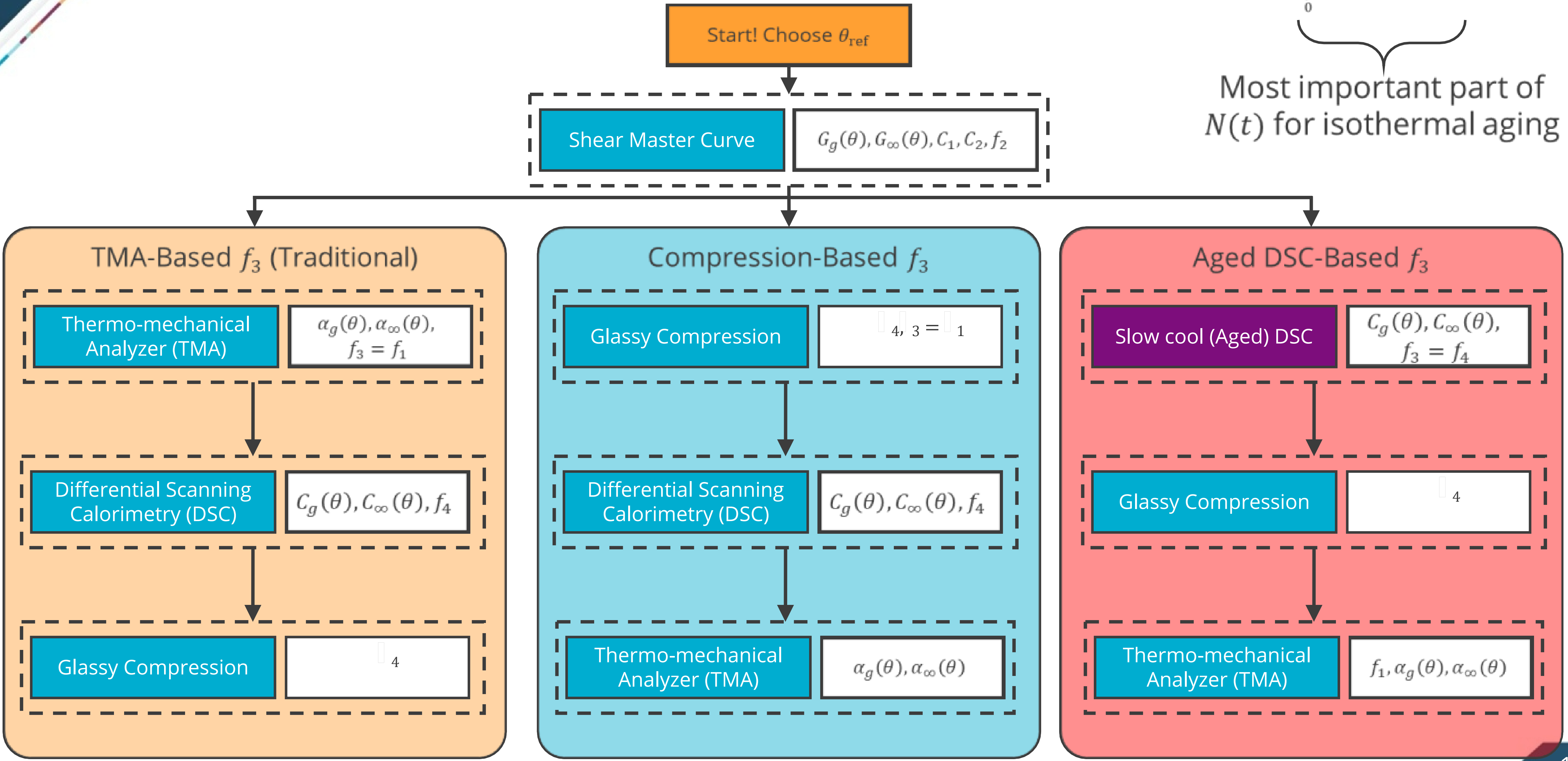




Alternative Calibration Approaches

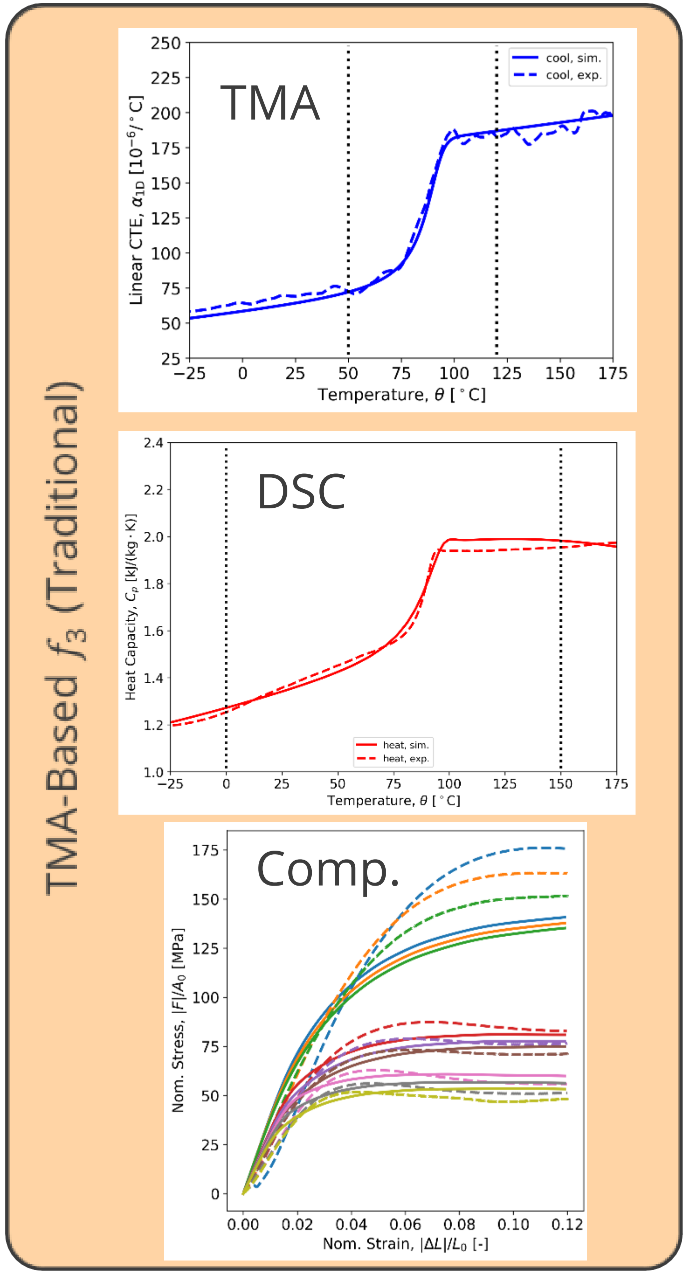
$$N(t) = \theta - \theta_{\mathrm{ref}} - \int_0^t f_3(t^* - s^*)\frac{\mathrm{d}\theta}{\mathrm{d}s}\mathrm{d}s + \cdots$$

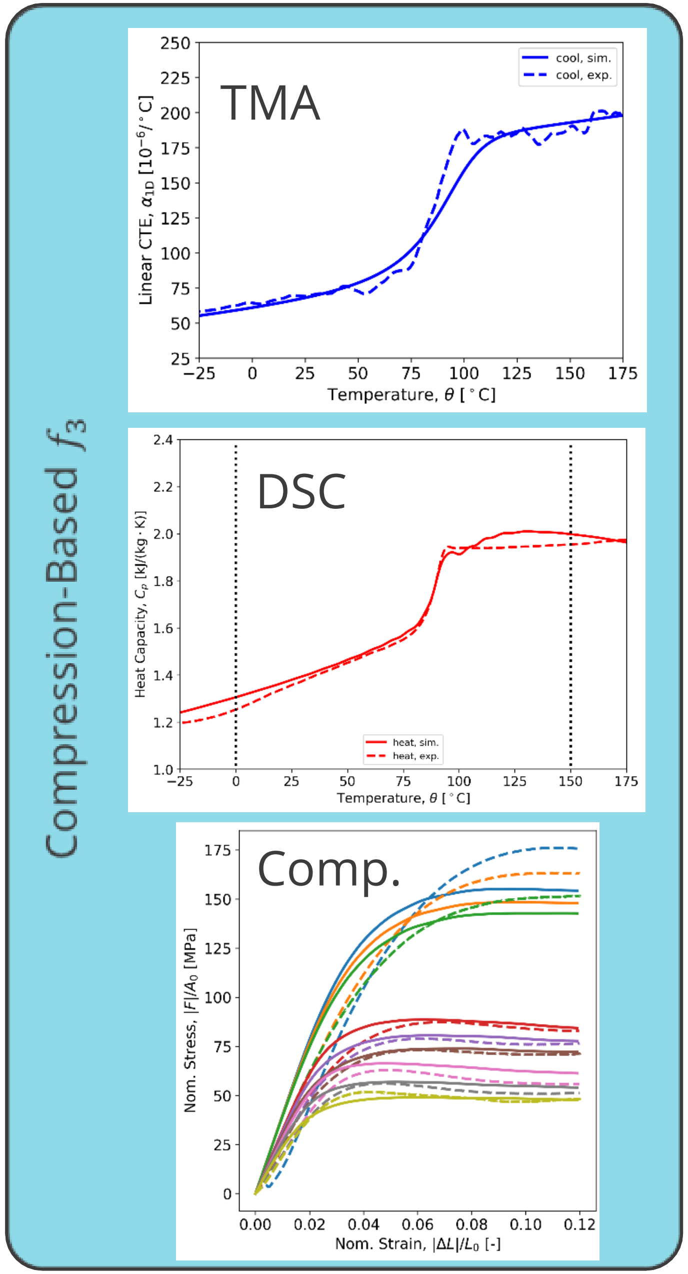
Most important part of $N(t)$ for isothermal aging

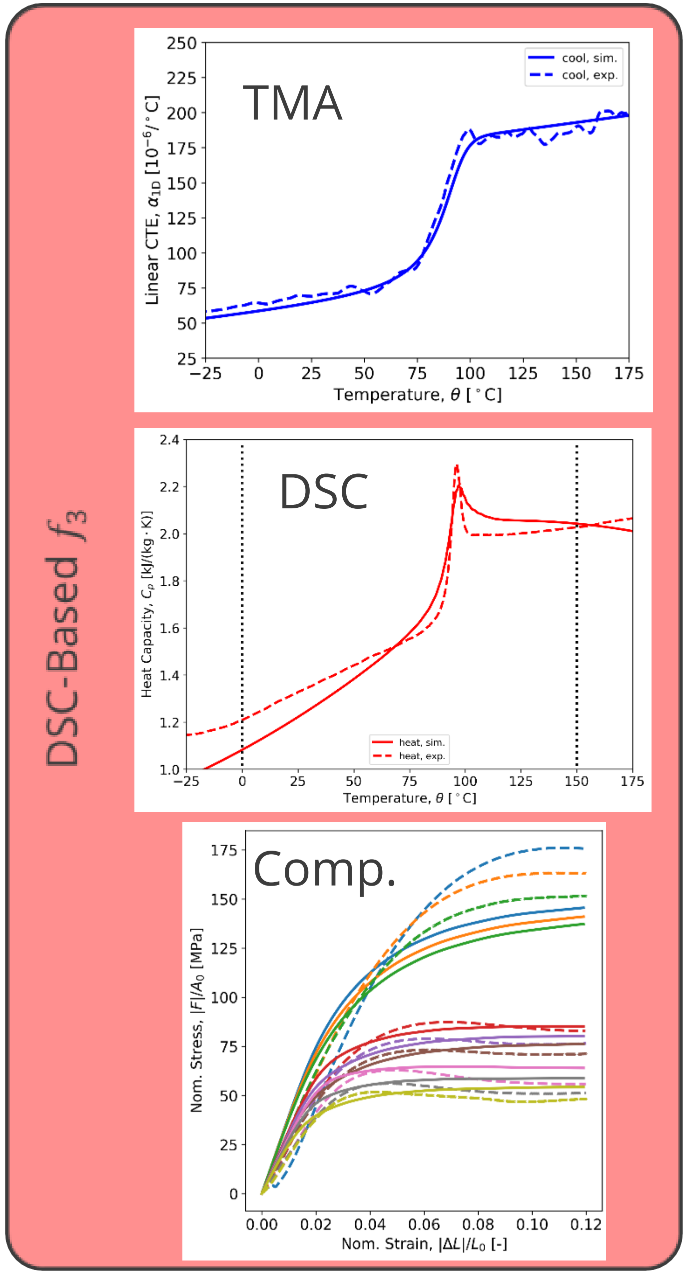


Calibration Fits: 828/T403

Solid - Model fit
Dashed - Experiments

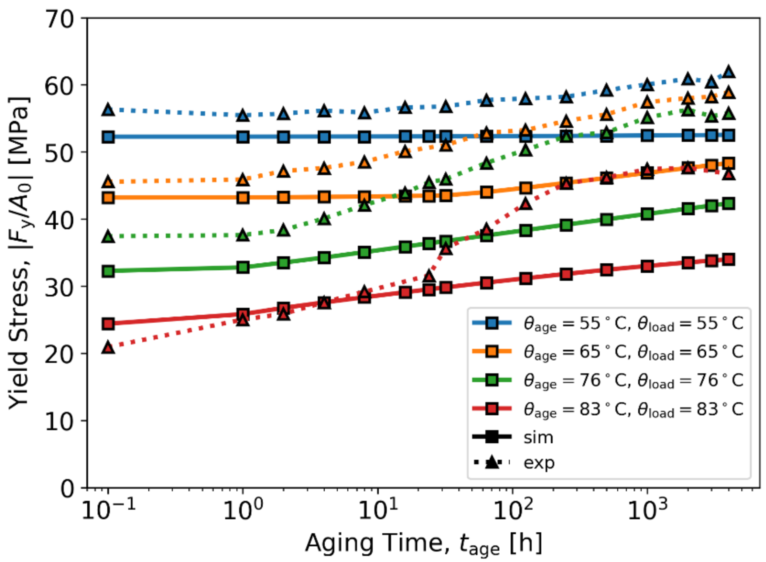


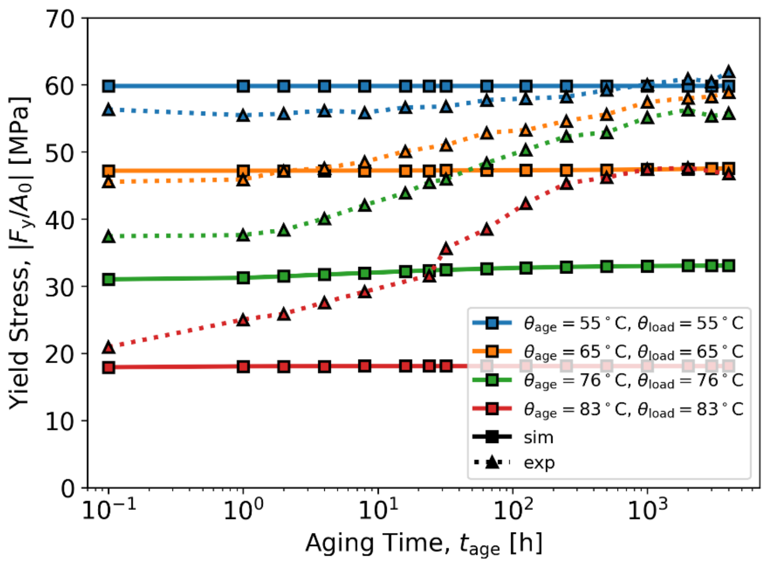




Yield Stress Evolution (828/T403)

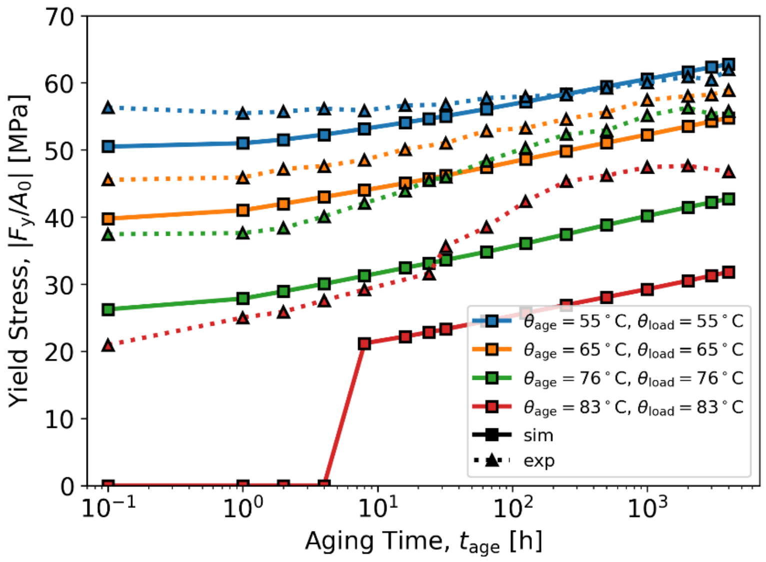
TMA f_3

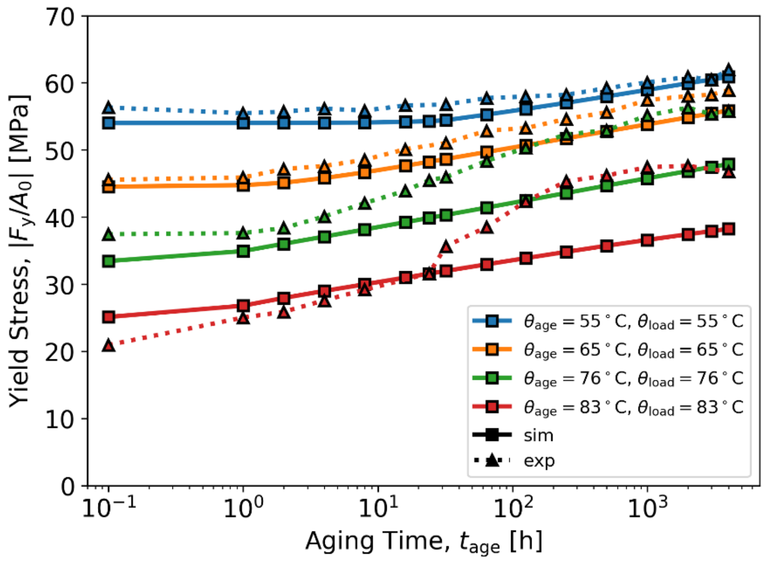




Legacy Calibration

Comp. f_3

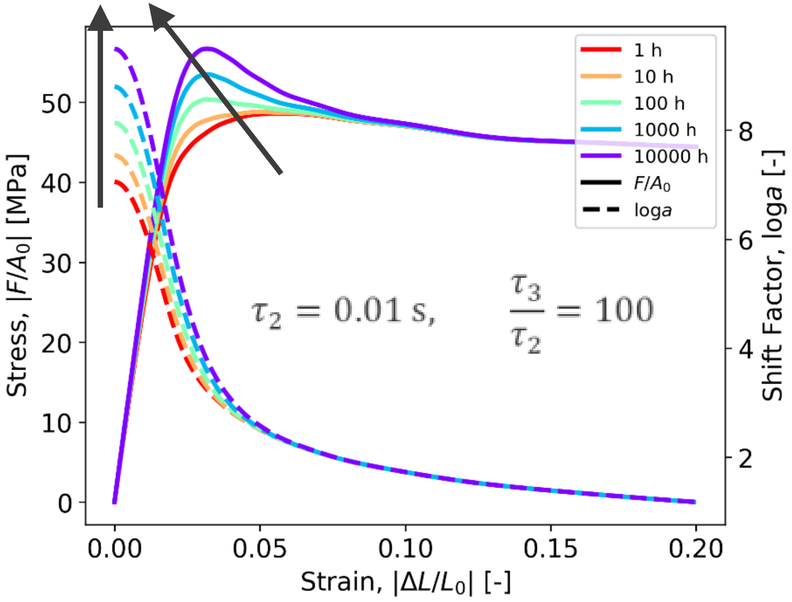




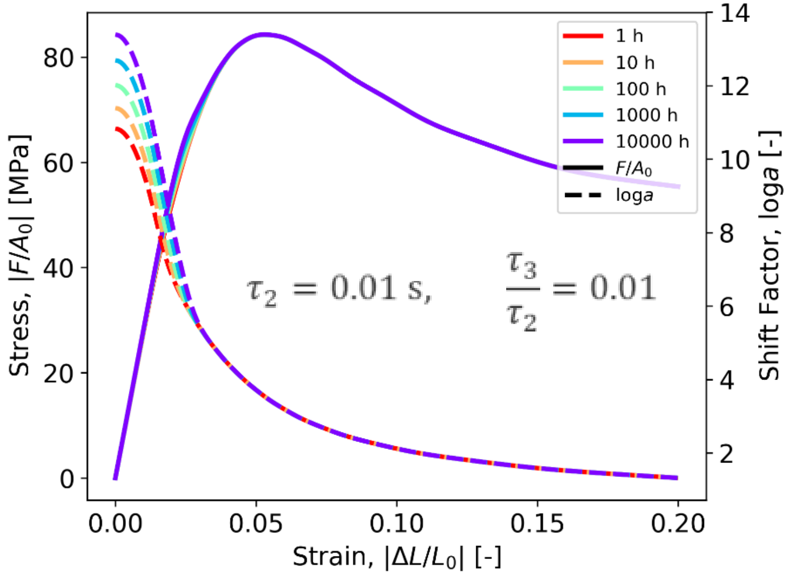
DSC f_3

What determines successful predictions of yield stress evolution?

Shift factor at start of loading increases → larger barrier to yield

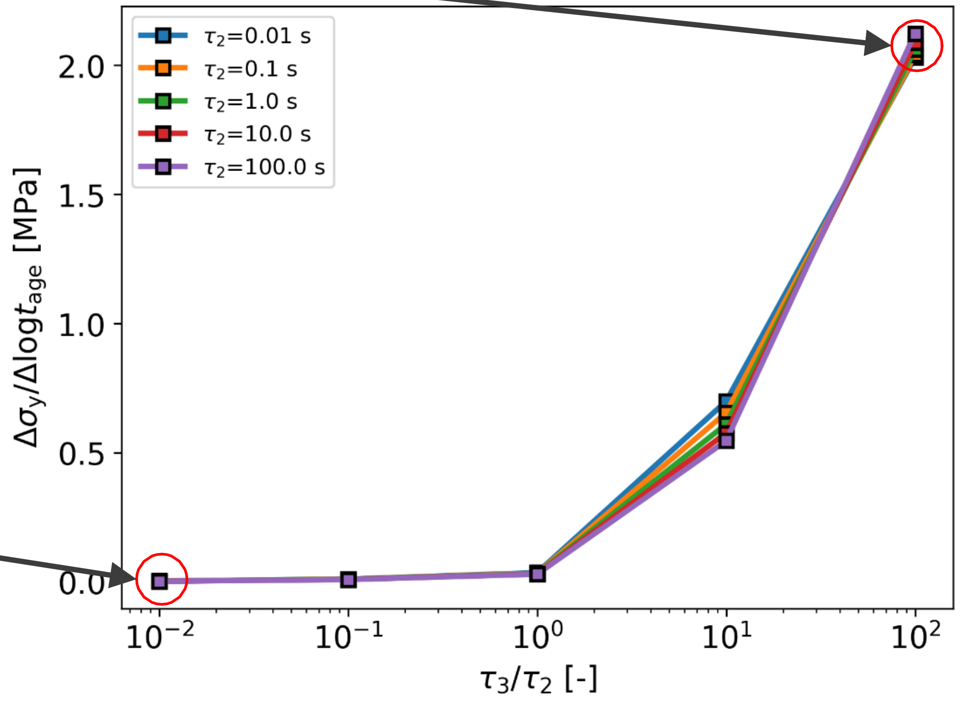


If tau2<tau3, the thermal history is forgotten before yield



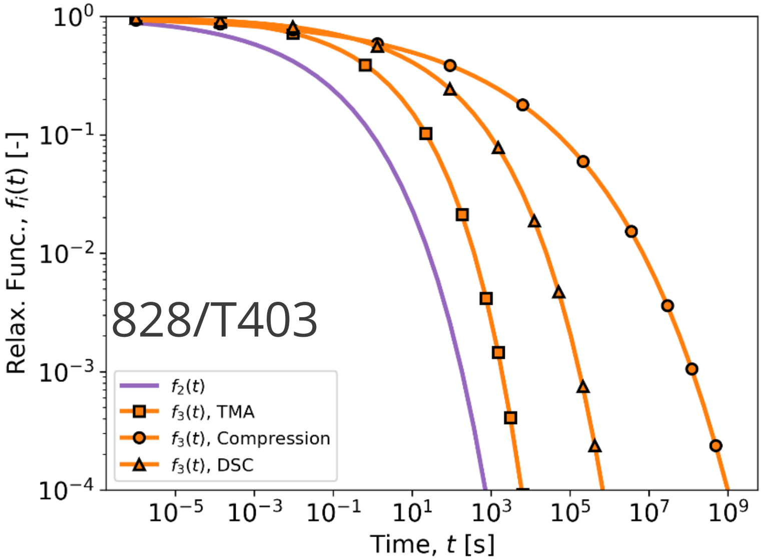
$$\theta_{age} = \theta_{ref} - 30\ °\mathrm{C}$$
$$C_1 = 20,$$
$$C_2 = 50$$

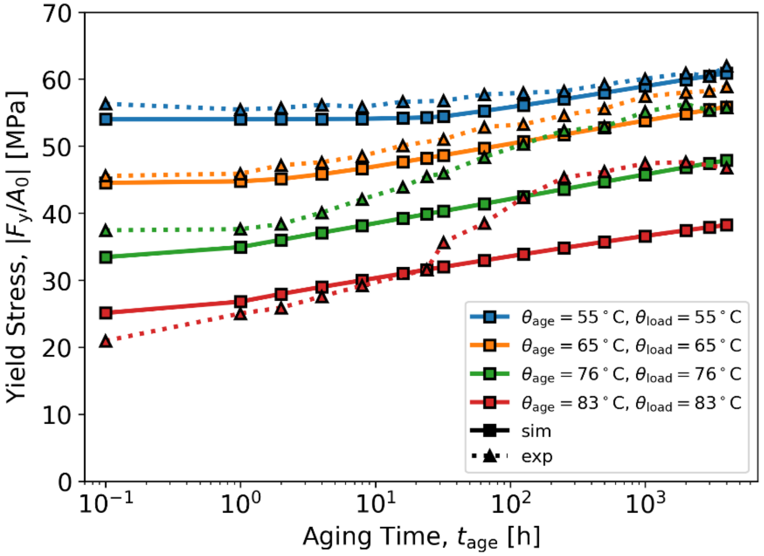
$$N(t) = \theta - \theta_{ref} - \int_0^t f_3(t^* - s^*)\frac{d\theta}{ds}ds + C_3\left(I_1 - I_{1,ref} - \int_0^t f_1(t^* - s^*)\frac{dI_1}{ds}ds\right) + C_4\int_0^t\int_0^t f_2(t^* - s^*, t^* - u^*)\frac{d\boldsymbol{H}^{dev}}{ds} : \frac{d\boldsymbol{H}^{dev}}{du}ds\,du$$



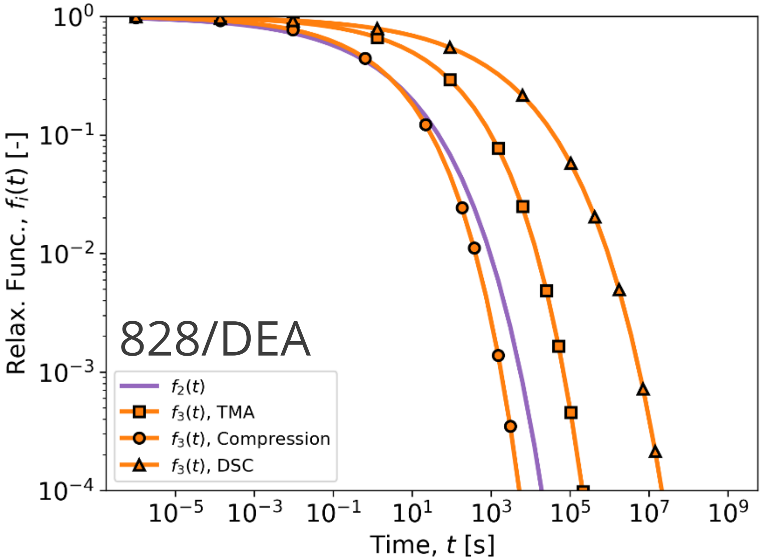
Yield stress evolution rate

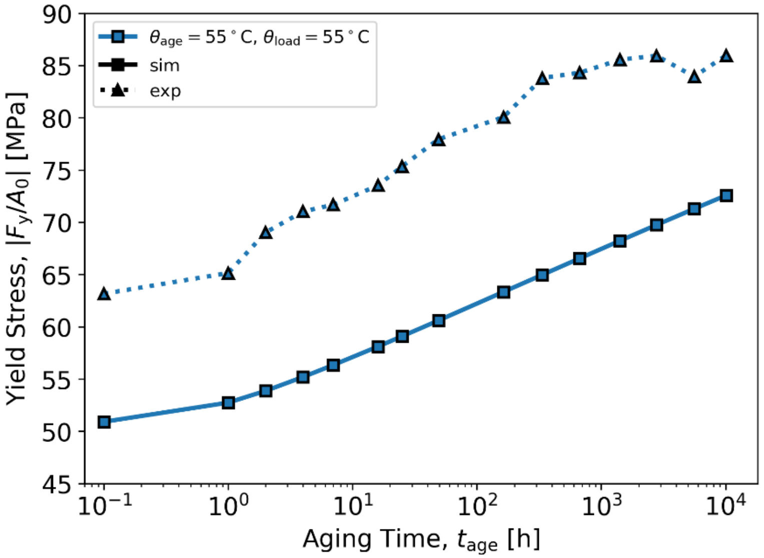
So why was the DSC method most successful?





828/T403	t_3'/t_2'
TMA-f_3	23.8
Compression-f_3	33,900
DSC-f_3	946.





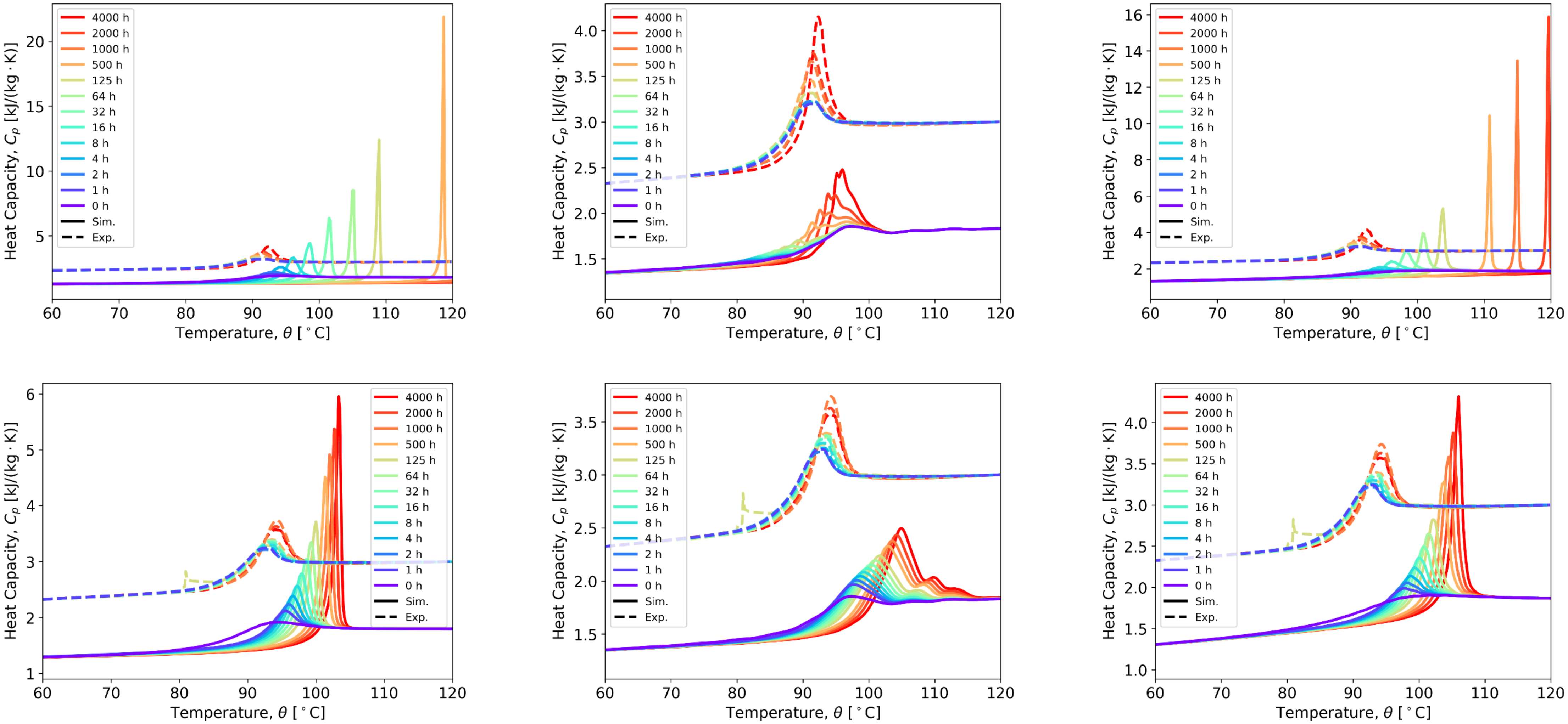
828/DEA	t_3'/t_2'
TMA-f_3	21.6
Compression-f_3	0.664
DSC-f_3	840.

- DSC method gives $t_3'/t_2' \approx 1000$, which seems to be the sweet spot for yield stress evolution at low aging temperatures
- Near Tg predictions are still inaccurate.
- The equilibrium yield stress is not predicted.

Enthalpy Recovery (828/T403)

Aging Temp. 55 °C

Aging Temp. 83 °C



TMA f_3

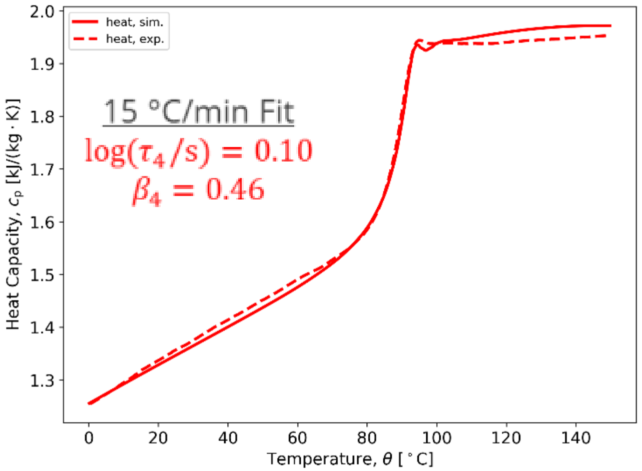
Compression f_3

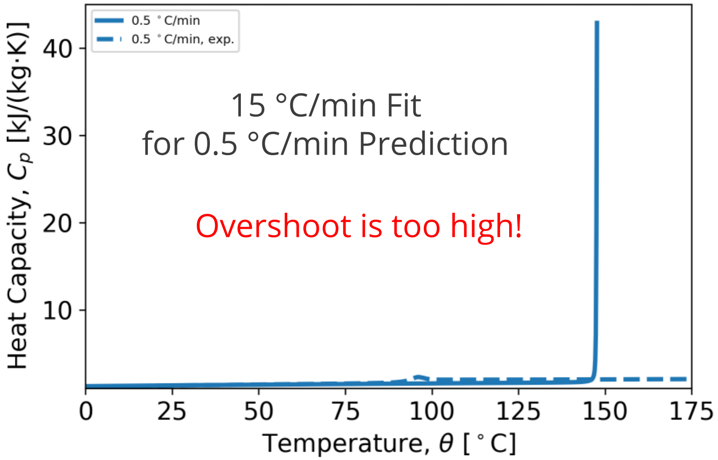
DSC f_3

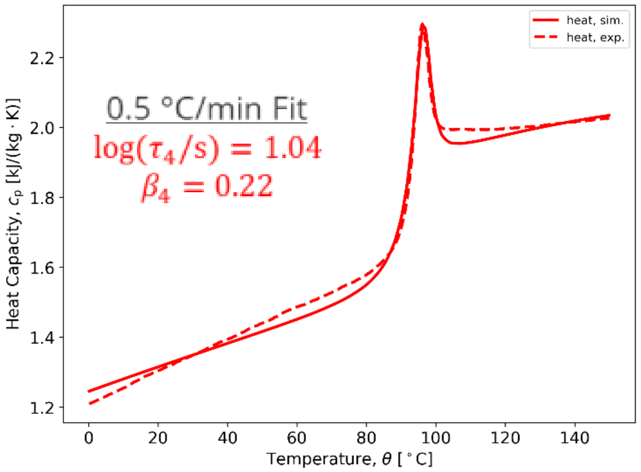
Enthalpy Recovery Parameter Studies

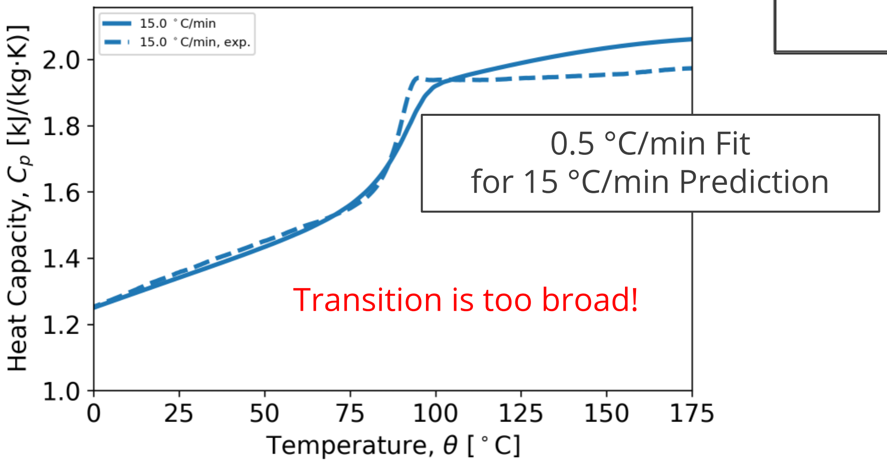
Revisit DSC-based $f_3 = f_4$ for 828/T403

- but use different cooling rates (0.5, 1, 5, 9, 13, 15 °C/min)
- reheating rate is constant (10 °C/min)





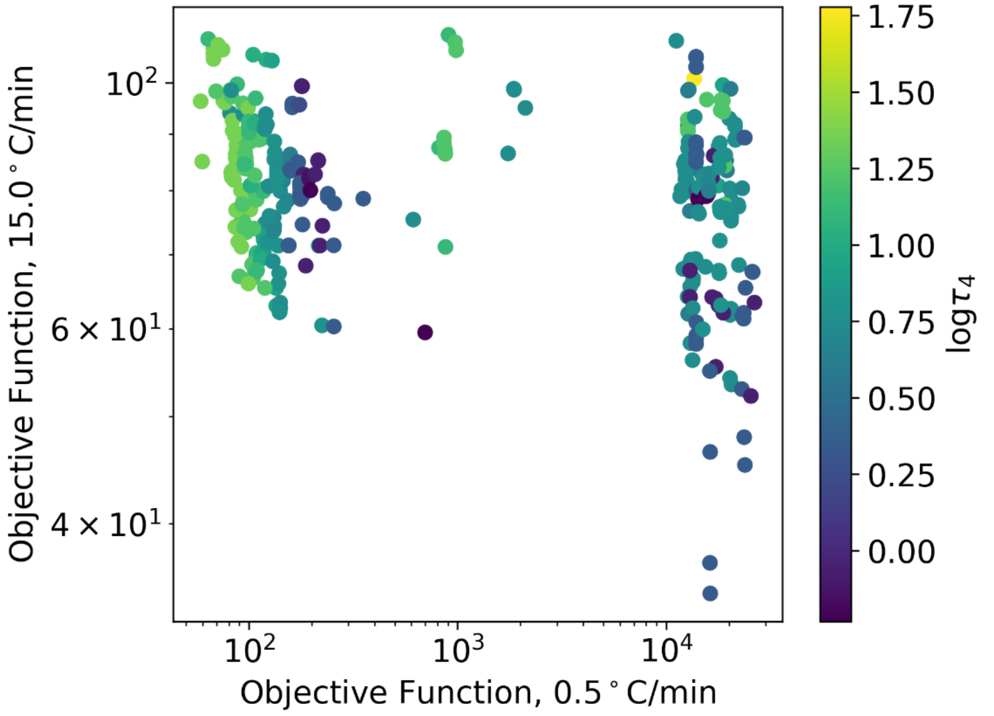




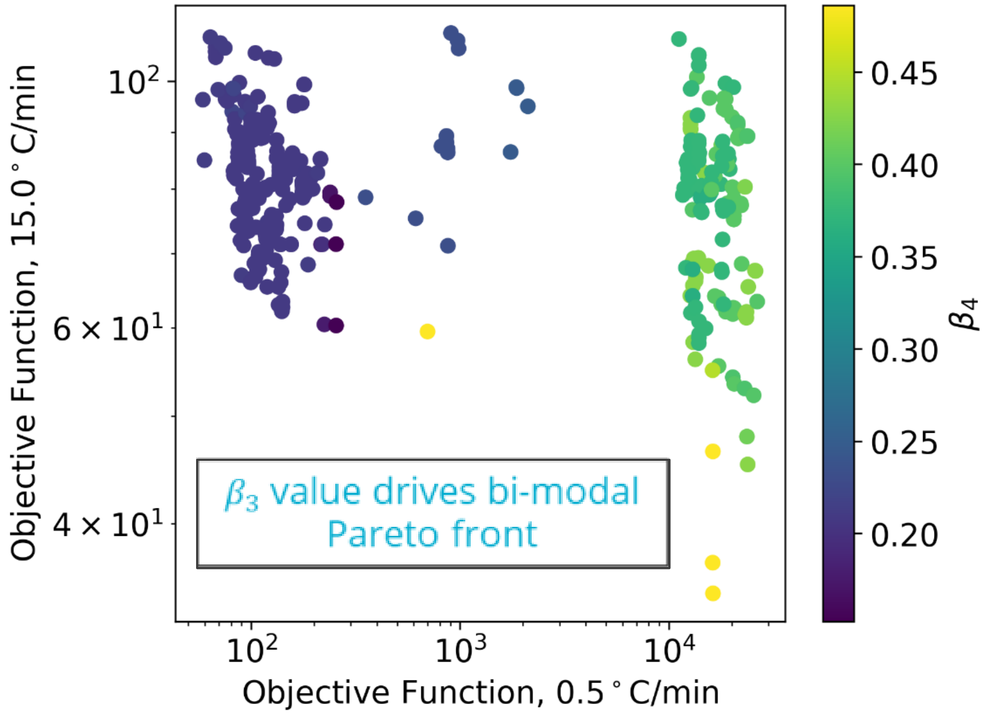
- Fitting to 0.5 C/min seems less bad overall, but *best fits for different levels of aging are clearly in conflict*
- Aging seems to favor
  - broader function (lower β)
  - Longer function (higher τ)

What determines successful predictions of enthalpy recovery?

Aged condition favors longer function (higher τ_3)
Unaged condition favors shorter function

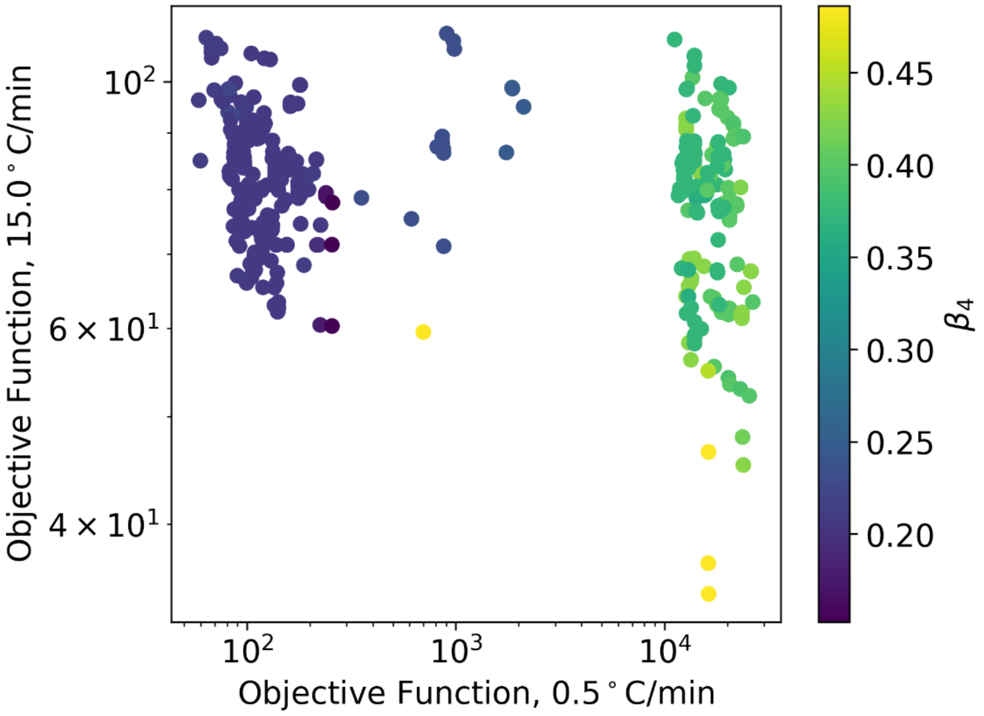


Aged condition favors broader function (lower β_3)
Unaged condition favors shorter function

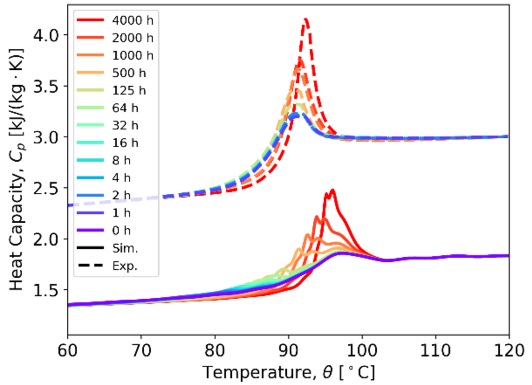


<u>MOGA</u> – multi-objective genetic algorithm
<u>Pareto front</u> – set of non-dominated points
Objective functions formed on all 6 cooling rates, but only slowest and fastest cooling rates shown here.

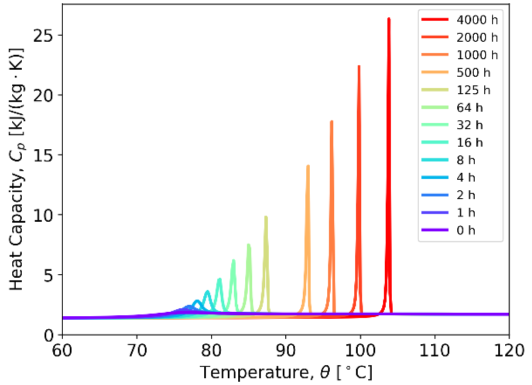
So why was the compression method most successful?



828/T403	τ_3 [s]	β_3
TMA-f_3	0.835	0.25
Compression-f_3	129	0.15
DSC-f_3	17.6	0.21



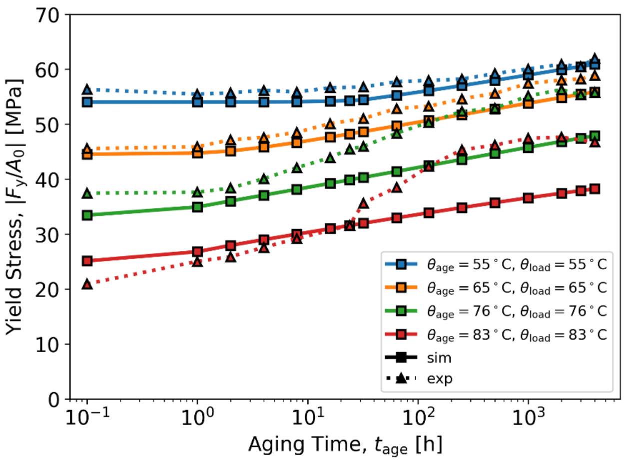
828/DEA	τ_3 [s]	β_3
TMA-f_3	41.0	0.26
Compression-f_3	1.42	0.27
DSC-f_3	890	0.22

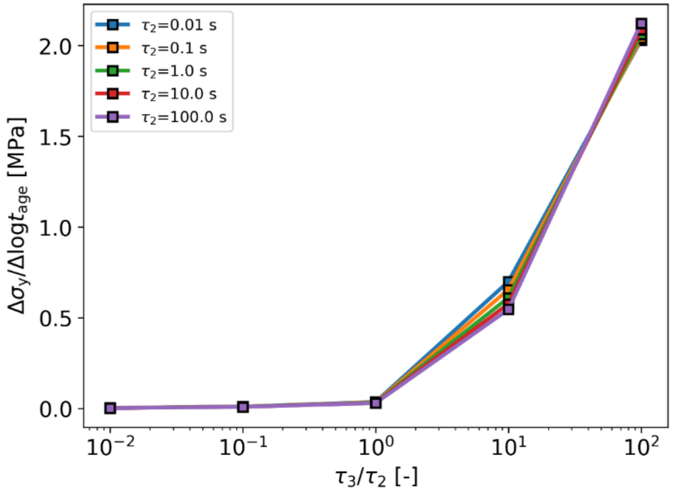


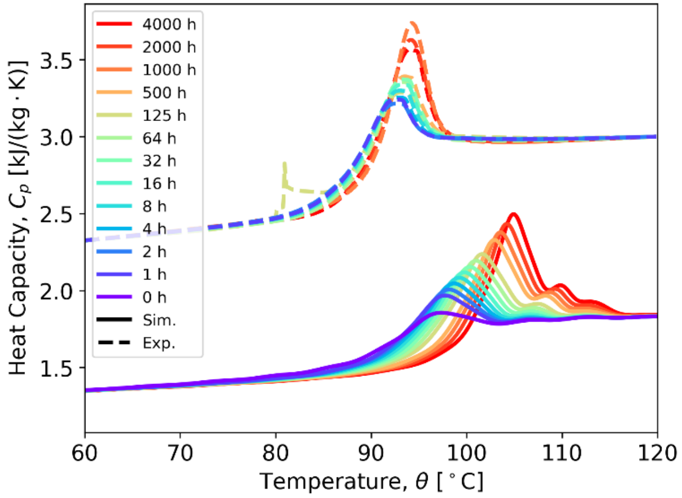
- Compression method does the best for 828/T403 simply because it gives the broadest relaxation function (low β)
- Likely a coincidence, since the success does not repeat for 828/DEA
- Does β_3 change with aging? This would imply the material is thermo-rheologically complex
- Does the WLF-shift factor lead to “over-aging”?

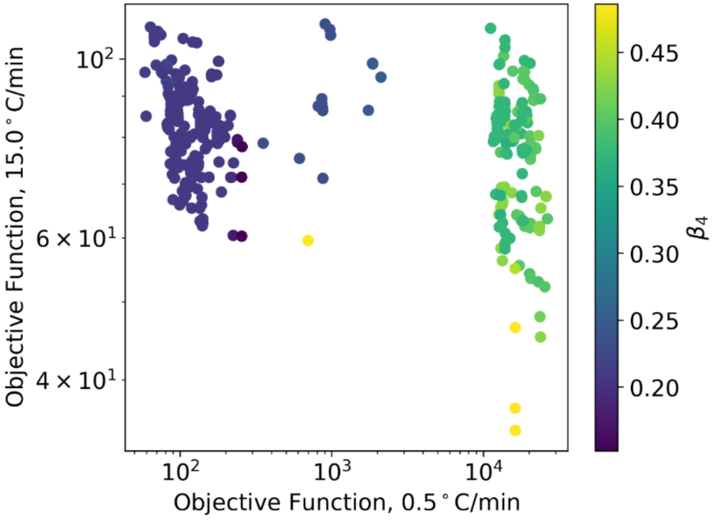
Conclusions

- SPEC was able to qualitatively predict a wide variety of viscoelastic and physical aging phenomenon
- But, you have to choose which behaviors to target in the calibration procedure
- This indicates model form errors
  - Need to implement a non-diverging equilibrium shift factor
  - Relaxation functions may change breadth with aging





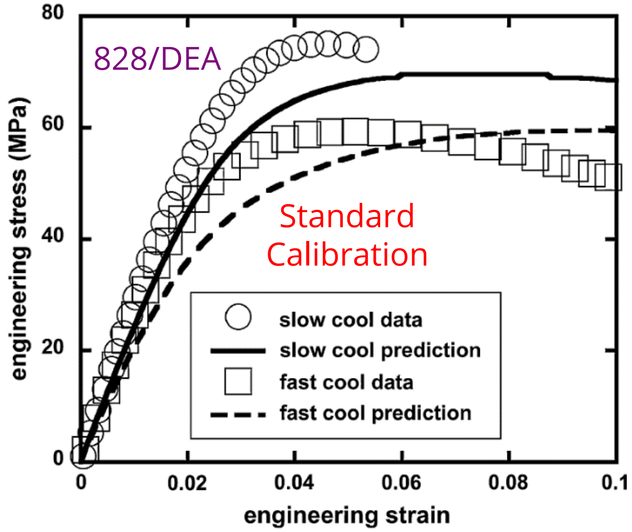


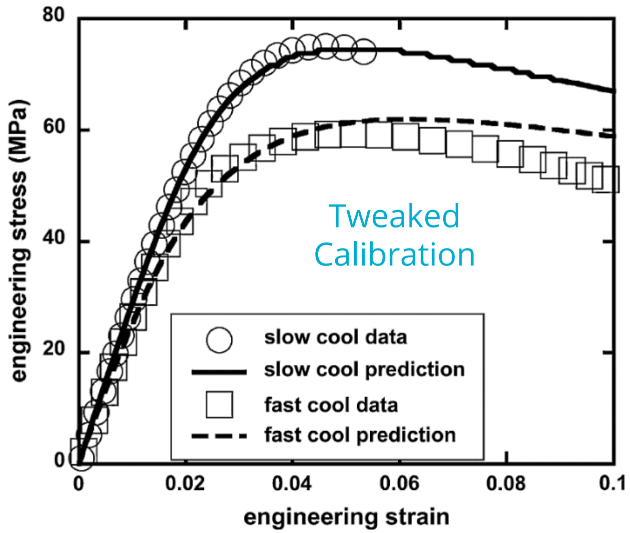


Thank you!

Previous attempts at modeling physical aging

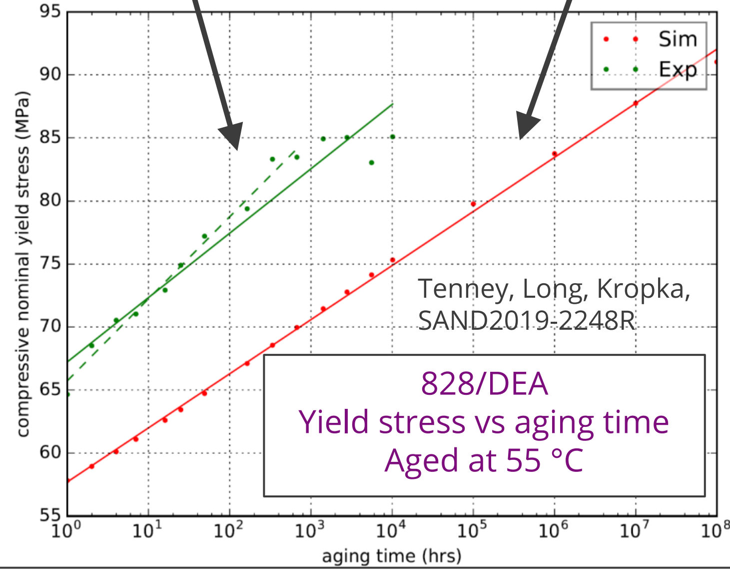
Adolf *et al.*, *Polymer*, 2004



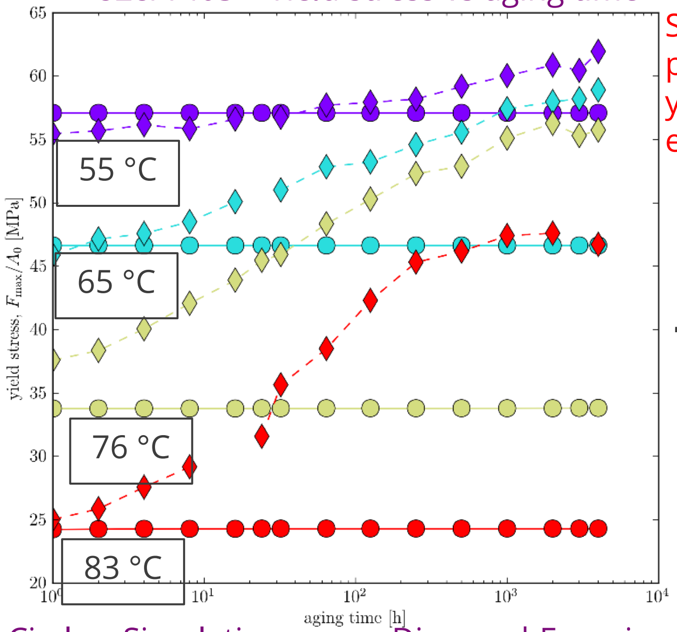


Experiments reach equilibrium

Simulations continue to evolve

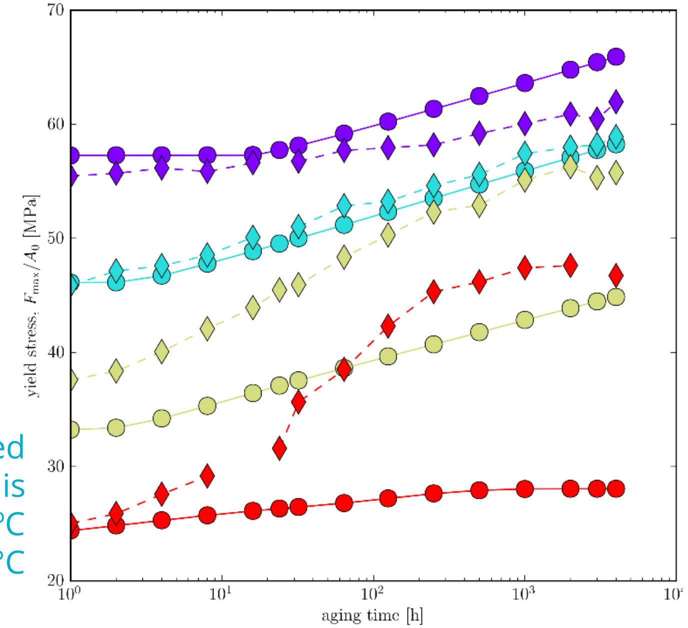


828/T403 – Yield stress vs aging time



Simulation predicts no yield stress evolution!

Tweaked calibration is close at 55 °C and 65 °C

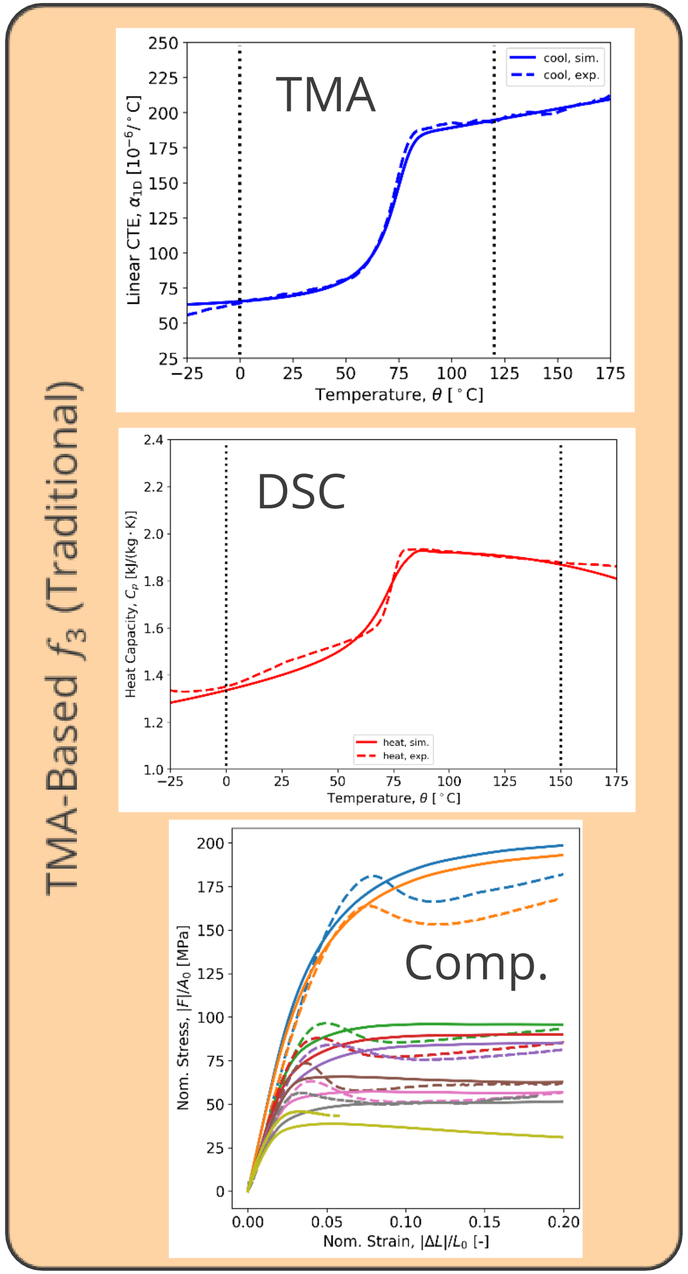


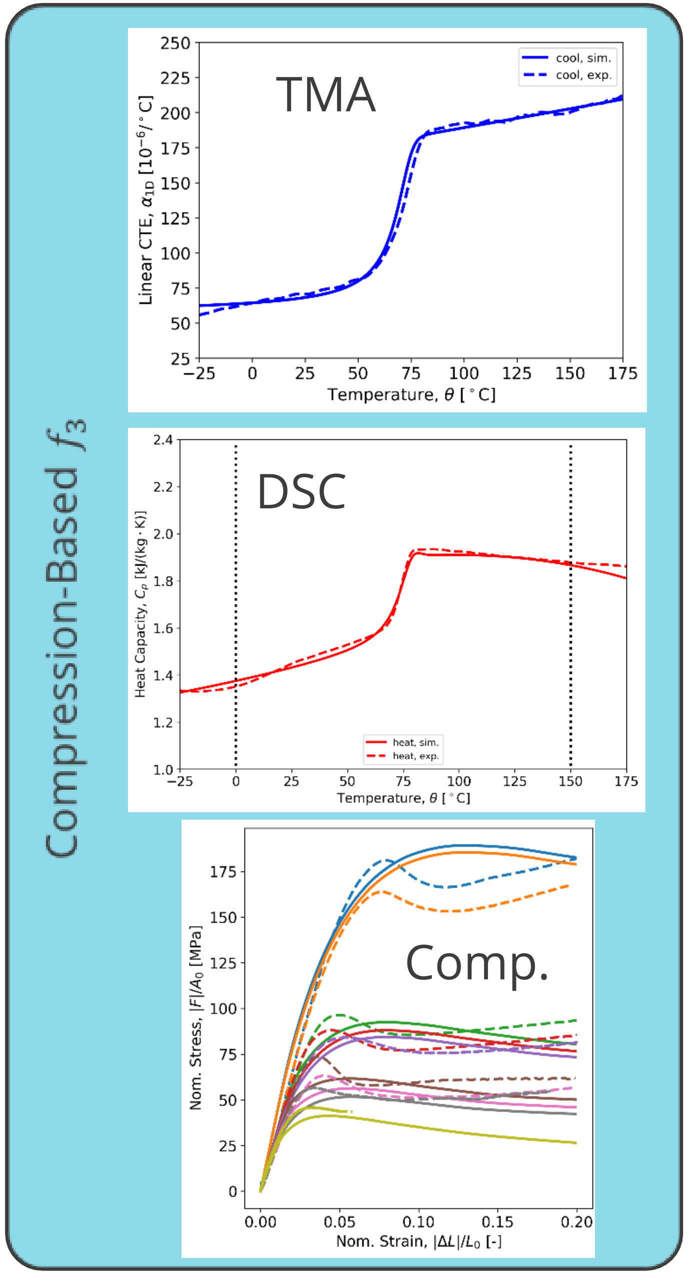
Circle – Simulation

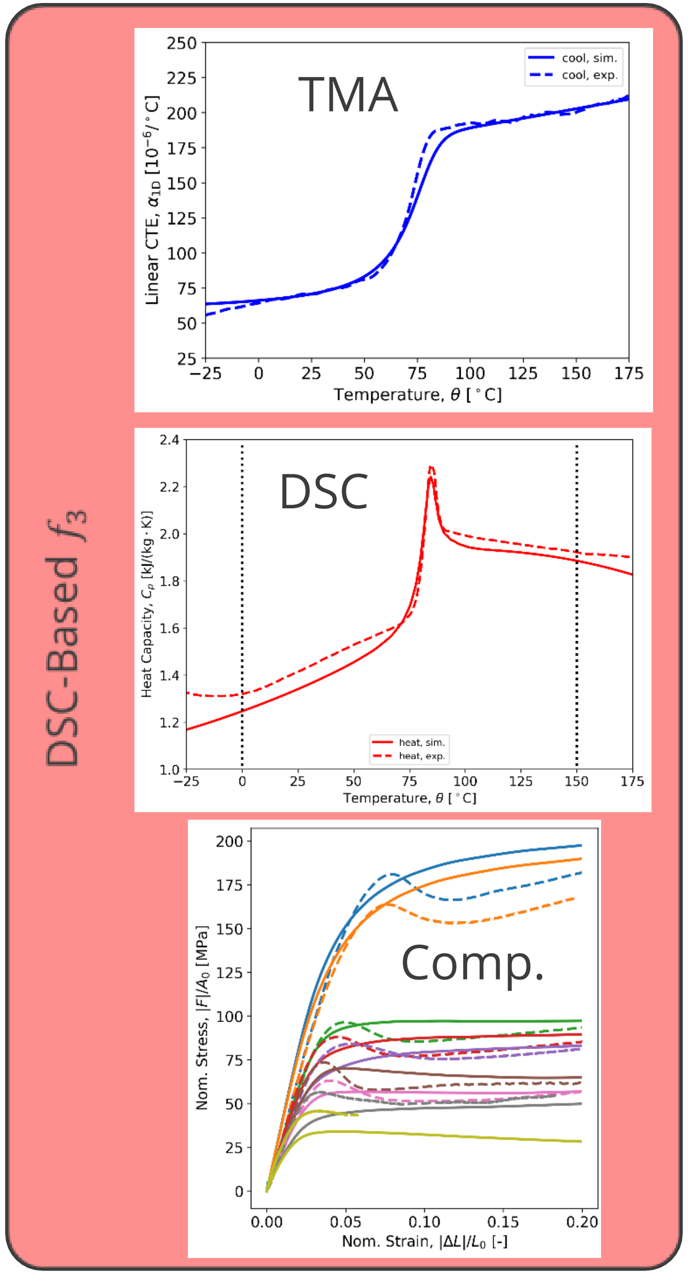
Diamond-Experiment

- Although SPEC can ***qualitatively*** predict physical aging, quantitative predictions are very sensitive to model parameterization.
- ***Objective:*** *Evaluate ability of SPEC to predict multiple measures of material evolution using a single set of parameters*
  - Search for a robust calibration procedure
  - Identify issues preventing accurate predictions
- 828/T403 (Tg ~ 90C)
- 828/DEA (Tg ~ 75C)

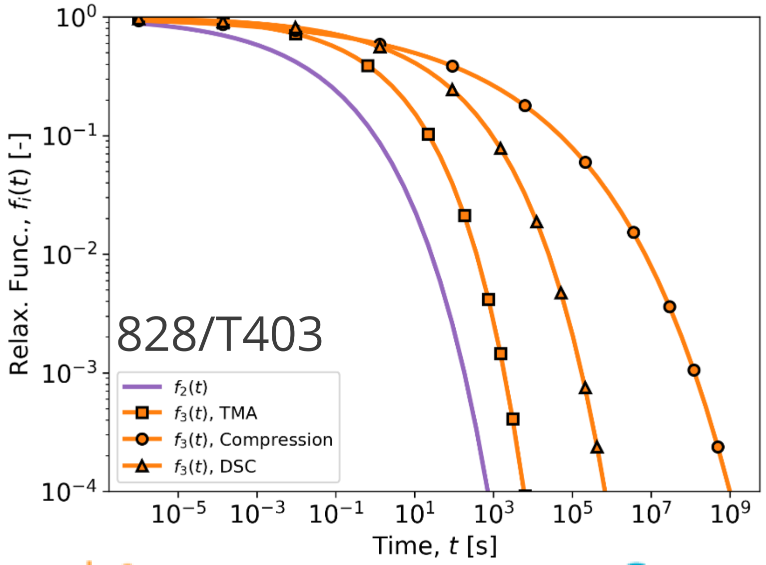
Calibration Fits: 828/DEA

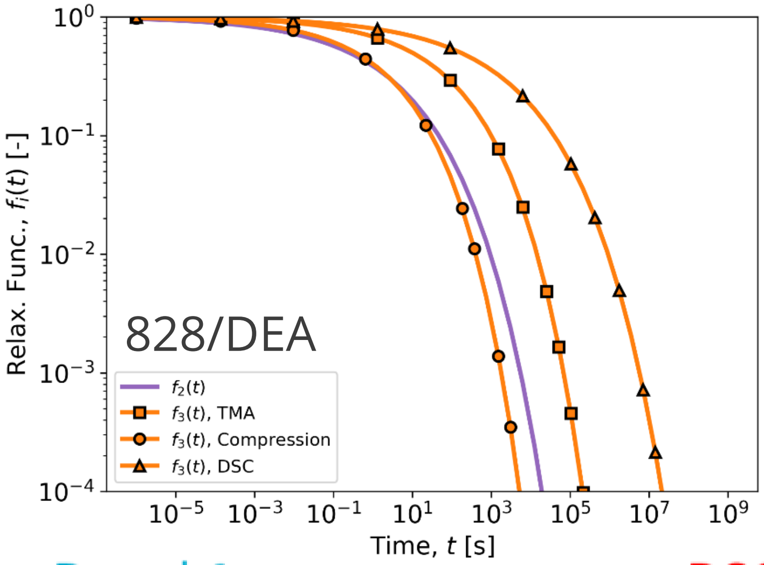




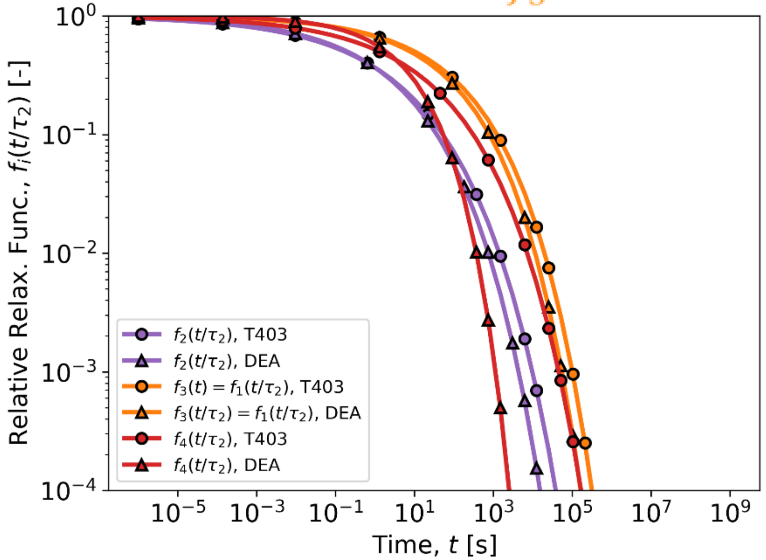


Relaxation Functions

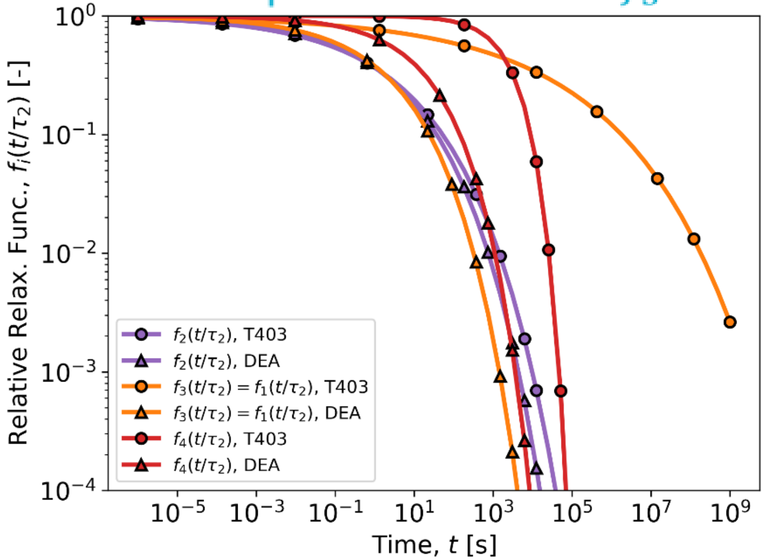




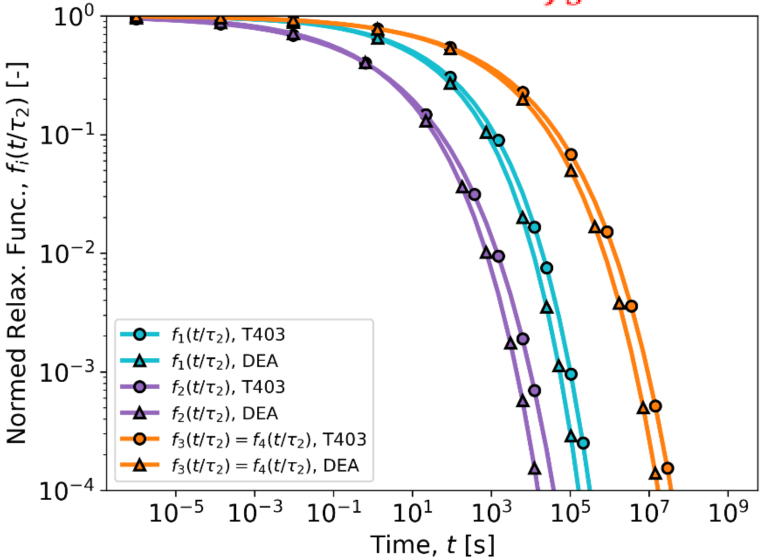
TMA-Based f_3



Compression-Based f_3



DSC-Based f_3



Normalized by shear characteristic time τ_2 (bottom row)

Model Parameterization for 828/T403

Table 4-1. SPEC parameters produced by the baseline calibration for 828T403.

Parameter	Value	Units	Experiment	Reference
K_g^{ref}	4.9	GPa	Legacy	[11], Table 3-1
K_g'	−12	MPa/K	Legacy	[11], Table 3-1
K_∞^{ref}	3.5	GPa	Legacy	[11], Table 3-1
K_∞'	−12	MPa/K	Legacy	[11], Table 3-1
G_g^{ref}	0.959	GPa	Shear master curve	Fig. 4-2c
G_g'	−2.959	MPa/K	Isofrequency temperature sweeps	Fig. 4-4
G_∞^{ref}	8.267	MPa	Shear master curve	Fig. 4-2c
G_∞'	22.918	kPa/K	Isofrequency temperature sweeps	Fig. 4-4
α_g^{ref}	211	10^{-6}/K	TMA	Fig. 4-6
α_g'	0.5	$10^{-6}/K^2$	TMA	Fig. 4-5
α_∞^{ref}	557	10^{-6}/K	TMA	Fig. 4-6
α_∞'	0.5	$10^{-6}/K^2$	TMA	Fig. 4-5
C_g^{ref}	0.695	$MJ/(m^3 \cdot K)$	DSC	Fig. 4-9
C_g'	1.98	$kJ/(m^3 \cdot K^2)$	DSC	Fig. 4-9
C_∞^{ref}	0.991	$MJ/(m^3 \cdot K)$	DSC	Fig. 4-9
C_∞'	1.82	$kJ/(m^3 \cdot K^2)$	DSC	Fig. 4-9
θ_{ref}	95	°C	Chosen	
$\hat{C}_1$	9.6	–	Shear master curve	Fig. 4-2a
$\hat{C}_2$	32.7	K	Shear master curve	Fig. 4-2a
C_3	900	K	Legacy	[11], Table 3-1
C_4	22500	K	Compression	Fig. 4-7
ρ	1176	kg/m^3	Legacy	[3], Table 4
τ_1	0.835	s	TMA	Fig. 4-6
β_1	0.25	–	TMA	Fig. 4-6
τ_2	0.0186	s	Shear master curve	Fig. 4-3
β_2	0.21	–	Shear master curve	Fig. 4-3
τ_3	0.835	s	TMA	Fig. 4-6
β_3	0.25	–	TMA	Fig. 4-6
τ_4	0.132	s	DSC	Fig. 4-9
β_4	0.22	–	DSC	Fig. 4-9

Table 4-3. SPEC parameters produced by the compression-focused calibration for 828T403. Only parameters that have changed from the baseline approach are listed here, see Table 4-1.

Parameter	Value	Units	Experiment	Reference
C_g^{ref}	0.983	$MJ/(m^3 \cdot K)$	DSC	Fig. 4-15
C_g'	1.97	$kJ/(m^3 \cdot K^2)$	DSC	Fig. 4-15
C_∞^{ref}	1.195	$MJ/(m^3 \cdot K)$	DSC	Fig. 4-15
C_∞'	1.38	$kJ/(m^3 \cdot K^2)$	DSC	Fig. 4-15
C_4	11600	K	Compression	Fig. 4-13
τ_1	129	s	Compression	Fig. 4-13
β_1	0.15	–	Compression	Fig. 4-13
τ_3	129	s	Compression	Fig. 4-13
β_3	0.15	–	Compression	Fig. 4-13
τ_4	49.8	s	DSC	Fig. 4-15
β_4	0.67	–	DSC	Fig. 4-15

Table 4-4. SPEC parameters produced by the DSC-focused calibration for 828T403. Only parameters that have chagned from the baseline approach are listed here, see Table 4-1.

Parameter	Value	Units	Experiment	Source
C_g^{ref}	0.996	$MJ/(m^3 \cdot K)$	DSC	Fig. 4-17
C_g'	3.86	$kJ/(m^3 \cdot K^2)$	DSC	Fig. 4-17
C_∞^{ref}	1.180	$MJ/(m^3 \cdot K)$	DSC	Fig. 4-17
C_∞'	1.54	$kJ/(m^3 \cdot K^2)$	DSC	Fig. 4-17
C_4	14700	K	Compression	Fig. 4-18
τ_3	17.6	s	DSC	Fig. 4-17
β_3	0.21	–	DSC	Fig. 4-17
τ_4	17.6	s	DSC	Fig. 4-17
β_4	0.21	–	DSC	Fig. 4-17

Model Parameterization for 828/DEA

Table 5-1. SPEC parameters produced by the baseline calibration for 828DEA.

Parameter	Value	Units	Experiment	Reference
K_g^{ref}	4.9	GPa	Legacy	[4], Table 3
K_g'	−12	MPa/K	Legacy	[4], Table 3
K_∞^{ref}	3.2	GPa	Legacy	[4], Table 3
K_∞'	−12	MPa/K	Legacy	[4], Table 3
G_g^{ref}	0.9	GPa	Legacy	[4], Table 3
G_g'	−4.2	MPa/K	Legacy	[4], Table 3
G_∞^{ref}	4.5	MPa	Legacy	[4], Table 3
G_∞'	0	kPa/K	Legacy	[4], Table 3
α_g^{ref}	220	$10^{-6}/\mathrm{K}$	TMA	Fig. 5-5
α_g'	0	$10^{-6}/\mathrm{K}^2$	TMA	Fig. 5-5
$\alpha_\infty^{\mathrm{ref}}$	562	$10^{-6}/\mathrm{K}$	TMA	Fig. 5-4
α_∞'	0.7	$10^{-6}/\mathrm{K}^2$	TMA	Fig. 5-4
C_g^{ref}	1.146	$\mathrm{MJ}/(\mathrm{m}^3\cdot\mathrm{K})$	DSC	Fig. 5-8
C_g'	1.29	$\mathrm{kJ}/(\mathrm{m}^3\cdot\mathrm{K}^2)$	DSC	Fig. 5-8
C_∞^{ref}	1.379	$\mathrm{MJ}/(\mathrm{m}^3\cdot\mathrm{K})$	DSC	Fig. 5-8
C_∞'	0.65	$\mathrm{kJ}/(\mathrm{m}^3\cdot\mathrm{K}^2)$	DSC	Fig. 5-8
θ_{ref}	75	°C	Chosen	
$\hat{C}_1$	12.6	–	Shear master curve	Fig. 5-1a
$\hat{C}_2$	40.1	K	Shear master curve	Fig. 5-1a
C_3	1000	K	Legacy	[4], Table 3
C_4	13700	K	Compression	Fig. 5-6
ρ	1176	kg/m^3	Legacy	[3], Table 4
τ_1	41.0	s	TMA	Fig. 5-5
β_1	0.26	–	TMA	Fig. 5-5
τ_2	1.25	s	Shear master curve	Fig. 5-2
β_2	0.23	–	Shear master curve	Fig. 5-2
τ_3	41.0	s	TMA	Fig. 5-5
β_3	0.26	–	TMA	Fig. 5-5
τ_4	6.80	s	DSC	Fig. 5-8
β_4	0.36	–	DSC	Fig. 5-8

Table 5-4. SPEC parameters produced by the compression-focused calibration for 828DEA. Only parameters that have changed from the baseline approach are listed here, see Table 5-1.

Parameter	Value	Units	Experiment	Reference
C_g^{ref}	1.135	$\mathrm{MJ}/(\mathrm{m}^3\cdot\mathrm{K})$	DSC	Fig. 5-16
C_g'	1.22	$\mathrm{kJ}/(\mathrm{m}^3\cdot\mathrm{K}^2)$	DSC	Fig. 5-16
C_∞^{ref}	1.300	$\mathrm{MJ}/(\mathrm{m}^3\cdot\mathrm{K})$	DSC	Fig. 5-16
C_∞'	0.83	$\mathrm{kJ}/(\mathrm{m}^3\cdot\mathrm{K}^2)$	DSC	Fig. 5-16
C_4	24800	K	Compression	Fig. 5-14
τ_1	1.42	s	Compression	Fig. 5-14
β_1	0.27	–	Compression	Fig. 5-14
τ_3	1.42	s	Compression	Fig. 5-14
β_3	0.27	–	Compression	Fig. 5-14
τ_4	15.8	s	DSC	Fig. 5-16
β_4	0.34	–	DSC	Fig. 5-16

Table 5-5. SPEC parameters produced by the DSC-focused calibration for 828DEA. Only parameters that have changed from the baseline approach are listed here, see Table 5-1.

Parameter	Value	Units	Experiment	Reference
C_g^{ref}	1.172	$\mathrm{MJ}/(\mathrm{m}^3\cdot\mathrm{K})$	DSC	Fig. 5-18
C_g'	2.16	$\mathrm{kJ}/(\mathrm{m}^3\cdot\mathrm{K}^2)$	DSC	Fig. 5-18
C_∞^{ref}	1.381	$\mathrm{MJ}/(\mathrm{m}^3\cdot\mathrm{K})$	DSC	Fig. 5-18
C_∞'	0.69	$\mathrm{kJ}/(\mathrm{m}^3\cdot\mathrm{K}^2)$	DSC	Fig. 5-18
C_4	9900	K	Compression	Fig. 5-19
τ_3	890.	s	DSC	Fig. 5-18
β_3	0.22	–	DSC	Fig. 5-18
τ_4	890.	s	DSC	Fig. 5-18
β_4	0.22	–	DSC	Fig. 5-18

Relaxation Function Parameters

TMA f_3

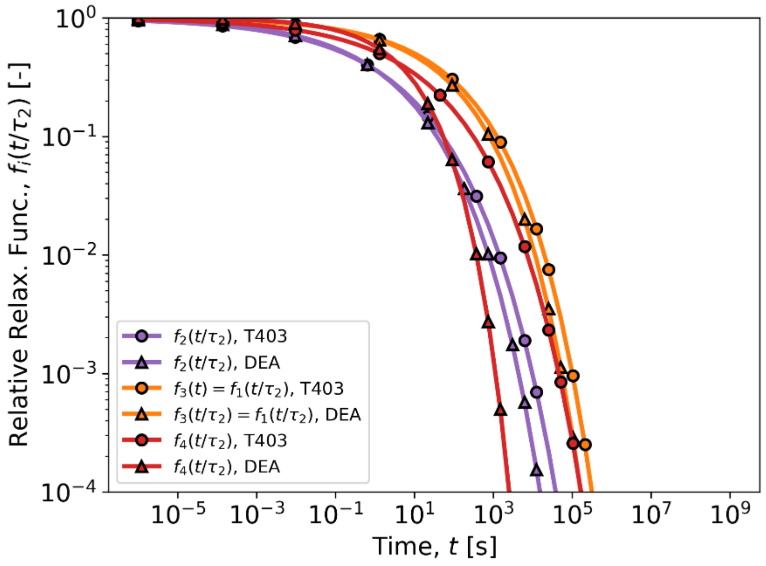
Parameter	828T403	828DEA	Units
$\tau_1 = \tau_3$	0.835	41.0	s
$\beta_1 = \beta_3$	0.25	0.26	
τ_2	0.0186	1.25	s
β_2	0.21	0.23	
τ_4	0.132	6.80	s
β_4	0.22	0.36	
$\tau_1/\tau_2 = \tau_3/\tau_2$	45	33	
τ_4/τ_2	7	5	

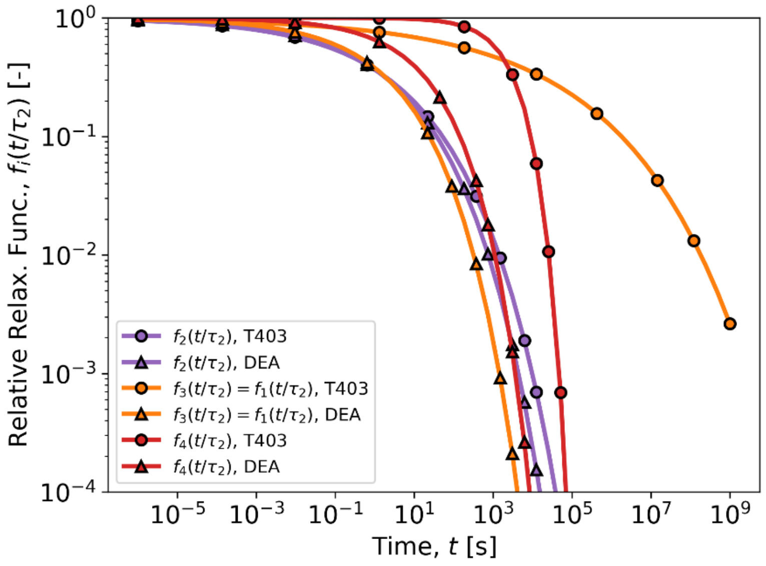
Compression f_3

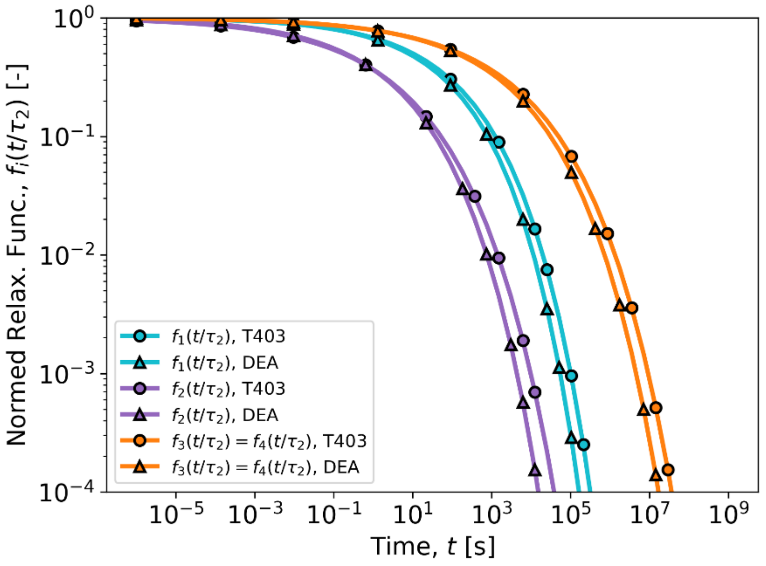
Parameter	828T403	828DEA	Units
$\tau_1 = \tau_3$	129	1.42	s
$\beta_1 = \beta_3$	0.15	0.27	
τ_2	0.0186	1.25	s
β_2	0.21	0.23	
τ_4	49.8	15.8	s
β_4	0.67	0.34	
$\tau_1/\tau_2 = \tau_3/\tau_2$	6935	1.1	
τ_4/τ_2	2667	13	

DSC f_3

Parameter	828T403	828DEA	Units
τ_1	0.835	41.0	s
β_1	0.25	0.26	
τ_2	0.0186	1.25	s
β_2	0.21	0.23	
$\tau_3 = \tau_4$	17.6	890.	s
$\beta_3 = \beta_4$	0.21	0.22	
τ_1/τ_2	45	33	
$\tau_3/\tau_2 = \tau_4/\tau_2$	946	712	

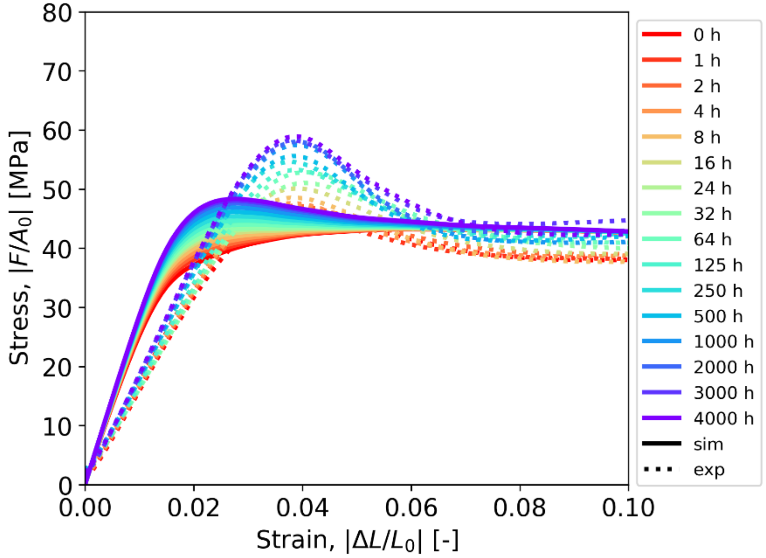


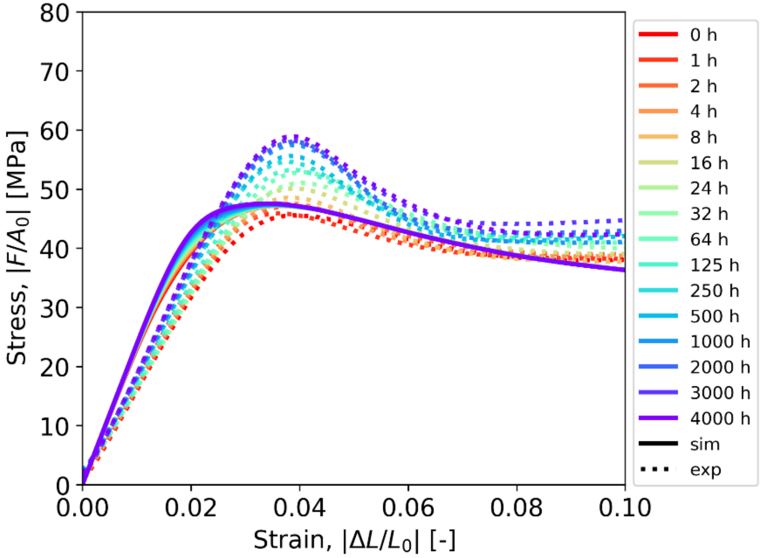




Yield Stress Evolution, Stress-strain curves (828/T403)

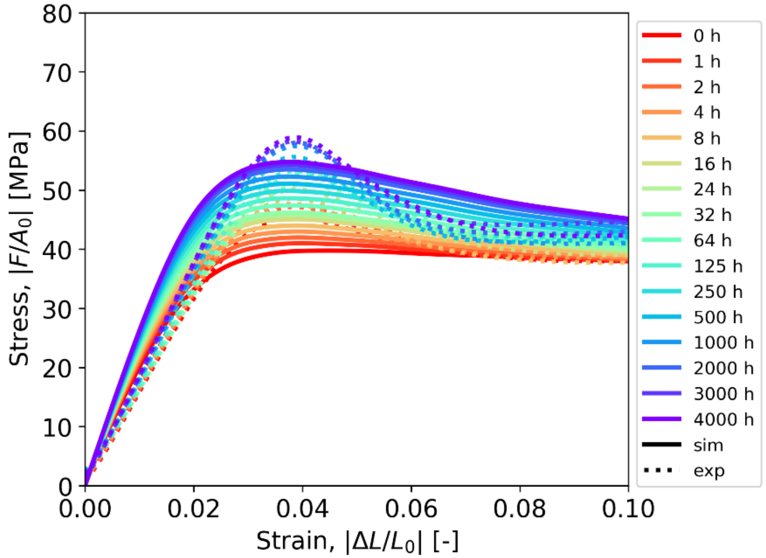
TMA f_3

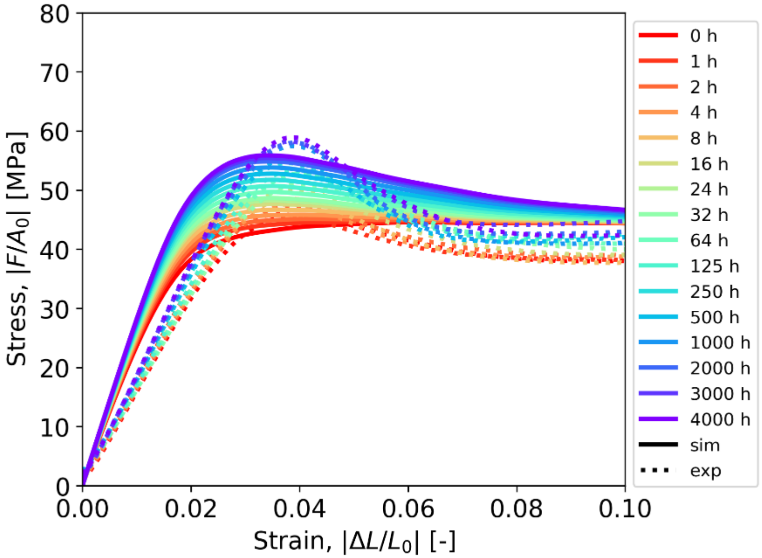




Legacy Calibration

Comp. f_3



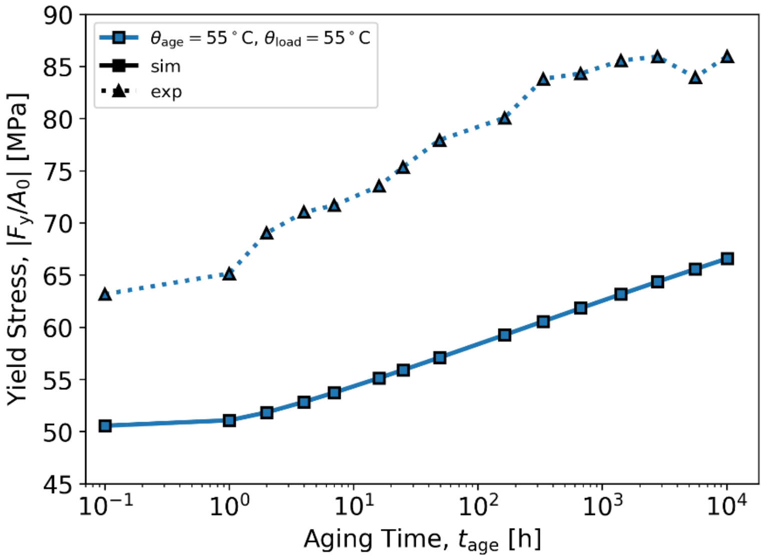


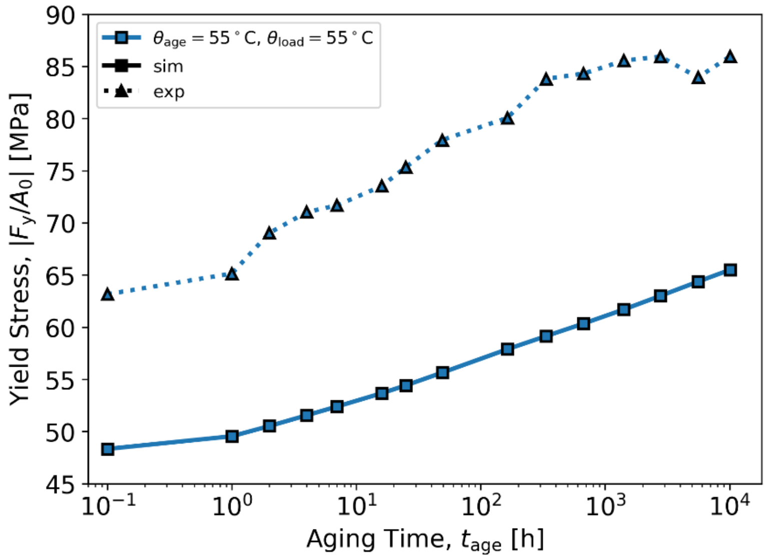
DSC f_3

Aged and Loaded at 65 °C

Yield Stress Evolution (828/DEA)

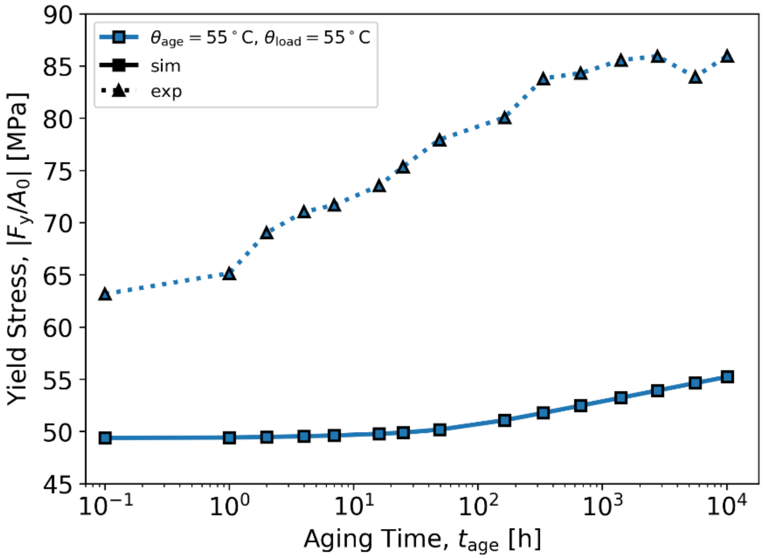
TMA f_3

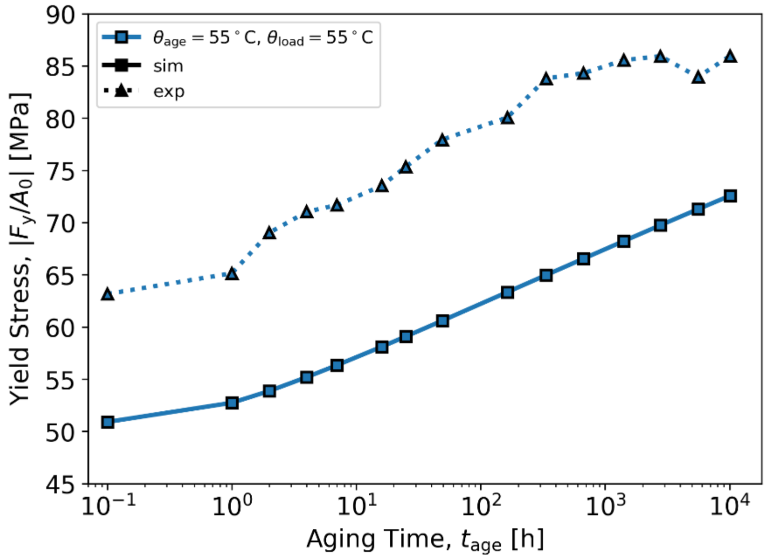




Legacy Calibration

Comp. f_3



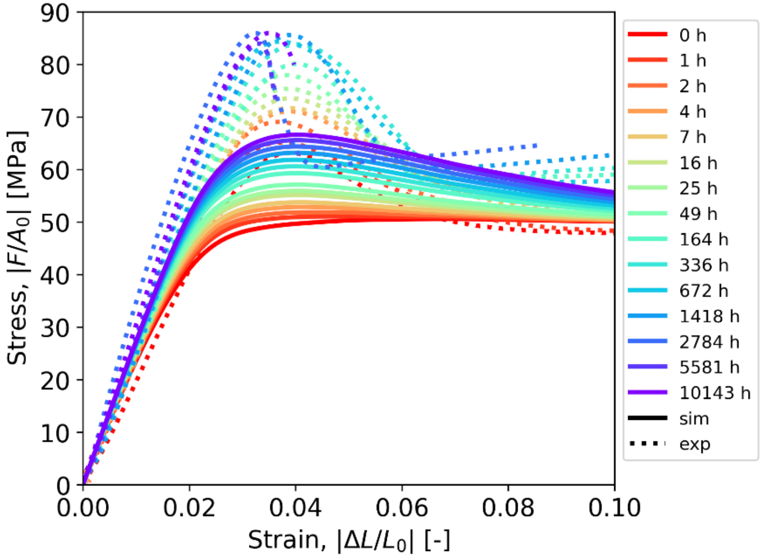


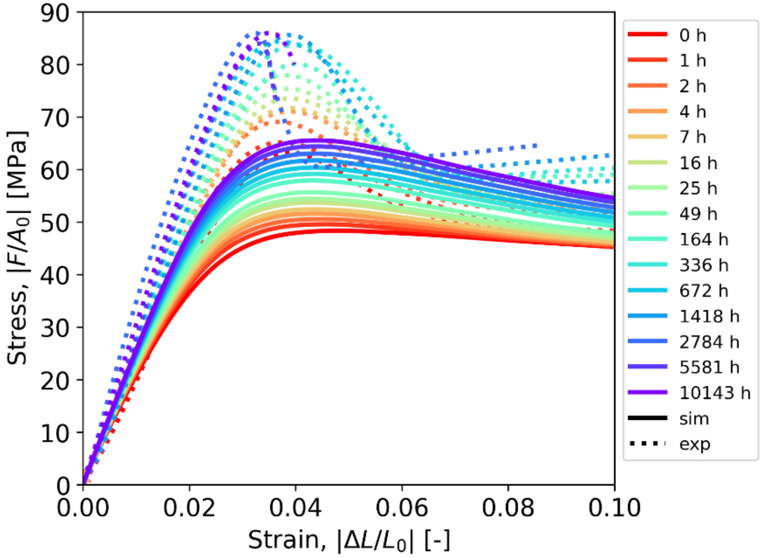
DSC f_3

Aged and Loaded at 55 °C

Yield Stress Evolution, Stress-strain curves (828/DEA)

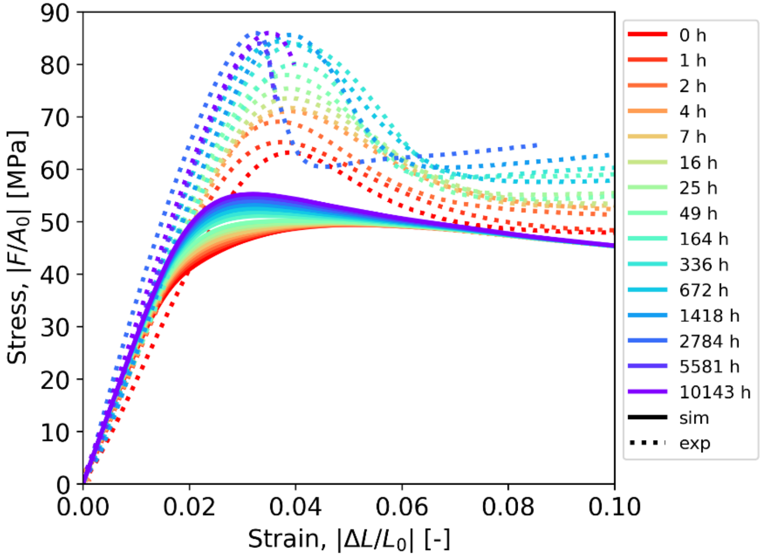
TMA f_3

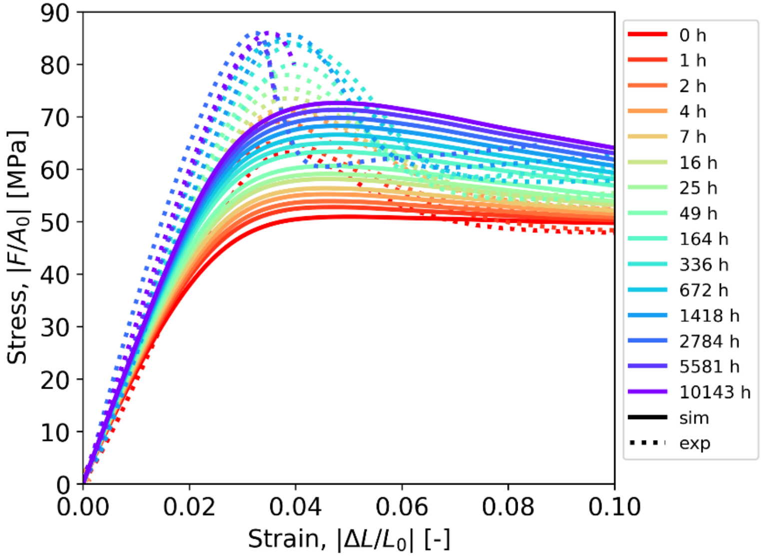




Legacy Calibration

Comp. f_3



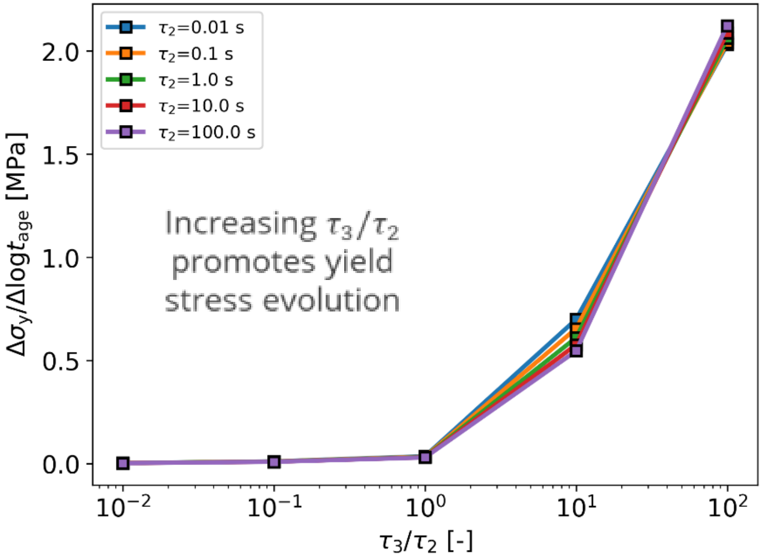


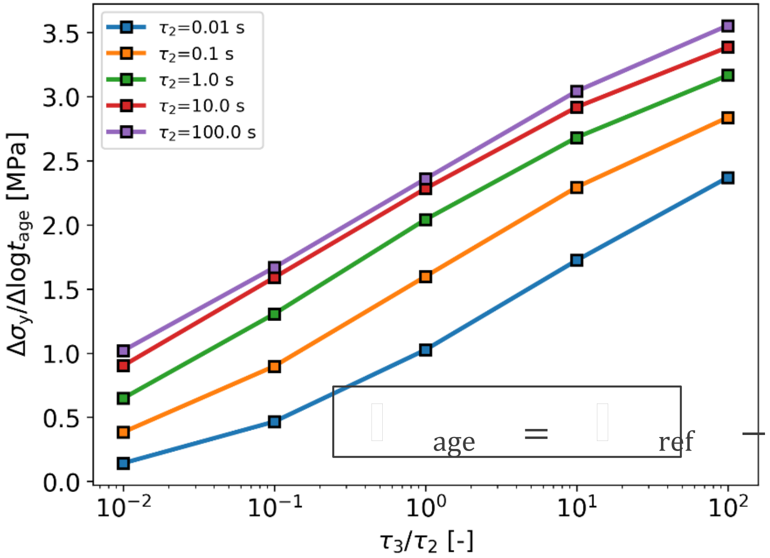
DSC f_3

Aged and Loaded at 55 °C

What determines successful yield stress evolution?

$$N(t) = \theta - \theta_{\mathrm{ref}} - \int_0^t f_3(t^* - s^*)\frac{\mathrm{d}\theta}{\mathrm{d}s}\mathrm{d}s + C_3\left(I_1 - I_{1,\mathrm{ref}} - \int_0^t f_1(t^* - s^*)\frac{\mathrm{d}I_1}{\mathrm{d}s}\mathrm{d}s\right) + C_4\int_0^t\int_0^t f_2(t^* - s^*, t^* - u^*)\frac{\mathrm{d}\boldsymbol{H}^{\mathrm{dev}}}{\mathrm{d}s}:\frac{\mathrm{d}\boldsymbol{H}^{\mathrm{dev}}}{\mathrm{d}u}\mathrm{d}s\mathrm{d}u$$

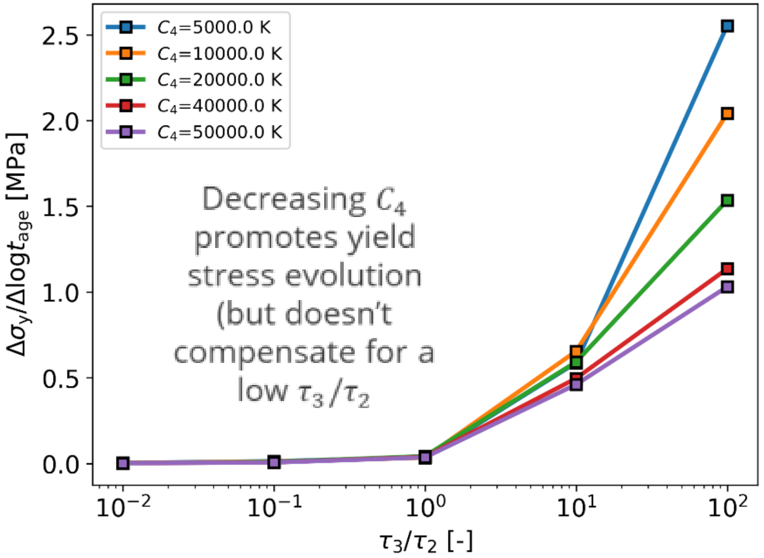


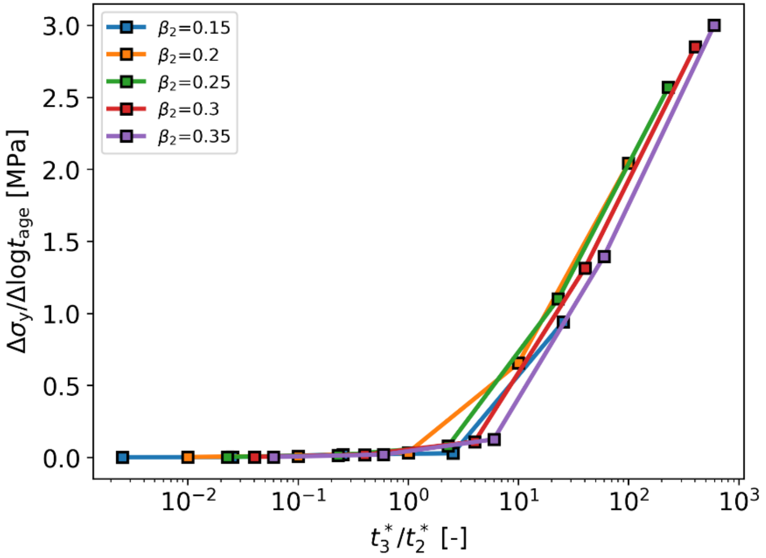


age = ref − 10 ° C

Near θ_g, yield stress evolution for $\frac{\tau_3}{\tau_2} < 1$ is possible, but small.

$\theta_{\mathrm{age}} = \theta_{\mathrm{ref}} - 30$ °C
$C_1 = 20,$
$C_2 = 50$



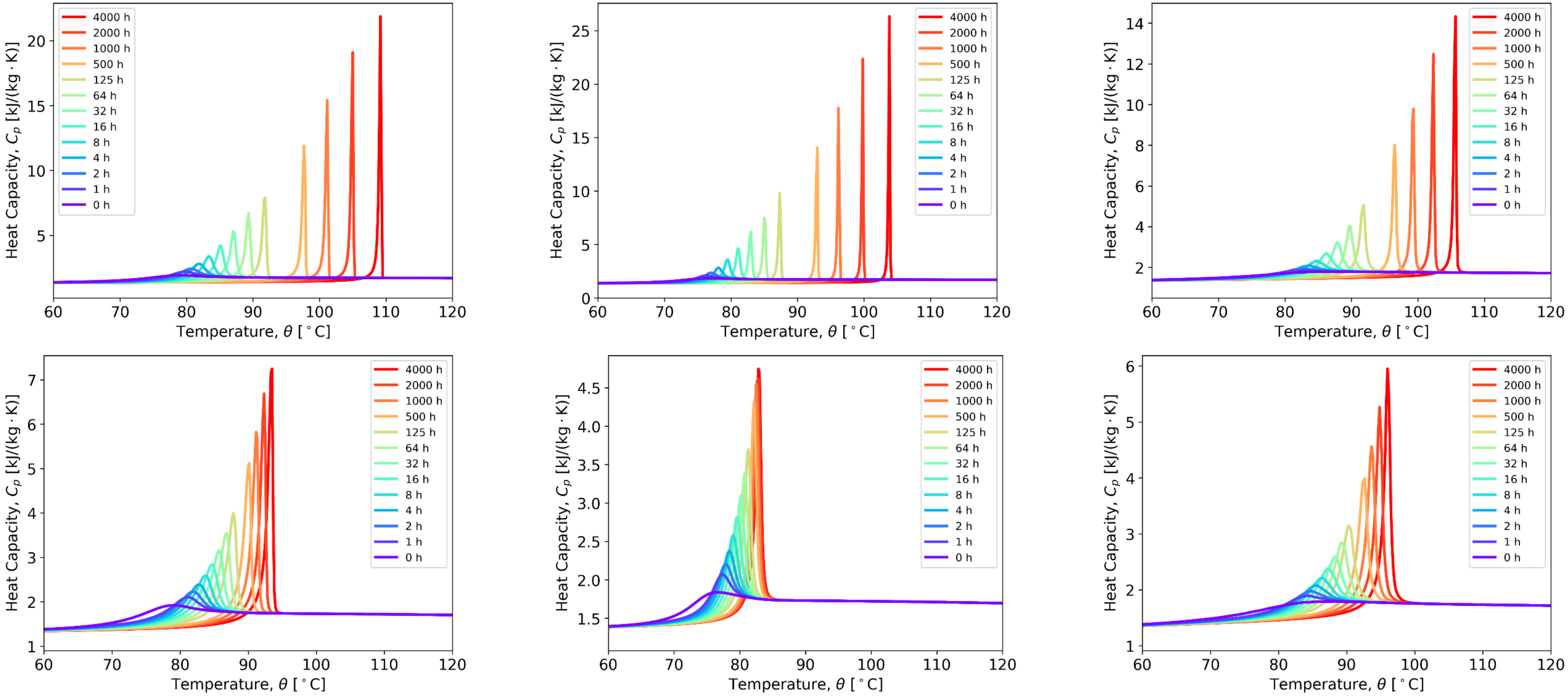


When breadth is also changing, τ_3/τ_2 is not meaningful. Instead, how long does it take to decay from 1 to 0.1?

Enthalpy Recovery (828/DEA)

Aging Temp. 55 °C

Aging Temp. 65 °C



TMA f_3

Compression f_3

DSC f_3