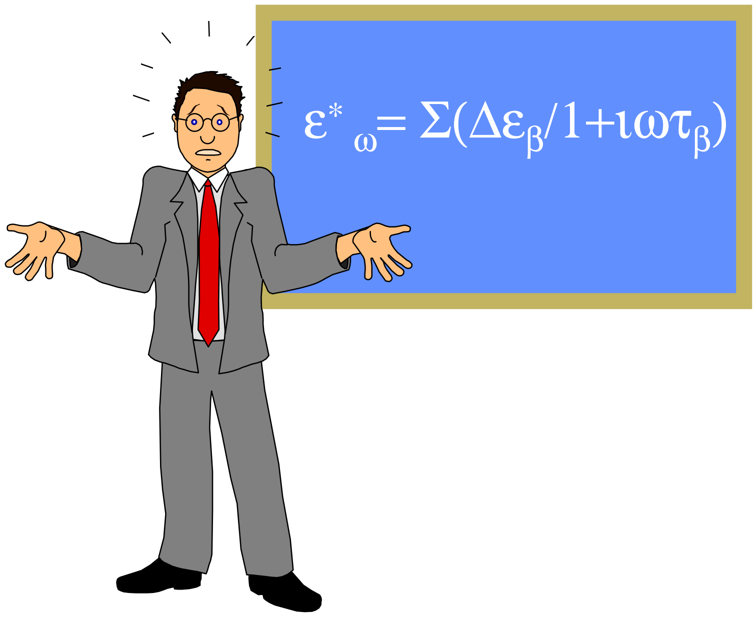
Dynamic Mechanical Analysis (DMA)
Basics and Beyond



Dr. Lin Li

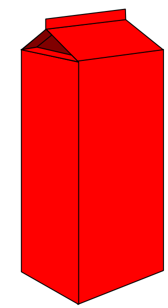
Thermal Analysis

PerkinElmer Inc.

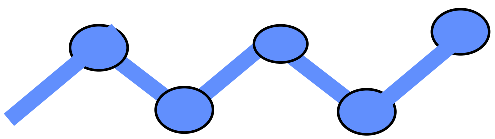
April 2000

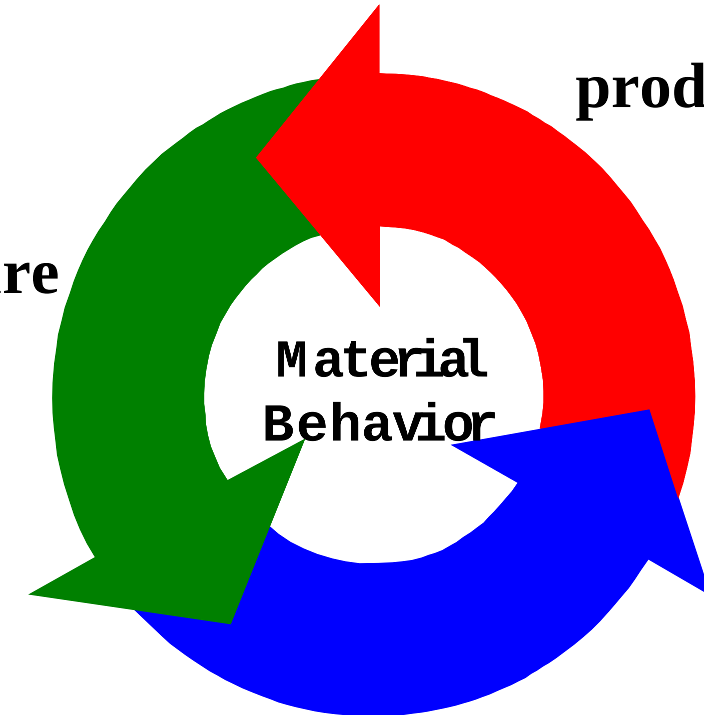
The DMA lets you relate:

product properties

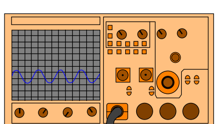


molecular structure





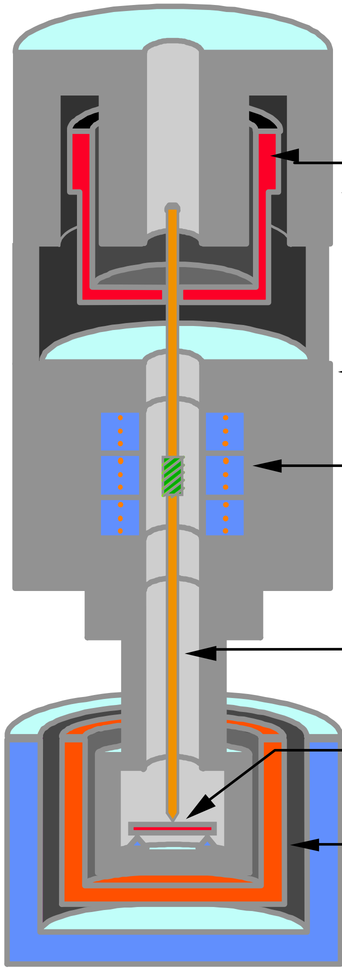
processing conditions



DMA Structure in general

<u>How the DMA works:</u>

- Constant inputs and outputs function as in the TMA
- A sine wave current is added to the force coil
- The resultant sine wave voltage of the LVDT is compared to the sine wave force
- The amplitude of the LVDT is related to the storage modulus, E' via the spring constant, k.
- The phase lag, δ, is related to the E" via the damping constant, D.



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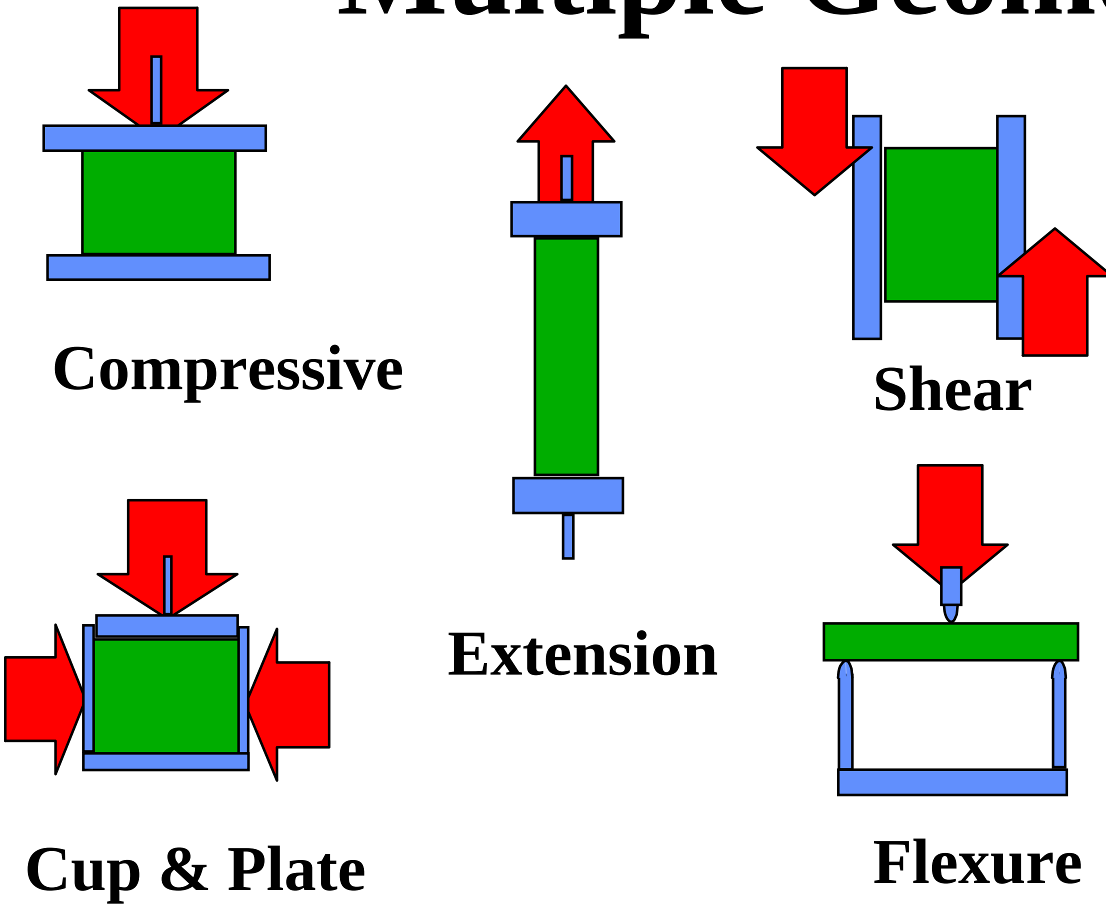
Outstanding Flexibility 1: Multiple Geometries



Parallel Plate
Cup & Plate
Tray & Plate
Sintered Plates
3 pt. Bending
4 pt. Bending
ASTM Flexure
Dual Cantilever
Single Cantilever
Extension
Shear Sandwich
Coaxial Cylinder
Paper Fold

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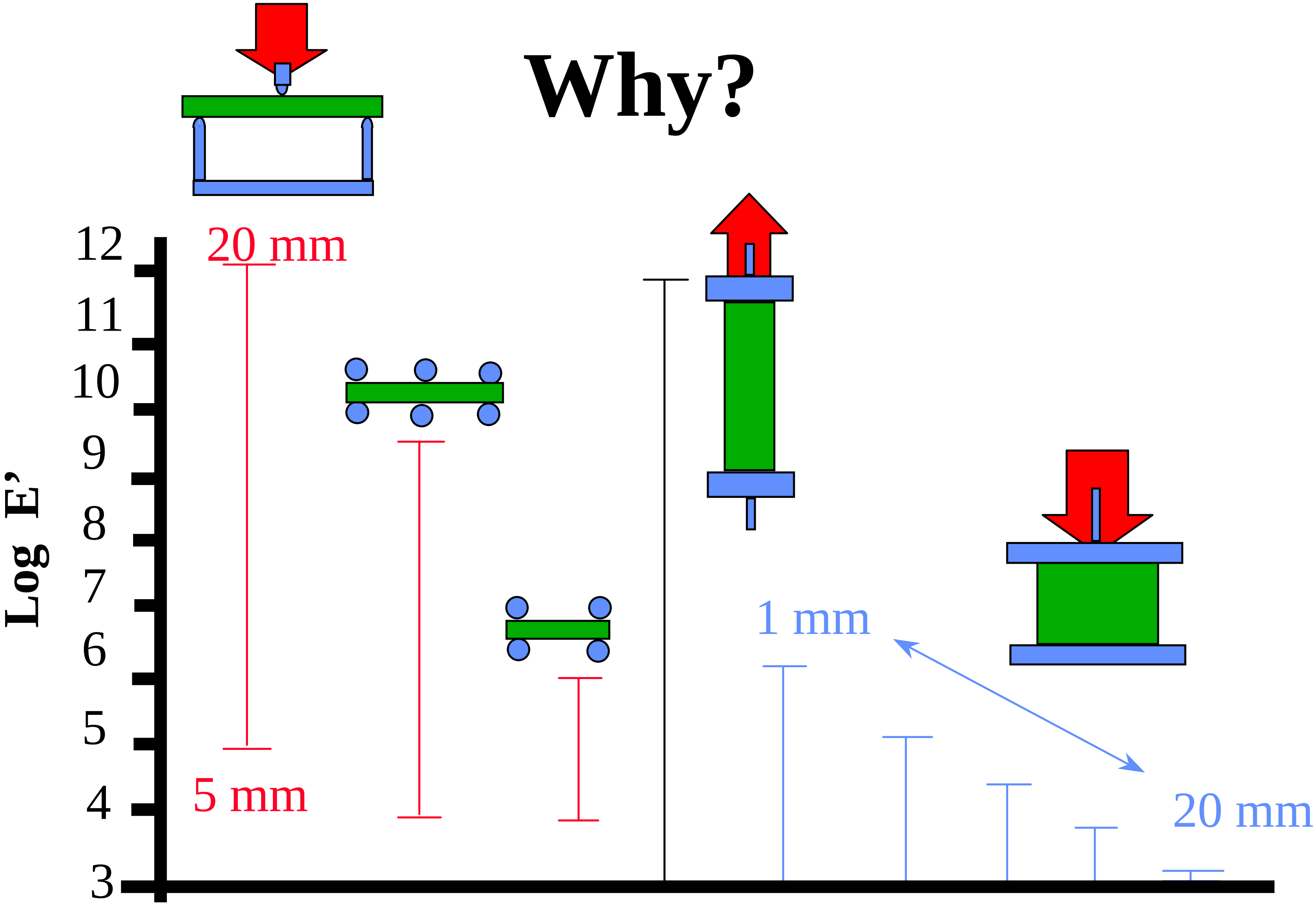
Why?



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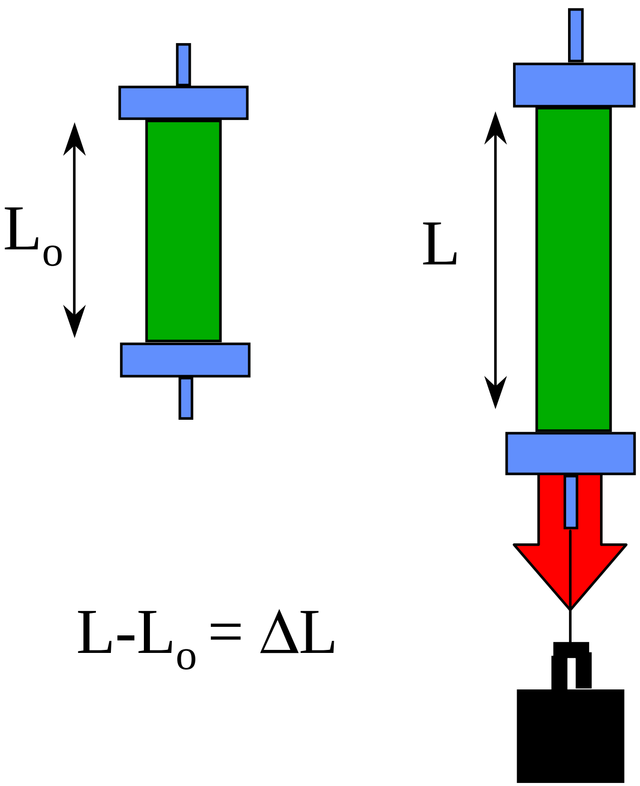
Stress Causes Strain...



$L - L_o = \Delta L$

Cauchy or Engineering Strain	$\varepsilon = \Delta L/L_o$
Henchy or True Strain	$\varepsilon = \ln(\Delta L/L_o)$
Kinetic Theory of Rubber Strain	$\varepsilon = 1/3\{L/L_o - (L_o/L)^2\}$
Kirchhoff Strain	$\varepsilon = 1/2\{(L/L_o)^2 - 1\}$
Murnaghan Strain	$\varepsilon = 1/2\{1 - (L_o/L)^2\}$

The different definitions of tensile strain become equivalent at very small deformations.

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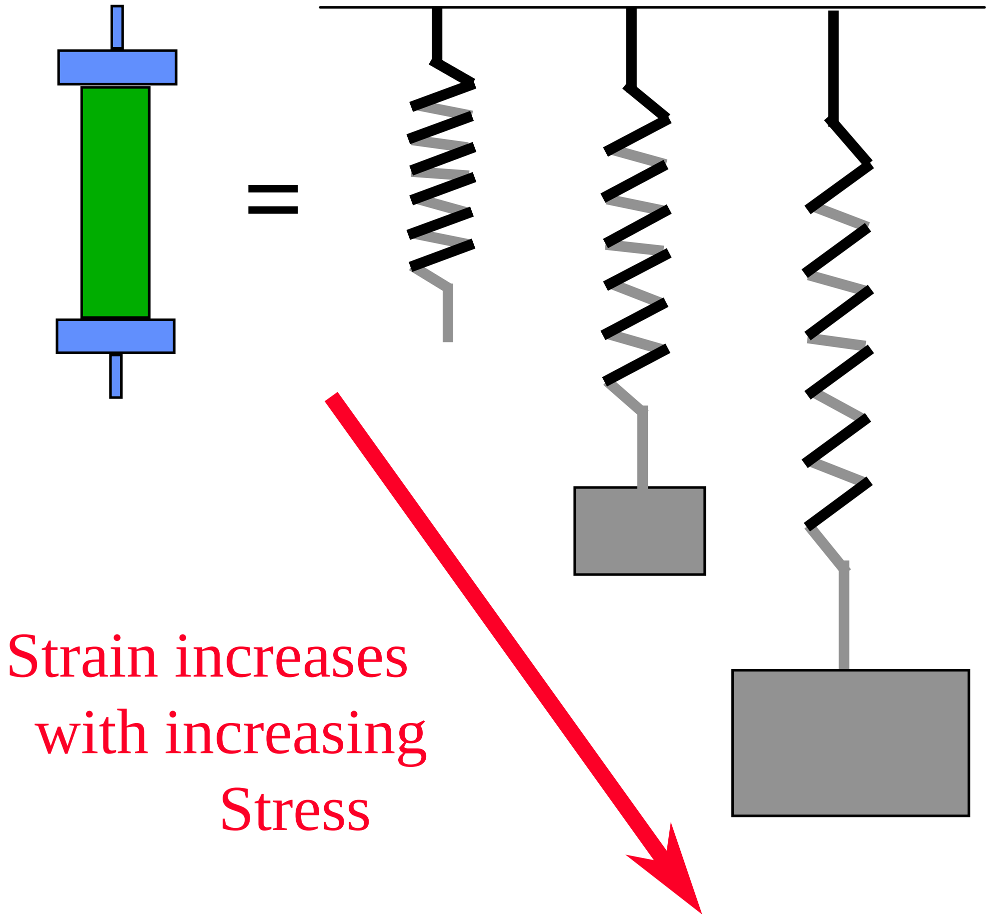
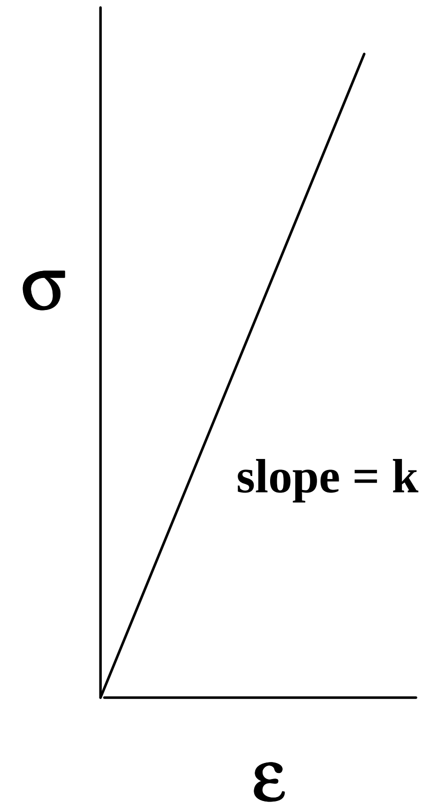
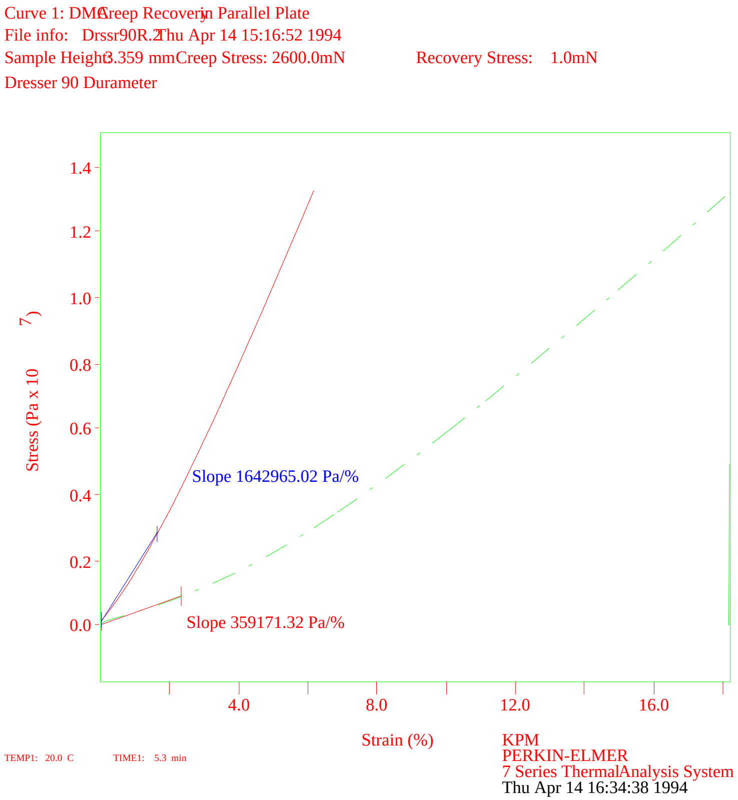
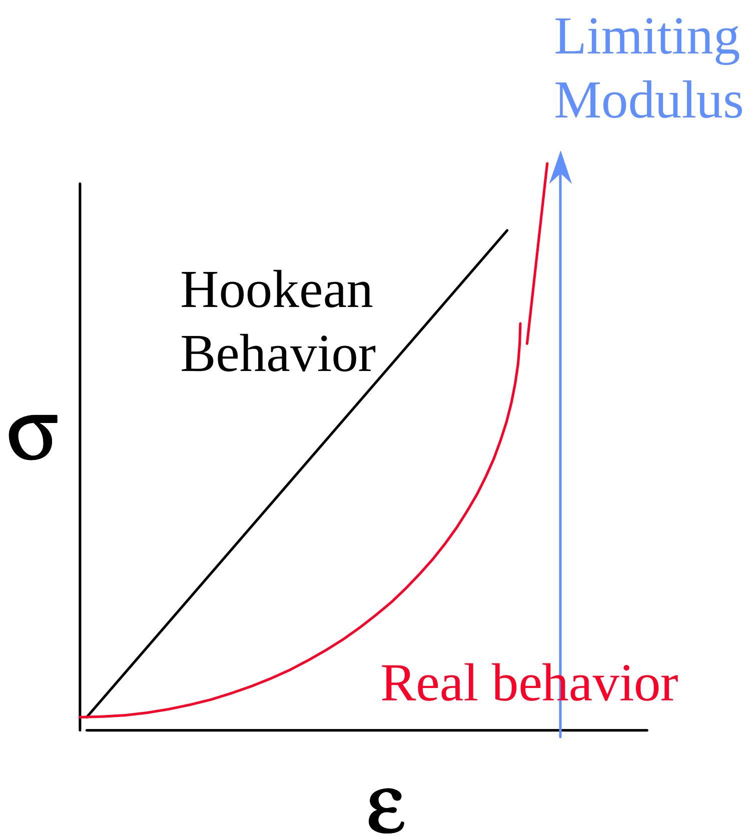
The Elastic Limit: Hooke's Law



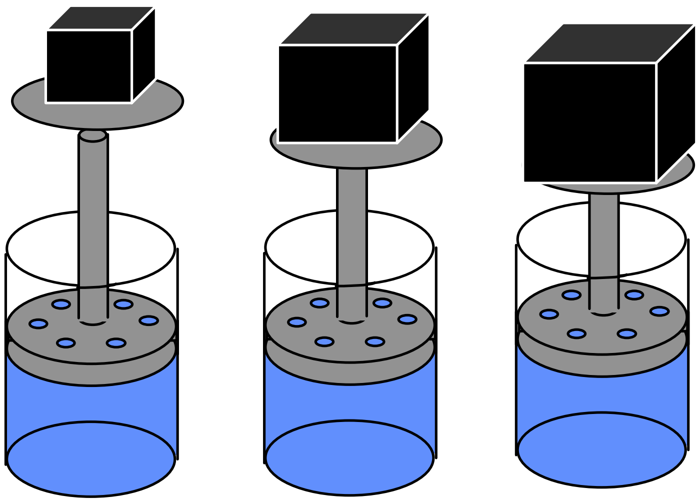


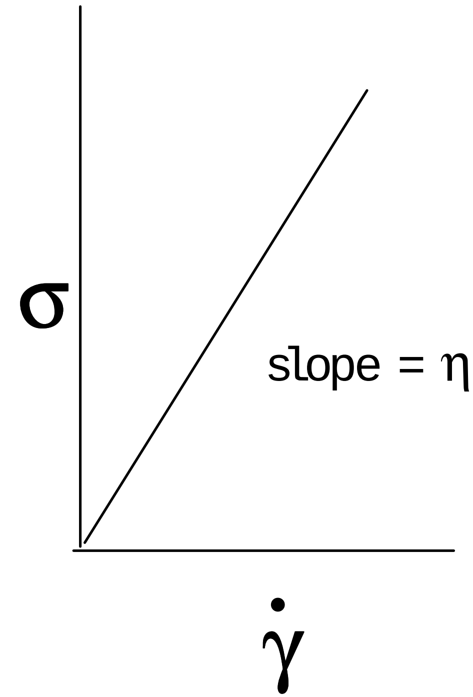
Real vs... Hookean Stress-Strain Curves





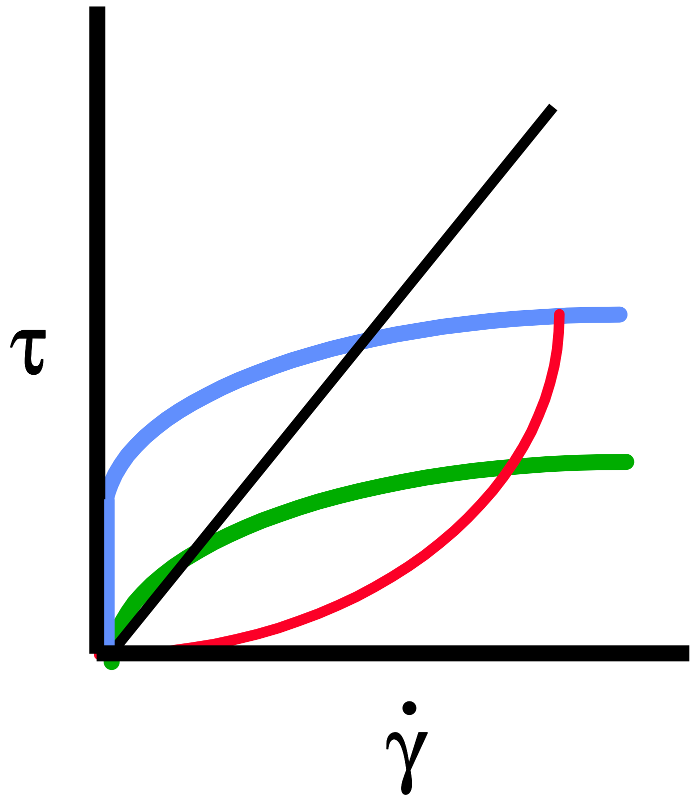
The Viscous Limit: Newtonian Behavior





The speed at which the fluid flows through the holes (the strain rate) increases with stress!!!

Viscosity Effects



- Newtonian behavior is linear and the viscosity is independent of rate.
- Pseudoplastic fluids get thinner as shear increases.
- Dilatant Fluids increase their viscosity as shear rates increase.
- Plastic Fluids have a yield point with pseudoplastic behavior.
- Thixotrophic and rheopectic fluids show viscosity-time nonlinear behavior. For example, the former shear thin and then reform its gel structure.

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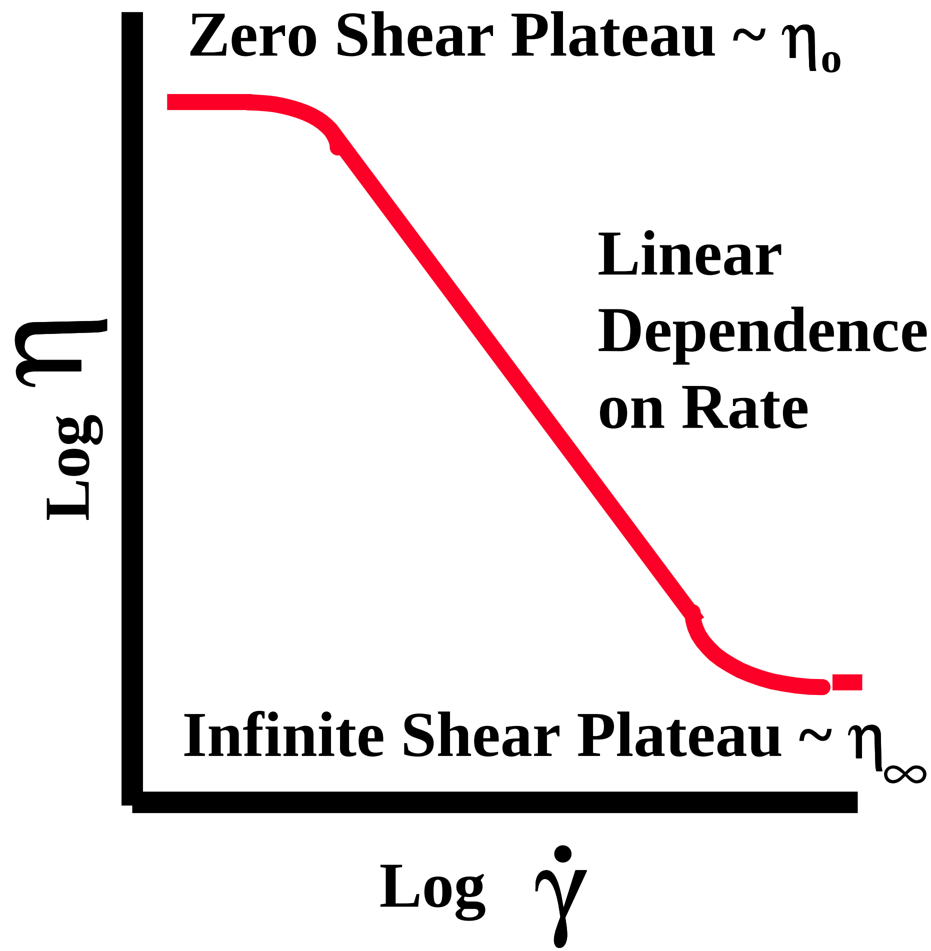
Polymers are Non-Newtonian Fluids!!!



- At low shear rates, the viscosity is controlled by MW. The material shows Newtonian behavior
- Viscosity shows a linear dependence on rate above the η_o region.
- At high rates, the material can no longer shear thin and a second plateau is reached.

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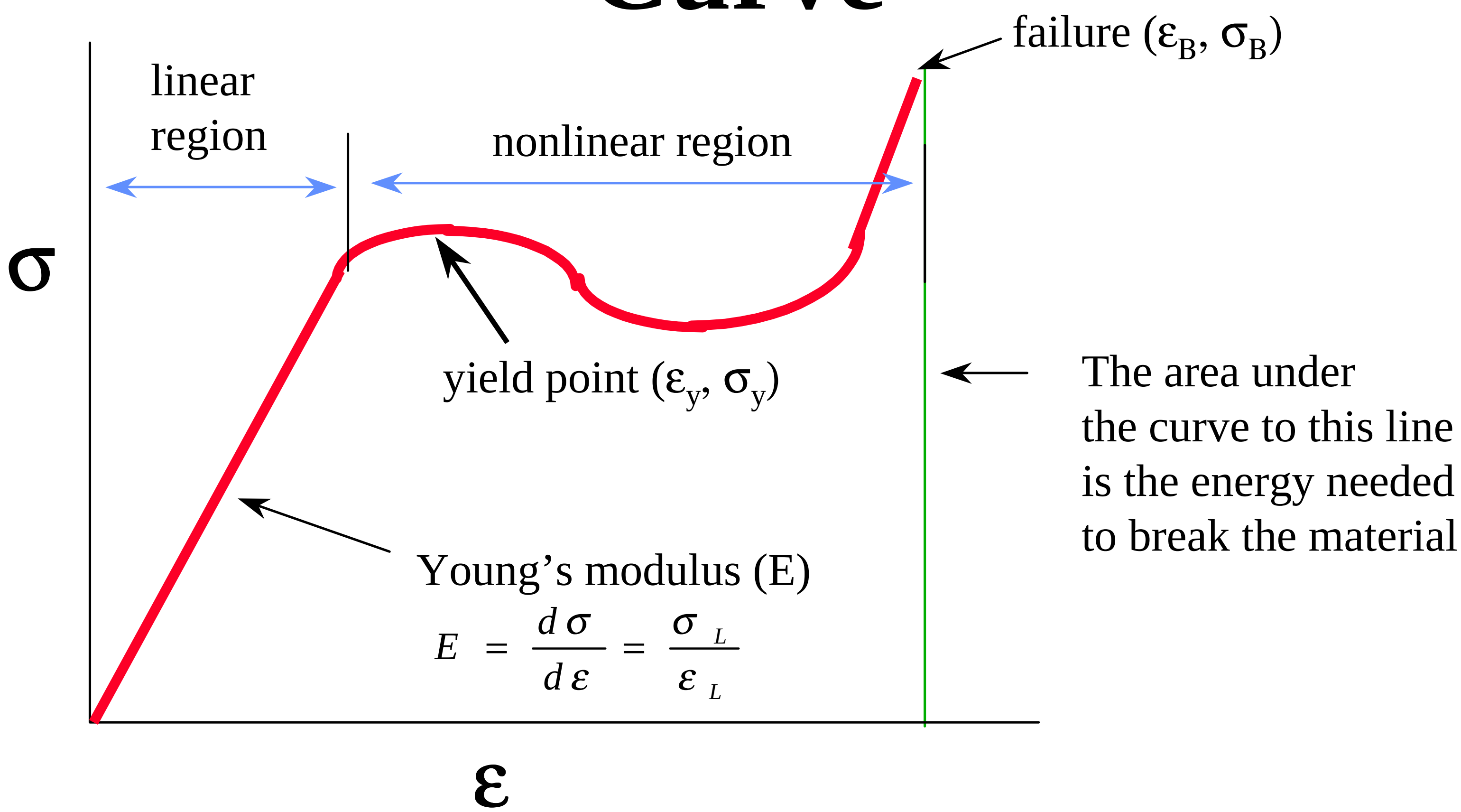
Analyzing a Stress-Strain Curve



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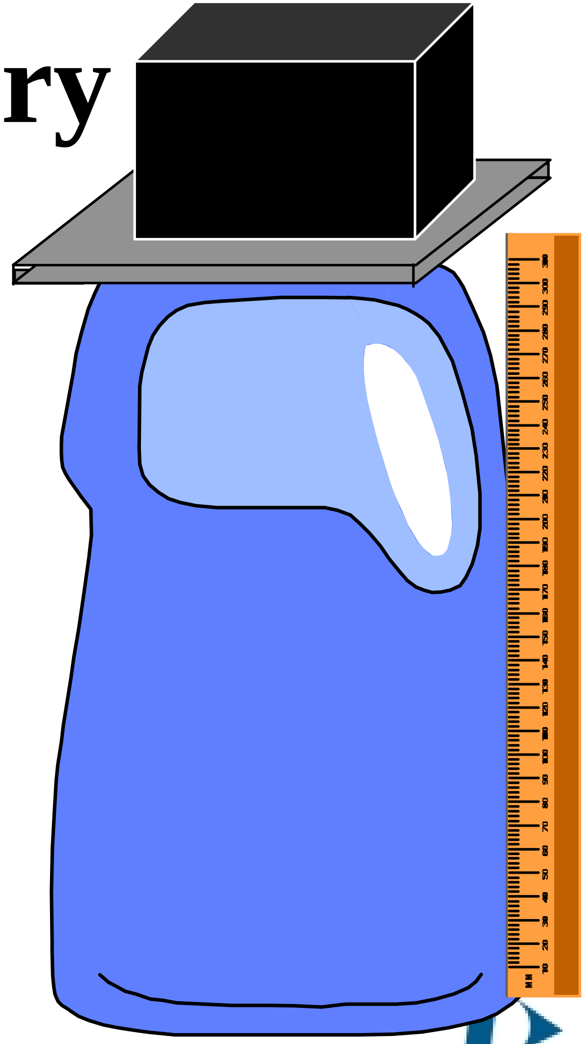
Under Continuos Loads: Creep Recovery



- Applying a constant load for long times and removing it from a sample.
- Allows one to see the distortion under constant load **and** also how well it recovers.

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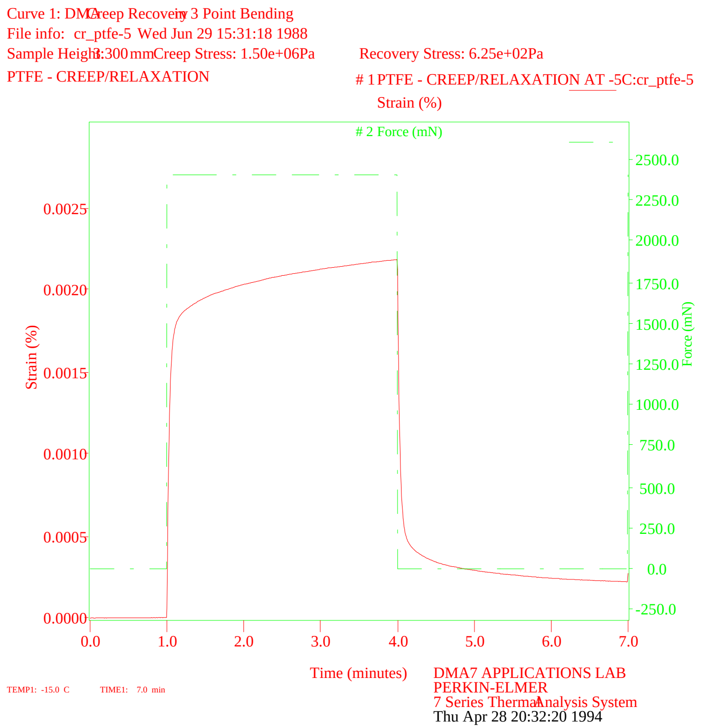
Creep is a fundamental engineering test.

- Creep is used as a basic test for design.
- By looking at both the creep and recovery parts of the curve, we can begin to examine how polymers relax.



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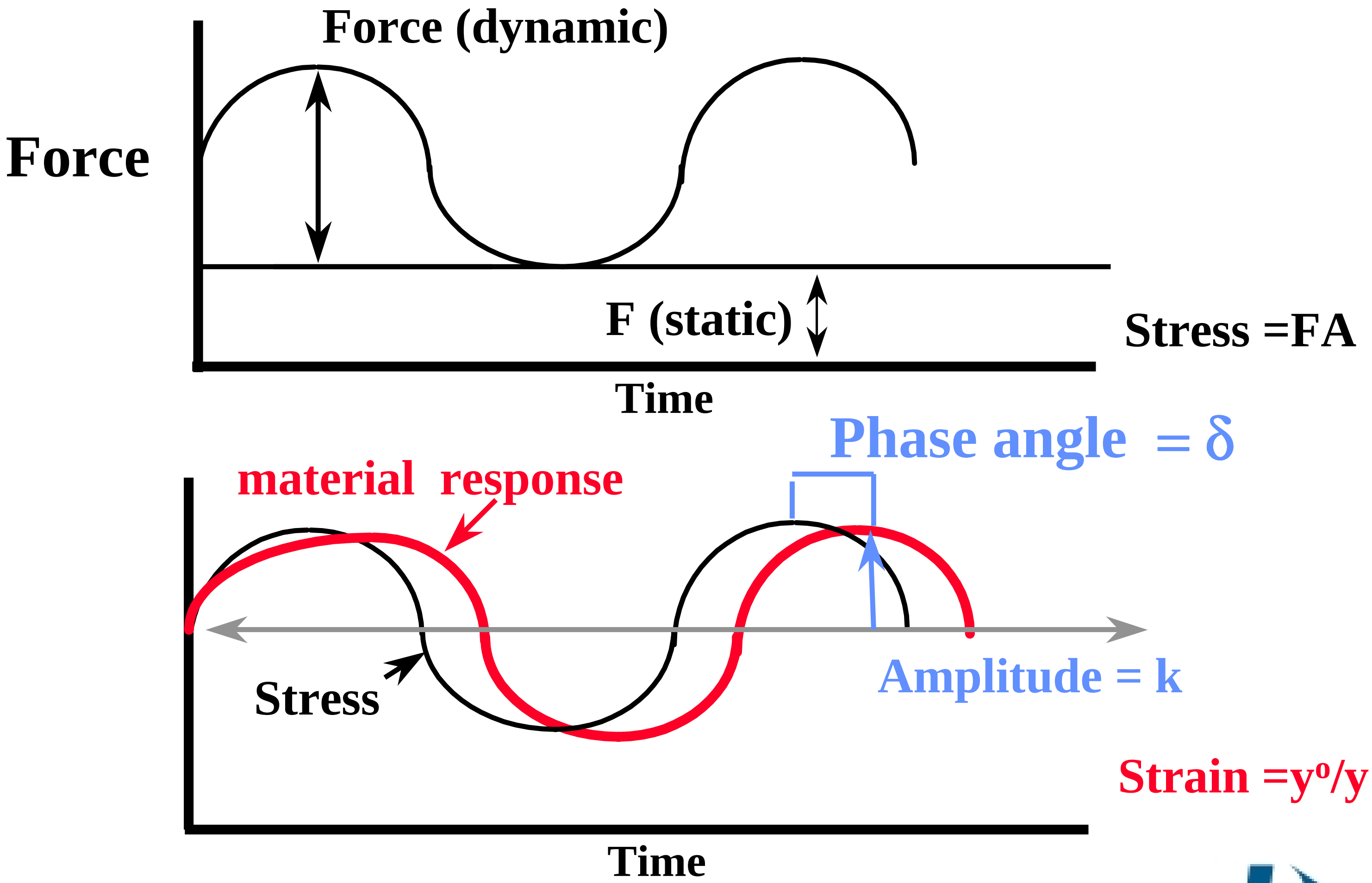
Dynamic Stress



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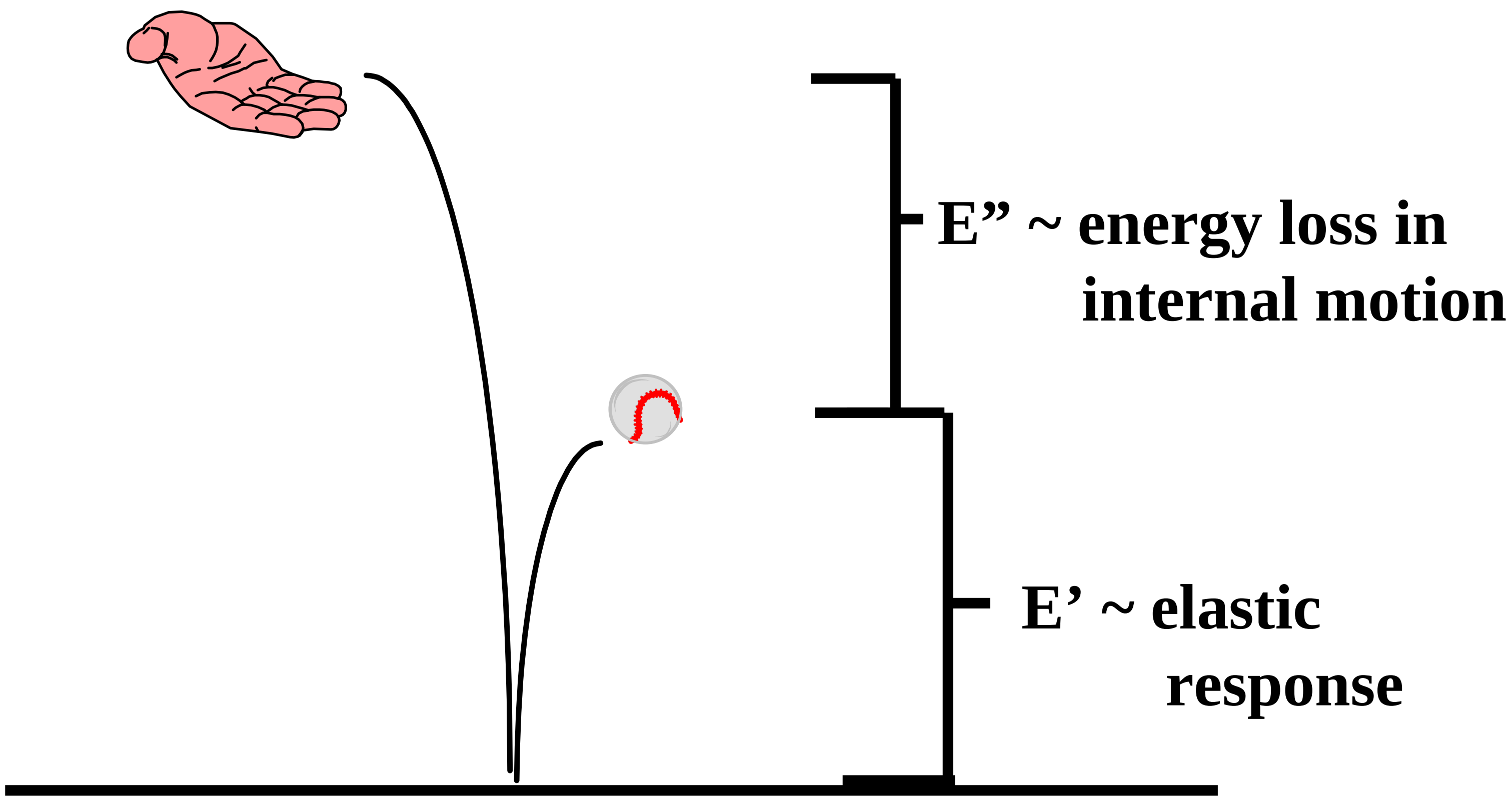
Why? Let’s bounce a ball.



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All this is calculated from δ and k:

- From k, we calculate E' (storage modulus)
- From δ, we calculate E'' (loss modulus)
- then:

$$\tan\delta = E''/E'$$

$$E^* = E' + iE'' = \mathrm{SQRT}(E'^2 + E''^2)$$

$$G^* = E^*/2(1+\nu)$$

$$\eta = 3G^*/\omega$$

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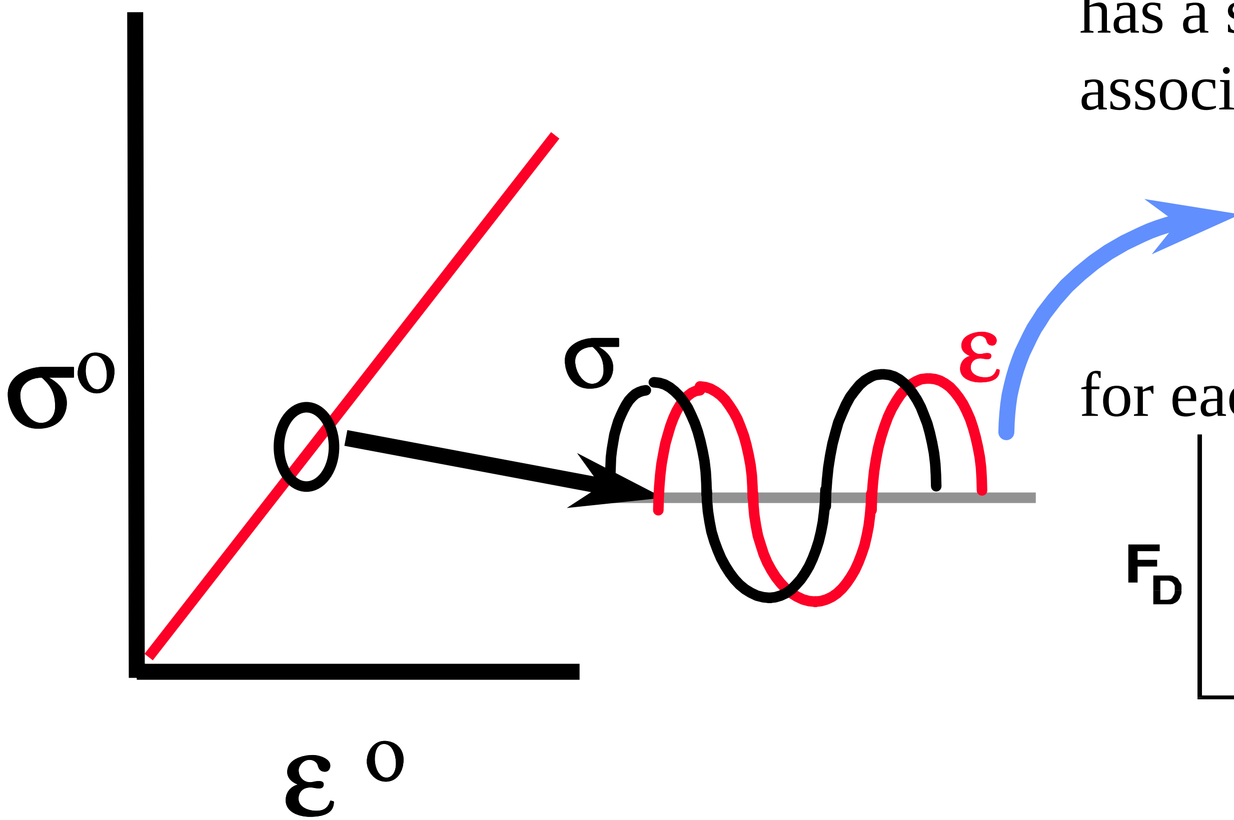
To apply this to materials...

Dynamic Stress Scan



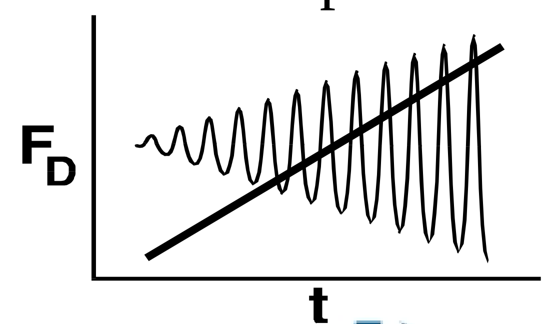
Since each part of the ramp has a sine wave stress associated with it, we get:

tan δ

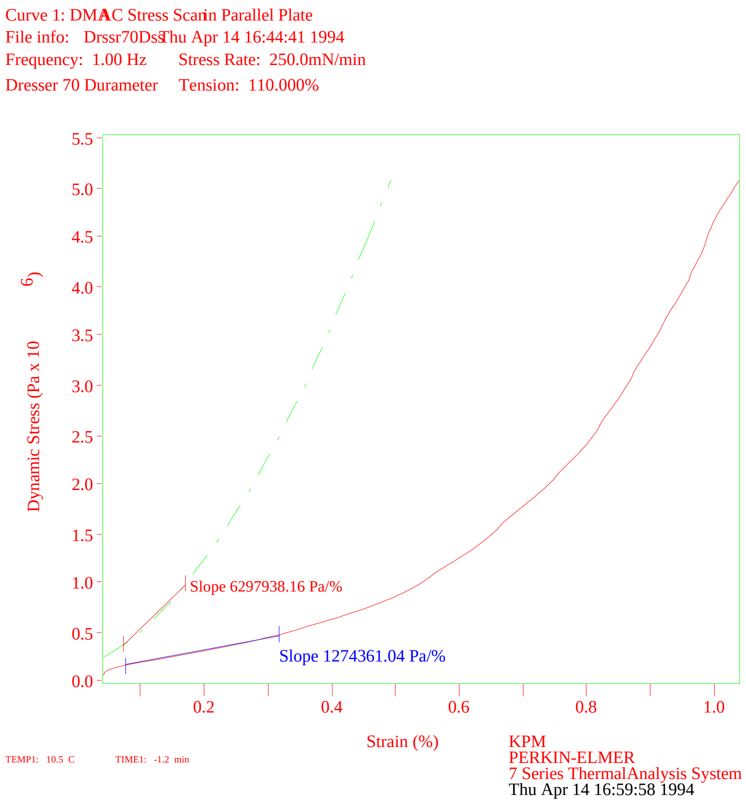
E^*, E', E"

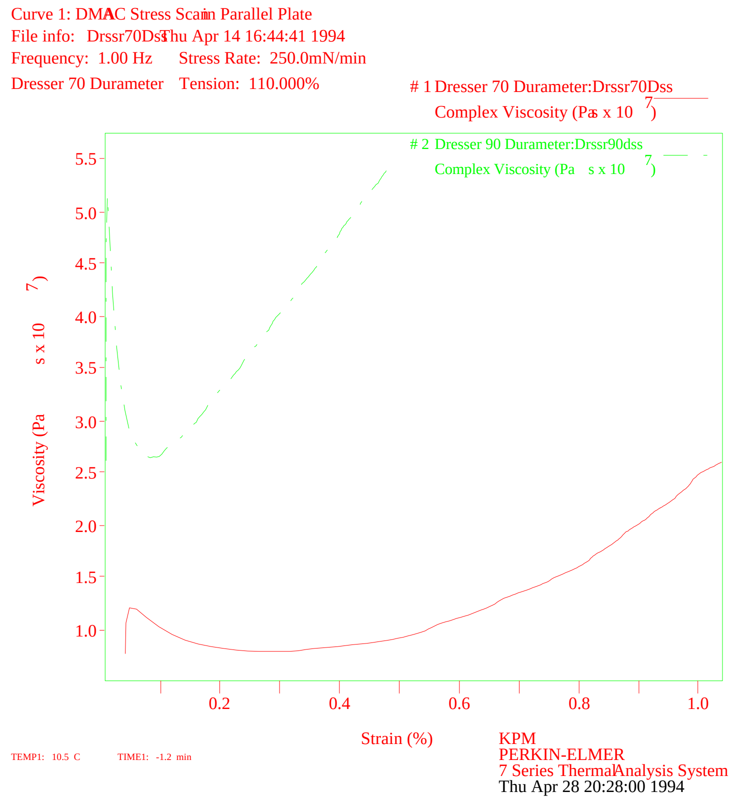
η

for each data point!!



For example, DSS Curves





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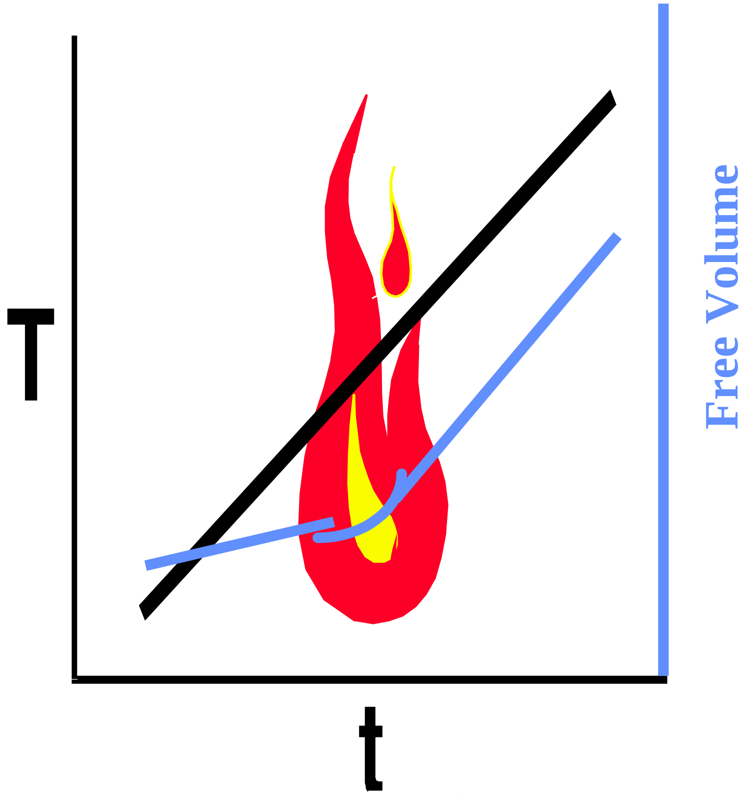
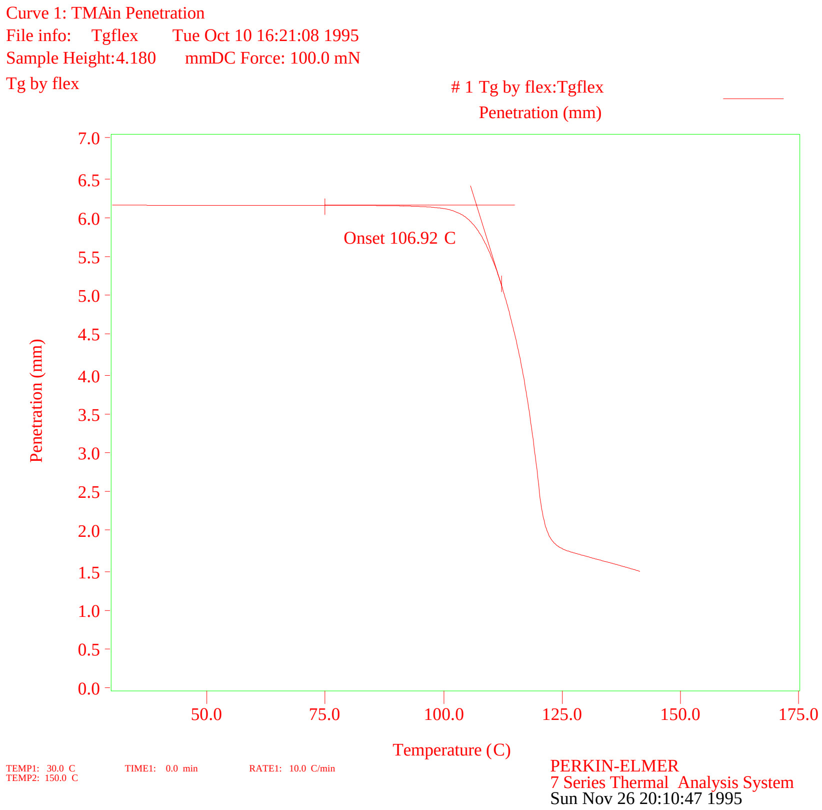
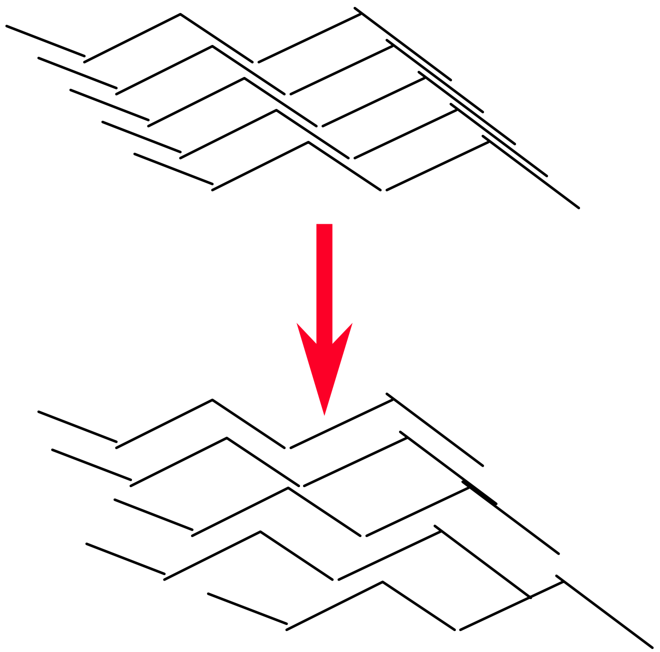
Now, let's induce temperature as a variable.

- We can heat the material under minimal load at a calibrated rate.
- This allows the material to change with temperature.
- These changes can be described in terms of free volume or relaxation times.

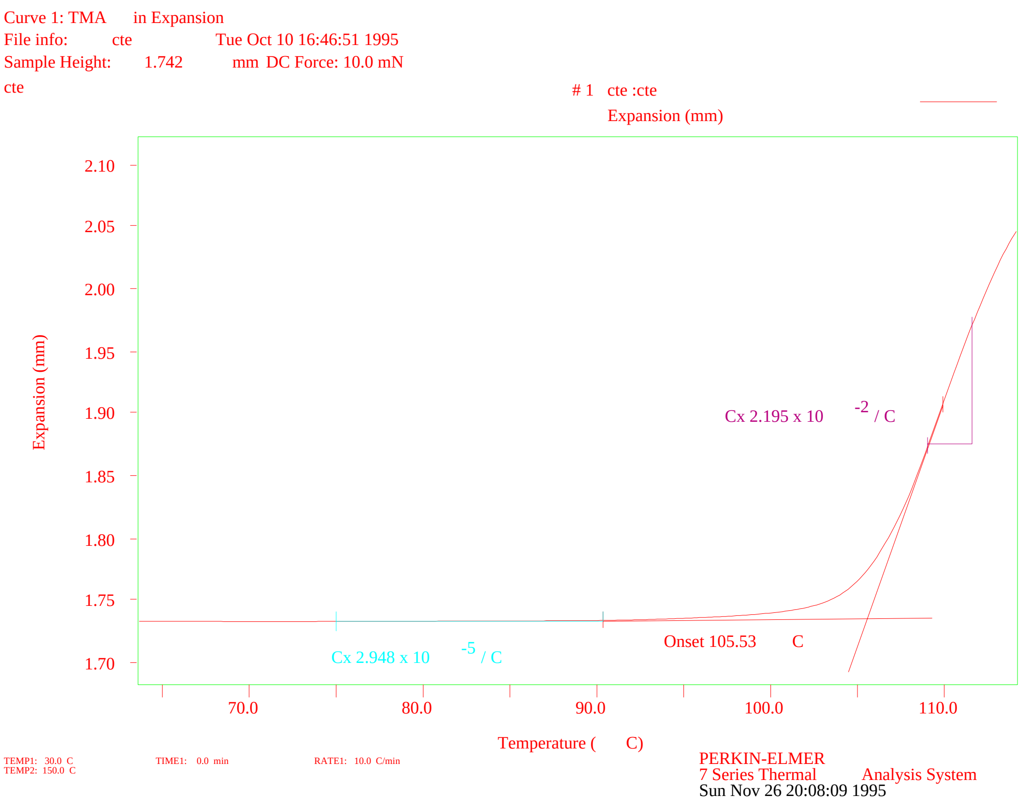


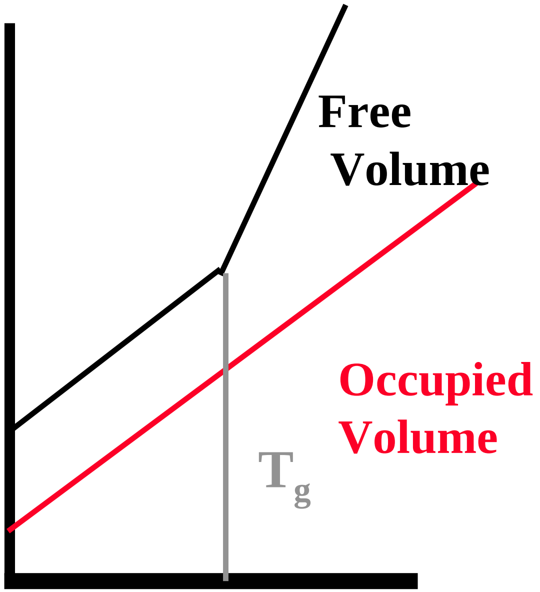
Thermomechanical Analysis as a starting Point.



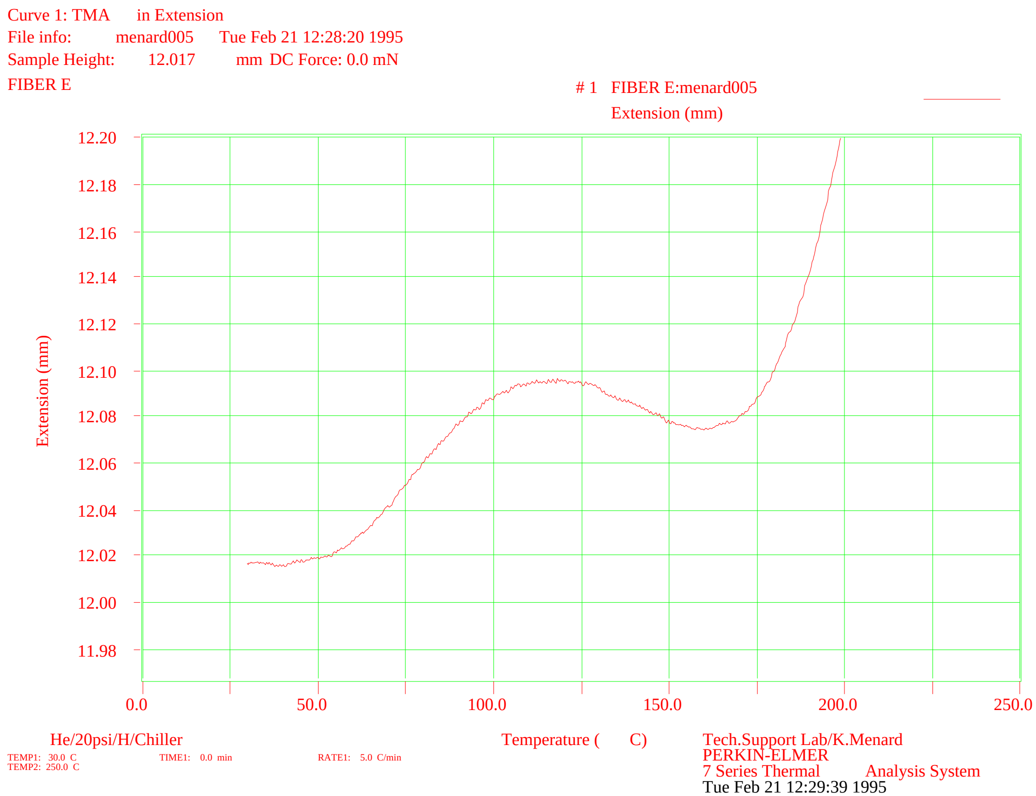


TMA - It's all free volume.





And it’s not just Tg.



(the traditional way to do heat set)

Time Temperature Scans at a Fixed Frequency

- hold frequency constant and vary temperature or time at temperature
- allows detection of transitions in material
- allows one to study cures
- most sensitive method for finding Tg
- can also get changes in dimension (TMA) while collecting DMA data
- Best probe of polymer relaxations as function of temperature

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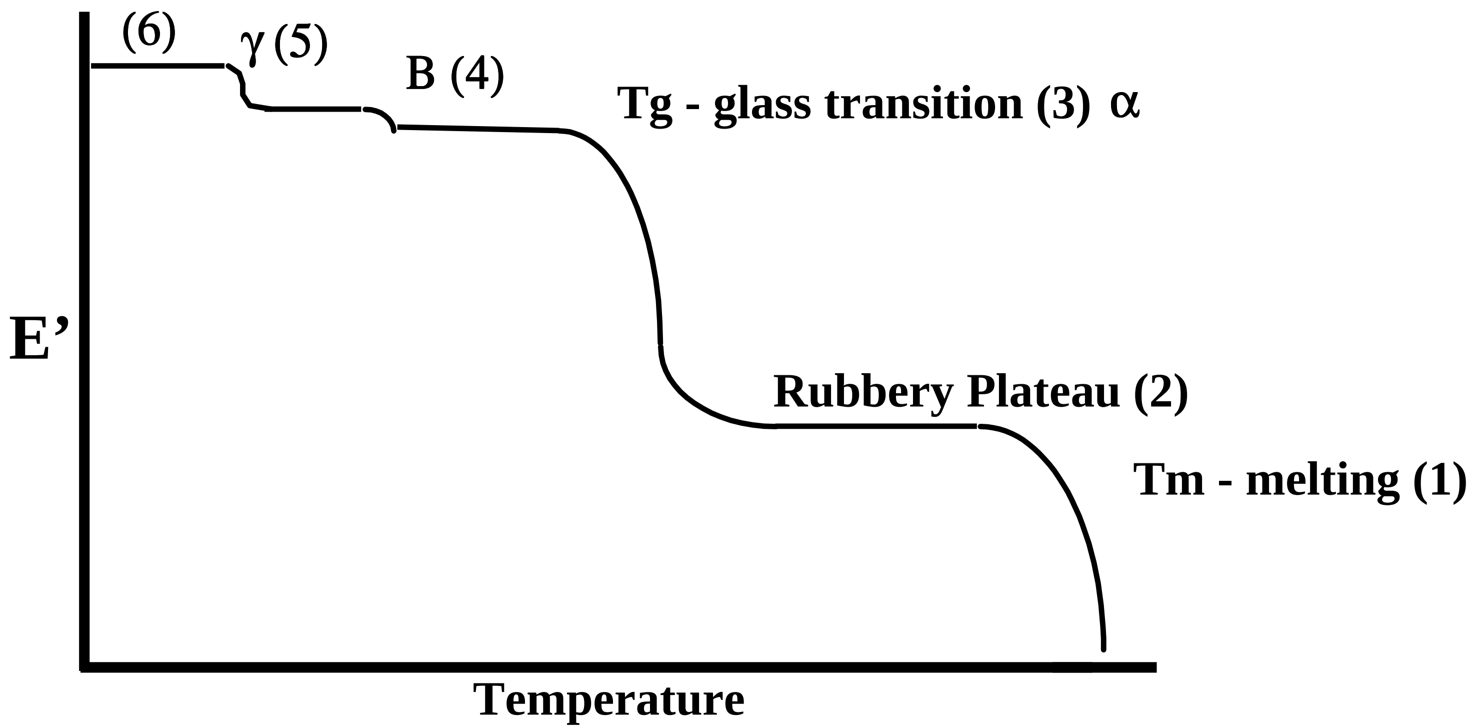
Idealized Multi-Event DMA Scan



(6)	(5)	(4)	(3)	(2)	(1)
local motions	**bend and stretch**	**side groups**	**gradual main chain**	**large scale chain**	**chain slippage**

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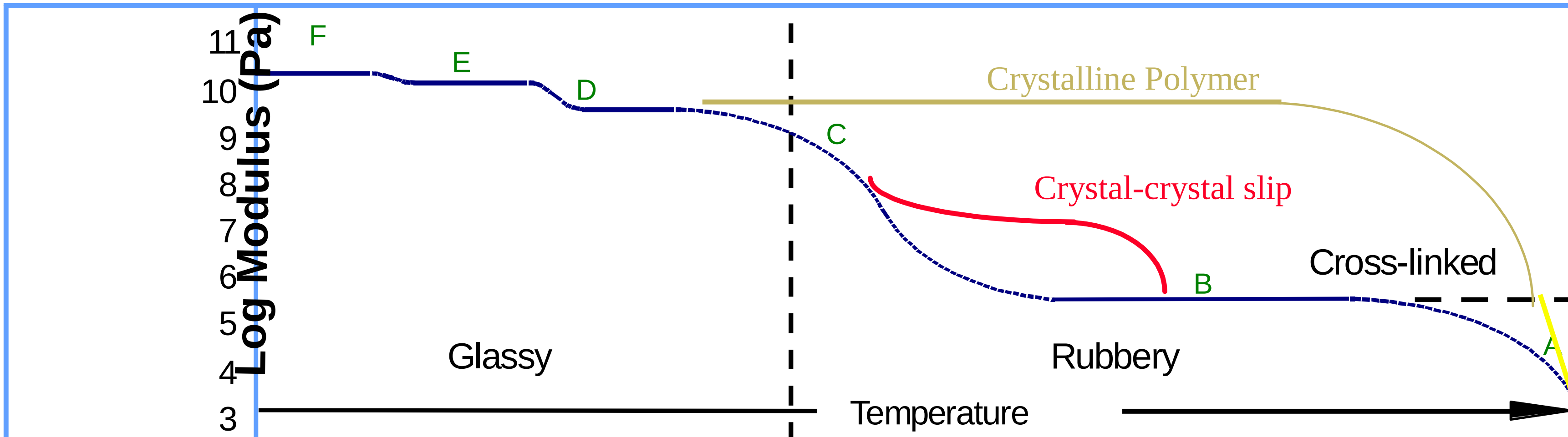
In more detail...



	F	E	D	C	B	A
Deformation	Secondary Dispersion	Hookean Behavior (gamma)	Second Transition (beta)	Primary Transition (alpha)	Highly Visco Elastic (rubbery)	Flow (melt)
Molecular Motion	Localized Motion	Bend & Stretch Bonds	Side Groups	Main Chain Gradual	Main Chain Large Scale Mobility	Chain Slipping
Unstrained State						
Strained State			Increasing			

R. Seymour, 1971

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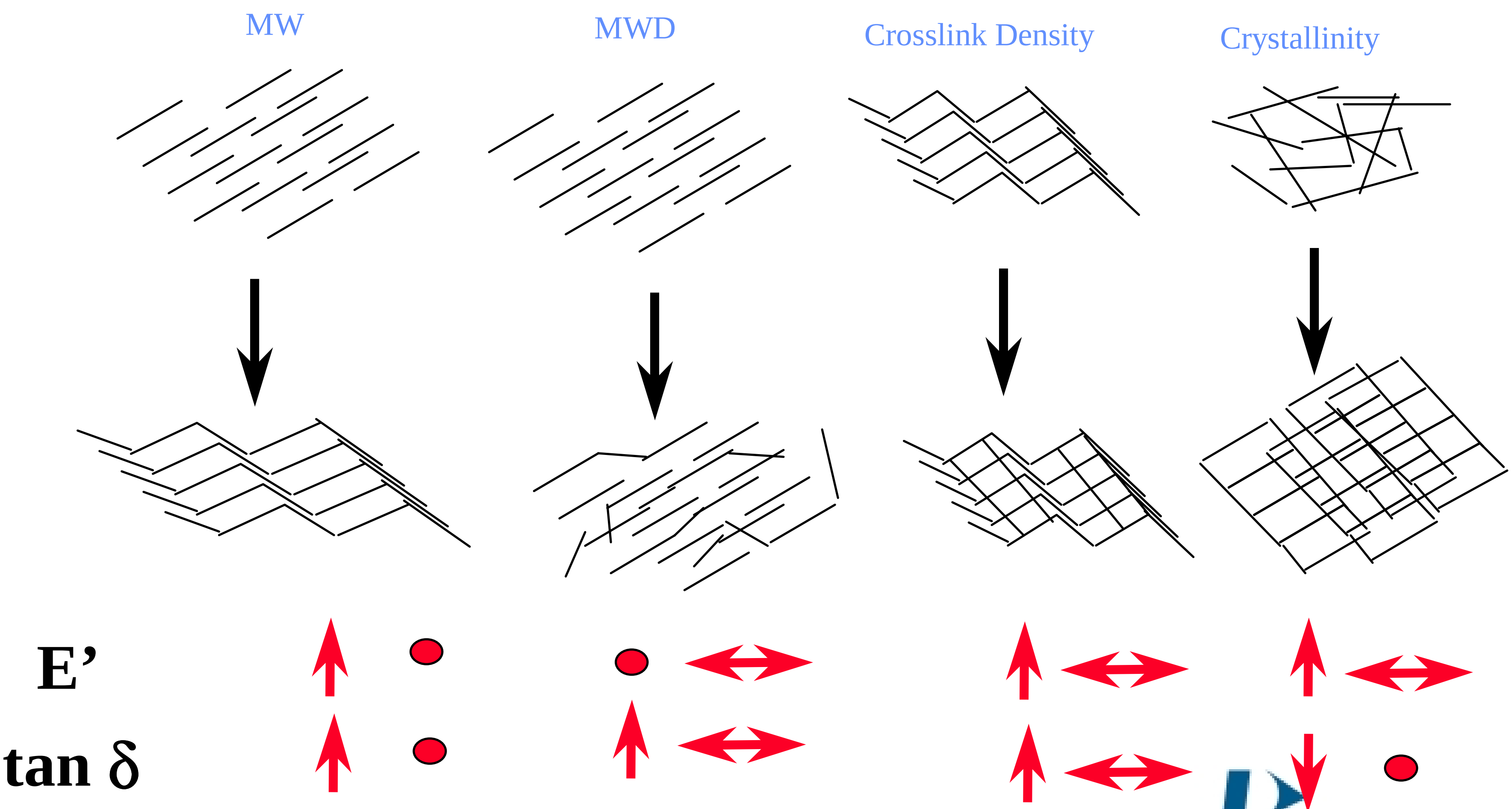
Common changes show as:



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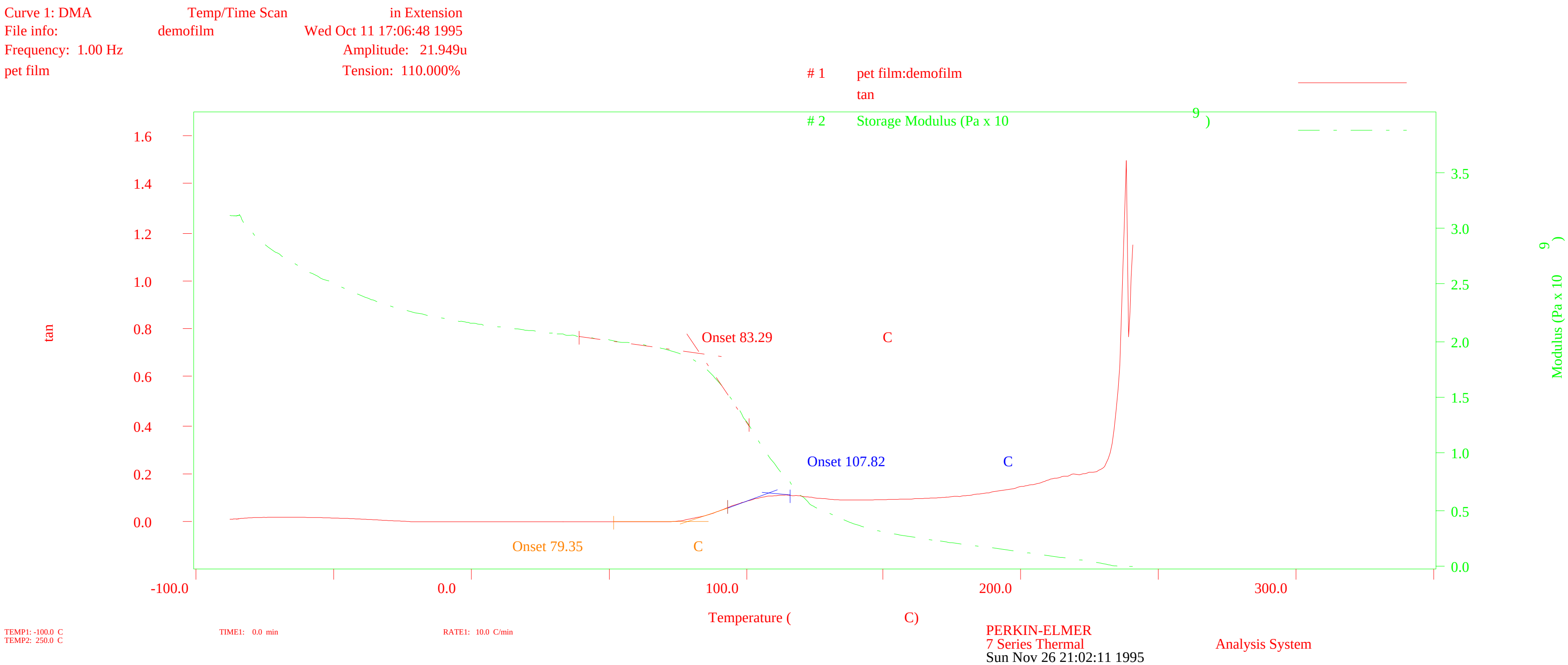
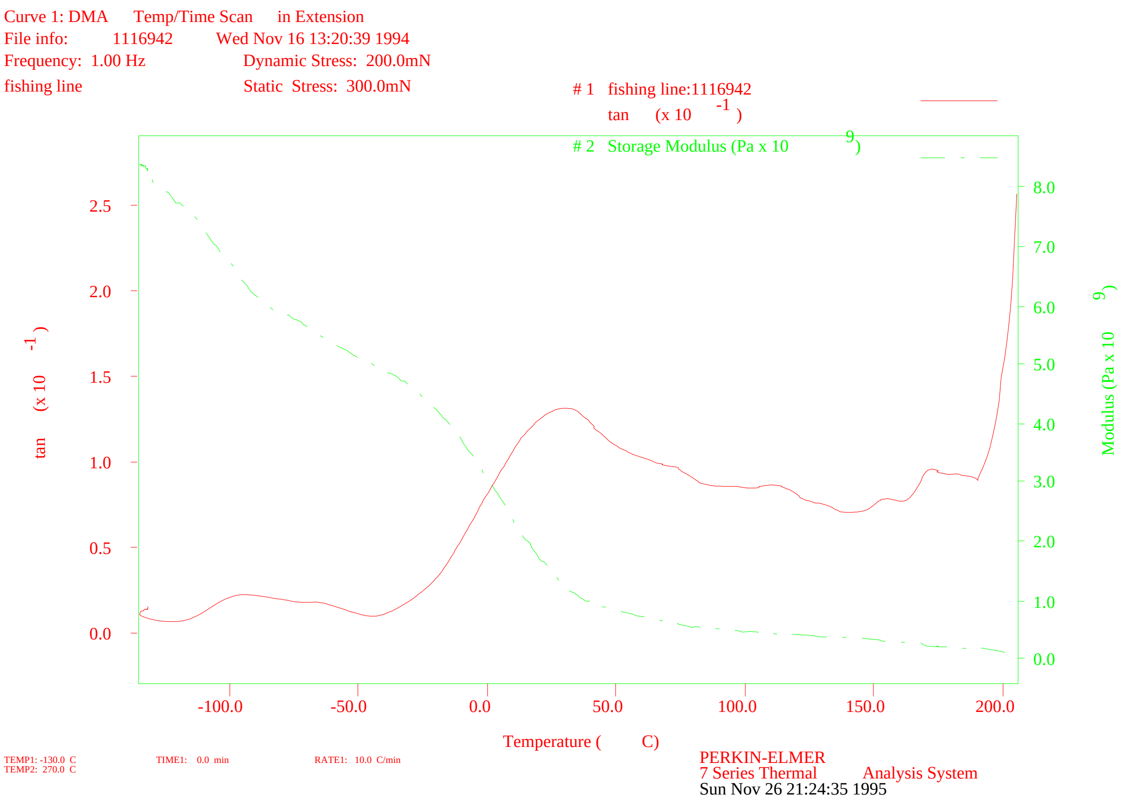
Tg are easily seen, as in PET Film



or in PP fishing line.



Sample prep can be minimal if only temperatures are needed.

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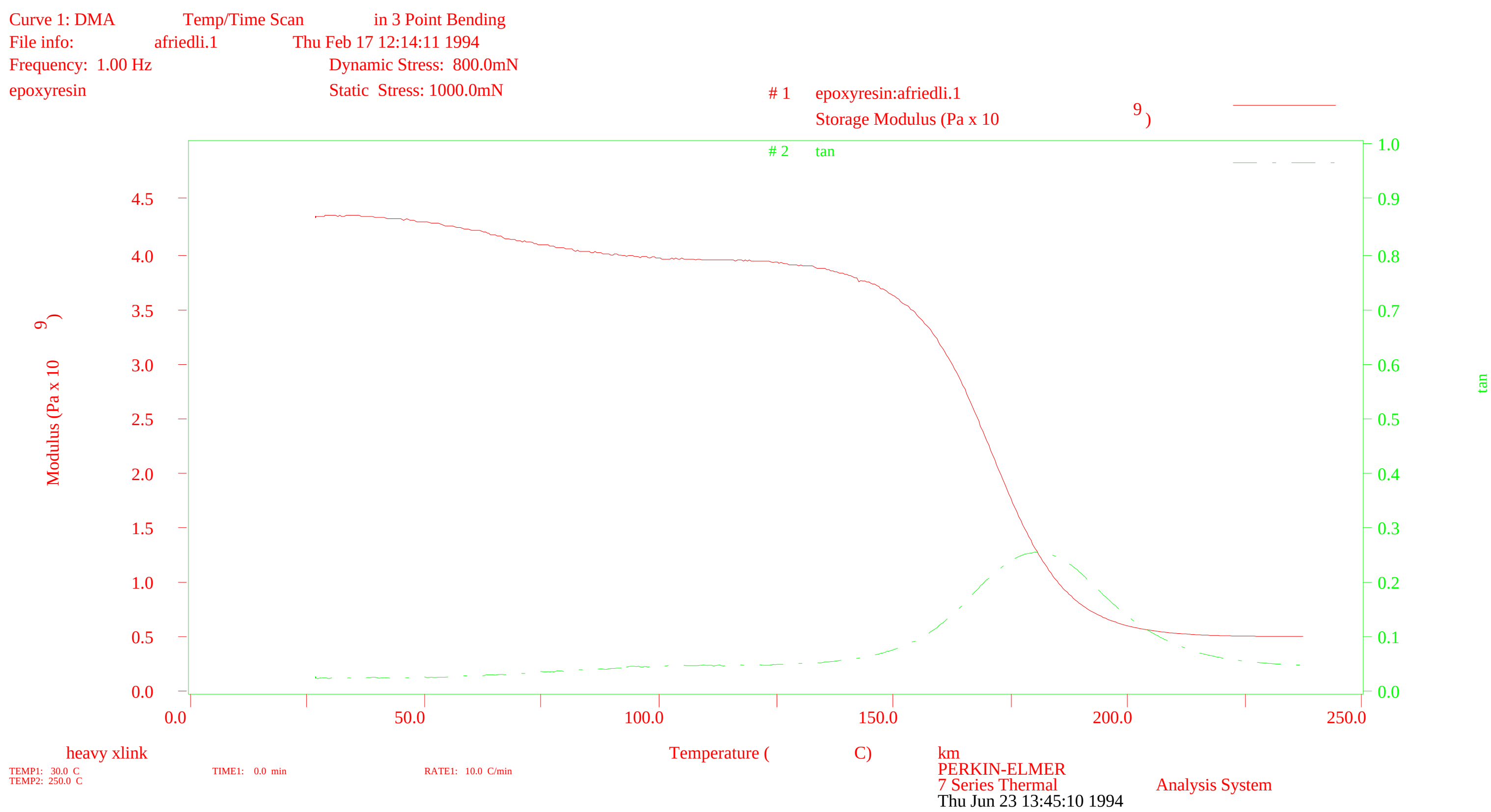
Transitions are clearly seen in highly crosslinked samples



This T_g is undetectable in the DSC !!!!!!

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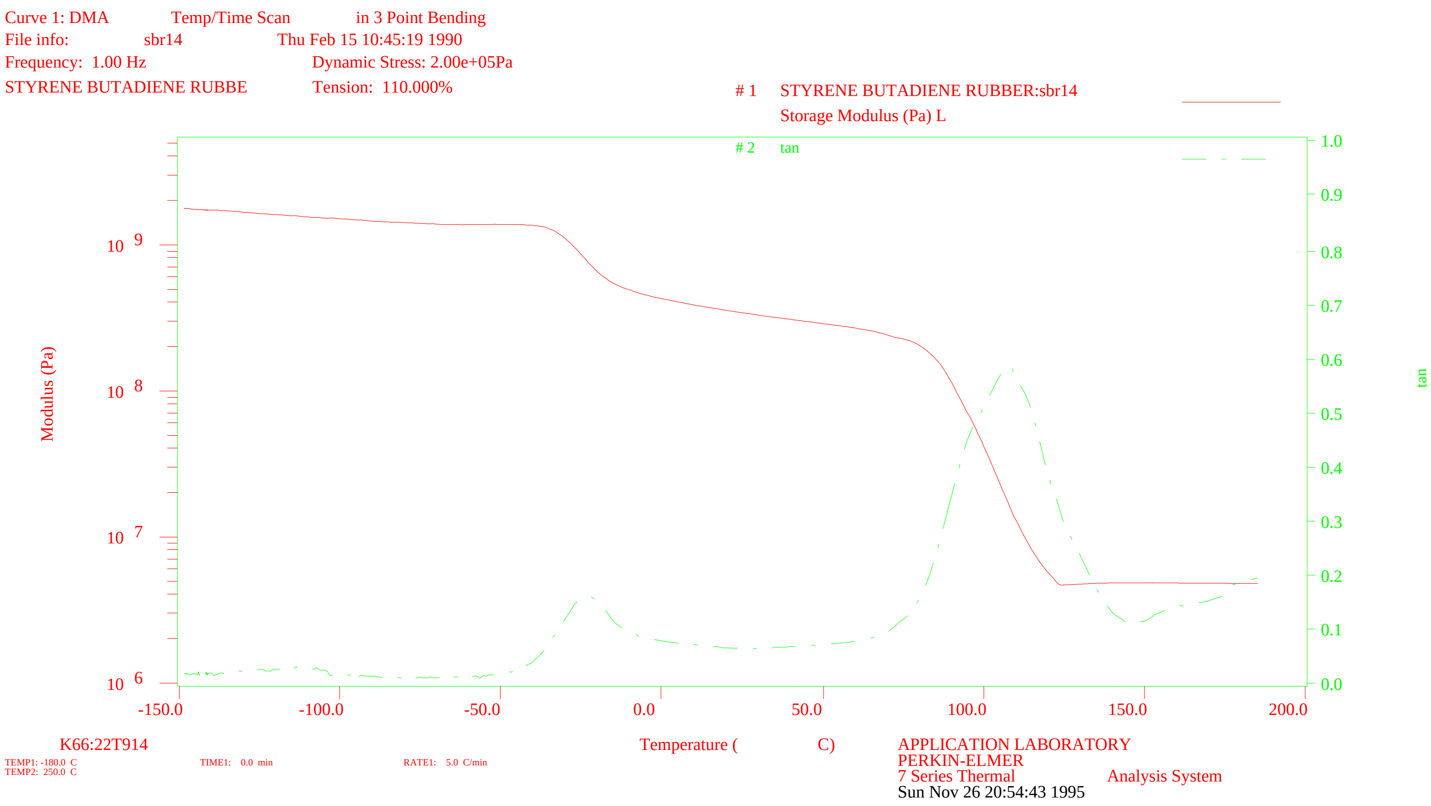
as well as in blends.



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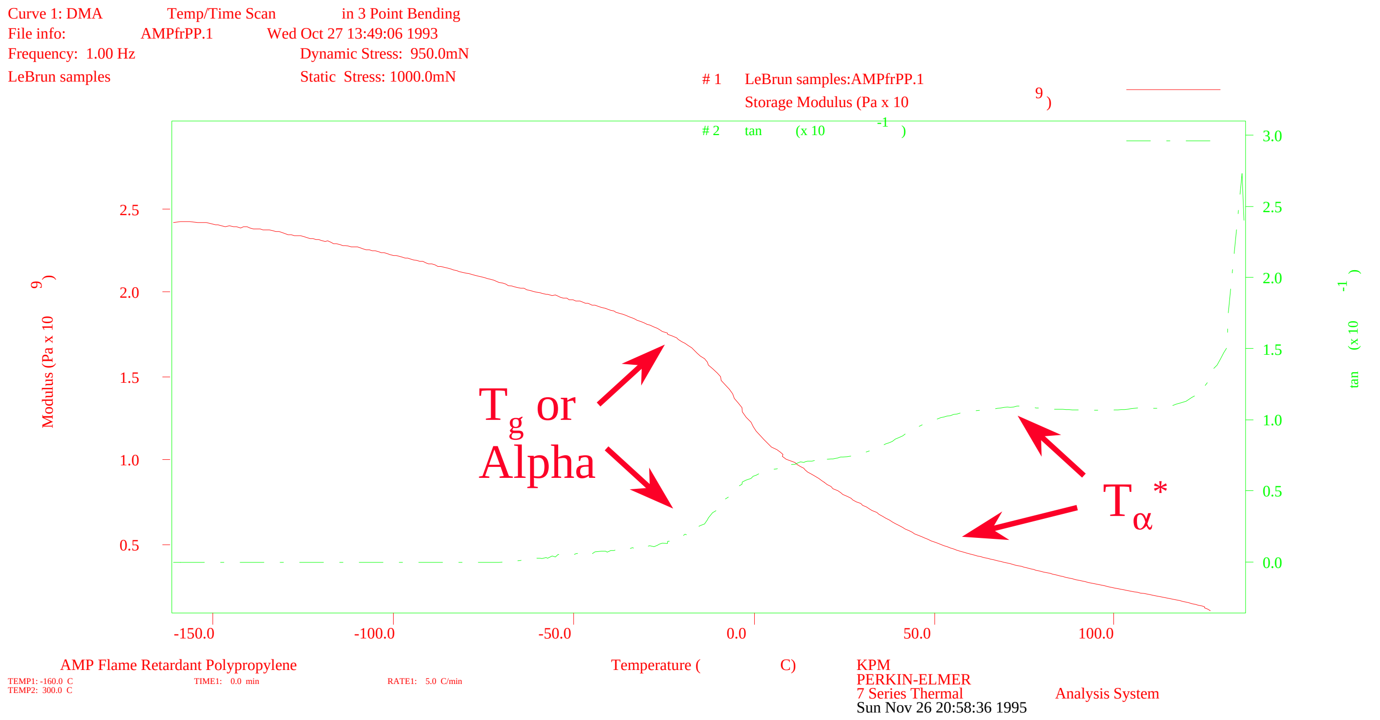
It's not always so simple:

For example, crystal-crystals slips can cause α^* transitions



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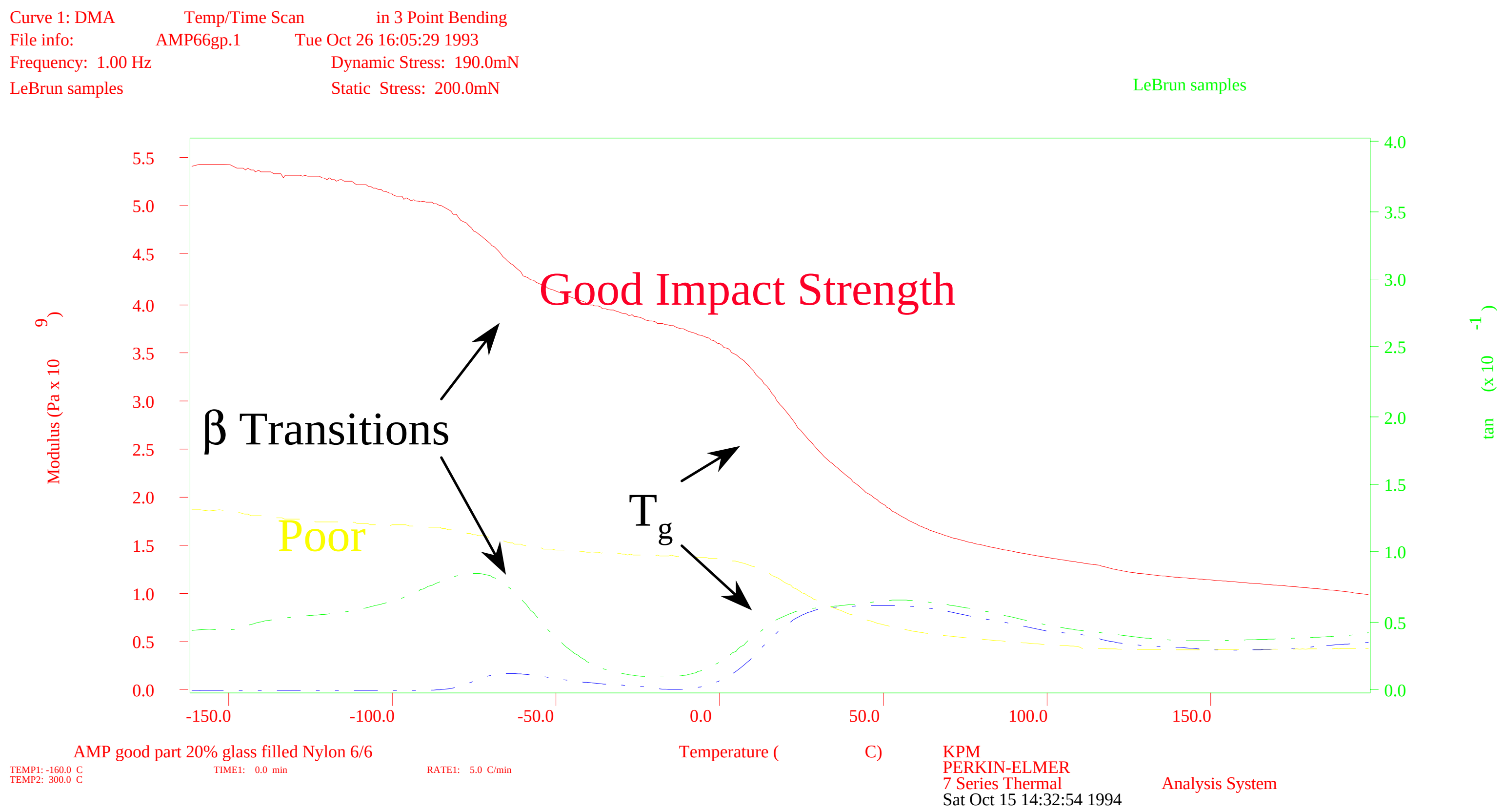
Higher Order Transitions affect toughness



Impact was good if T_g/T_β was 3 or less.

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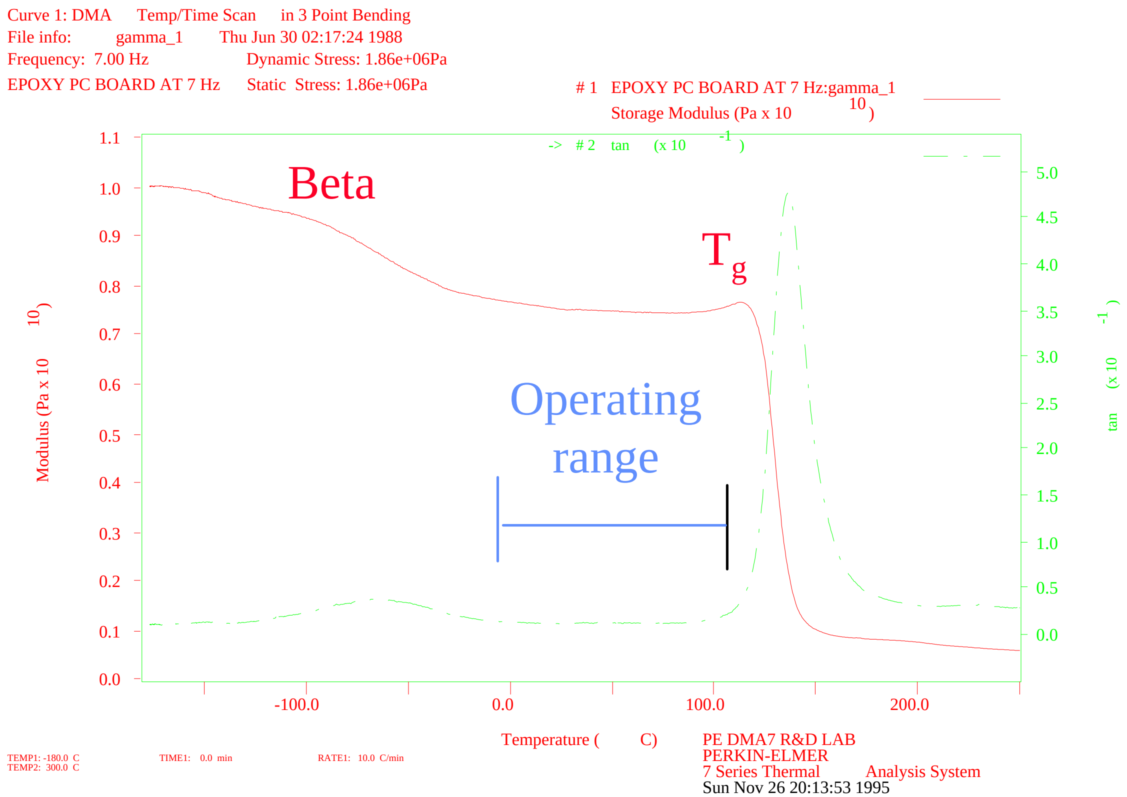
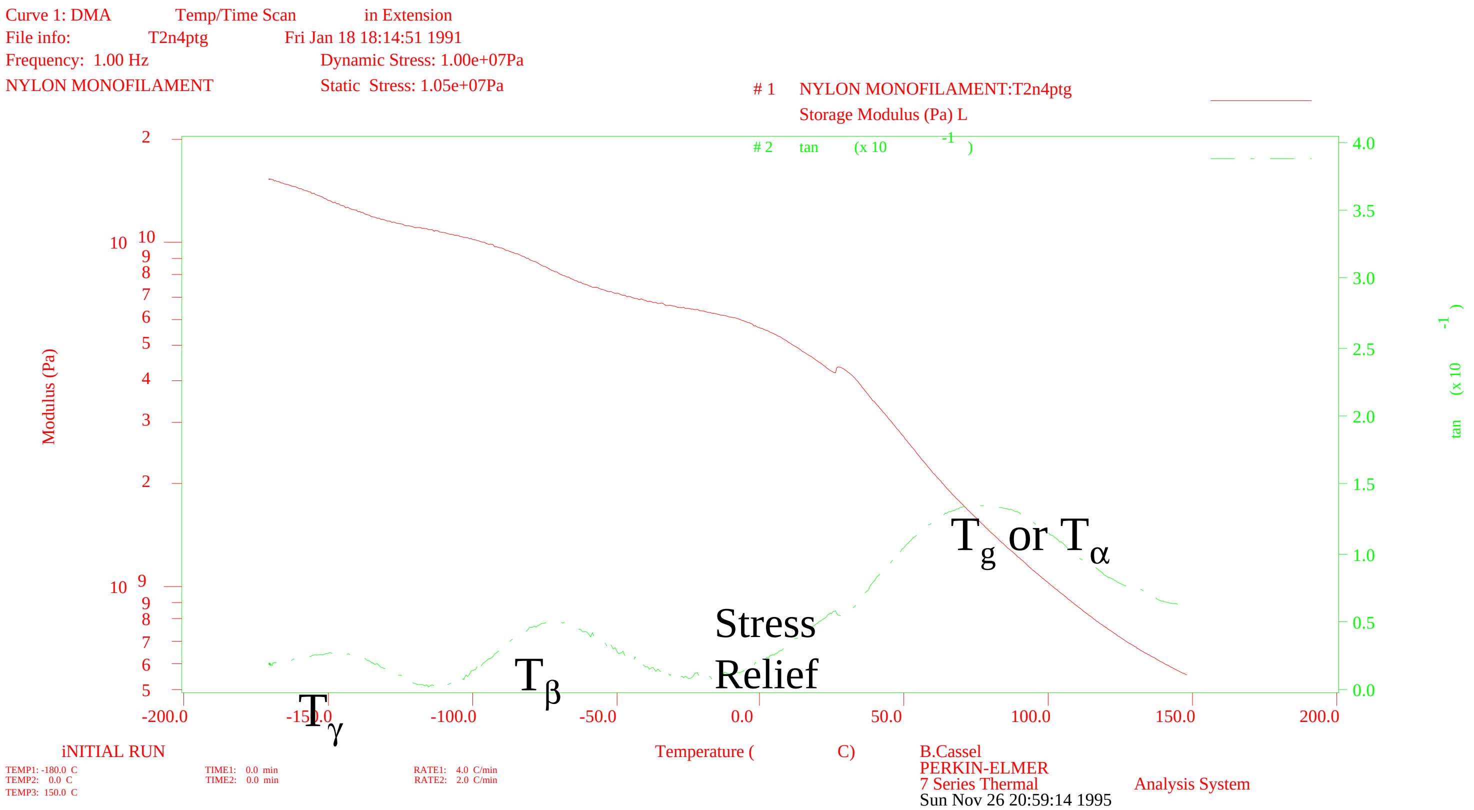
...and also define operating range.



It can get complex...



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Curing of Thermosets

- can be studied at constant temperature or by a temperature ramp
- can get minimum viscosity, gelation point (time), vitrification point, and activation energies from DMA curve
- can adapt instrument to do simultaneous DEA-DMA to follow cure to completion
- cure studies are not limited to polymeric systems but include food products like cakes and cookies

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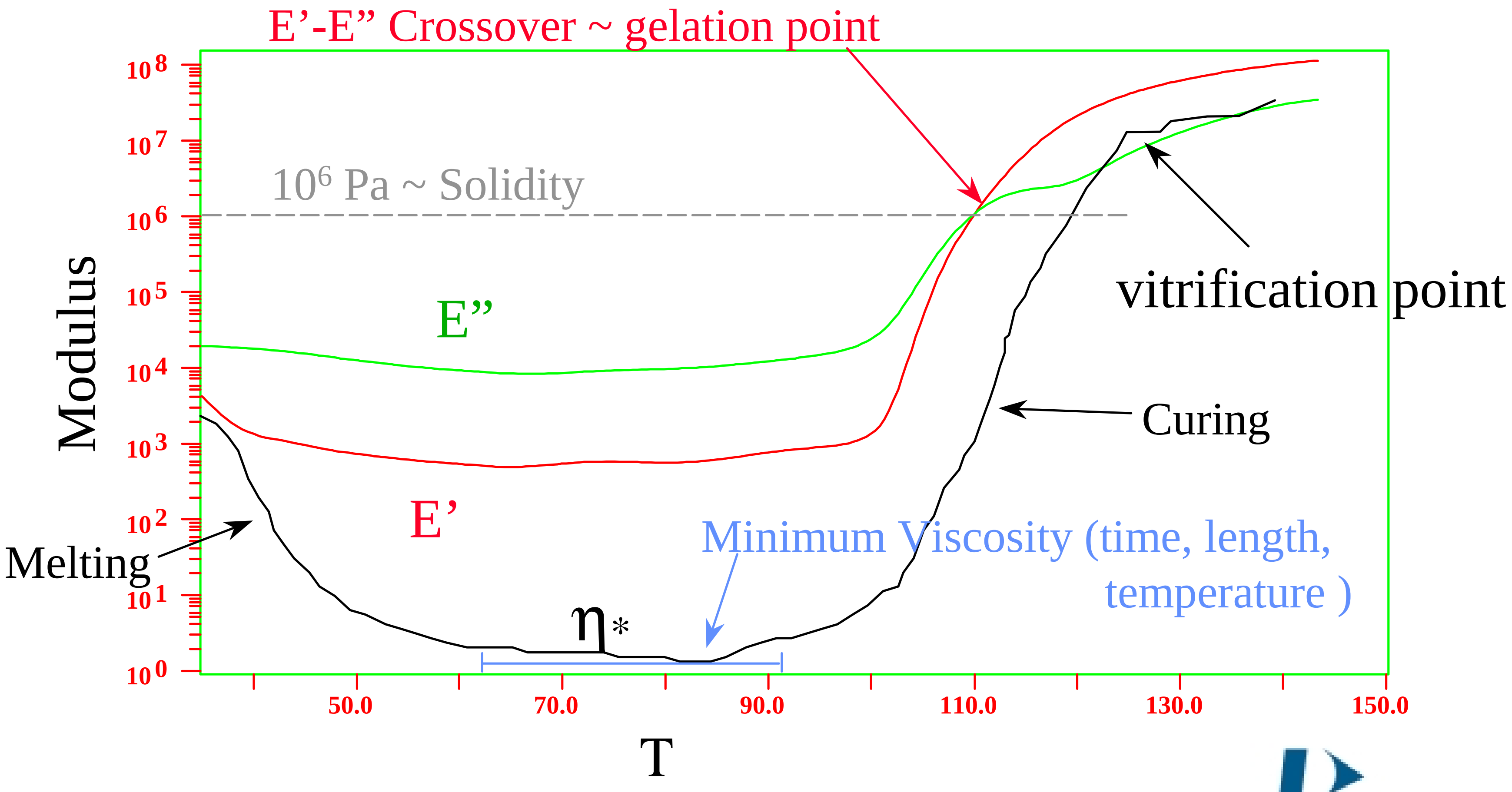
Analysis of a Cure by DMA



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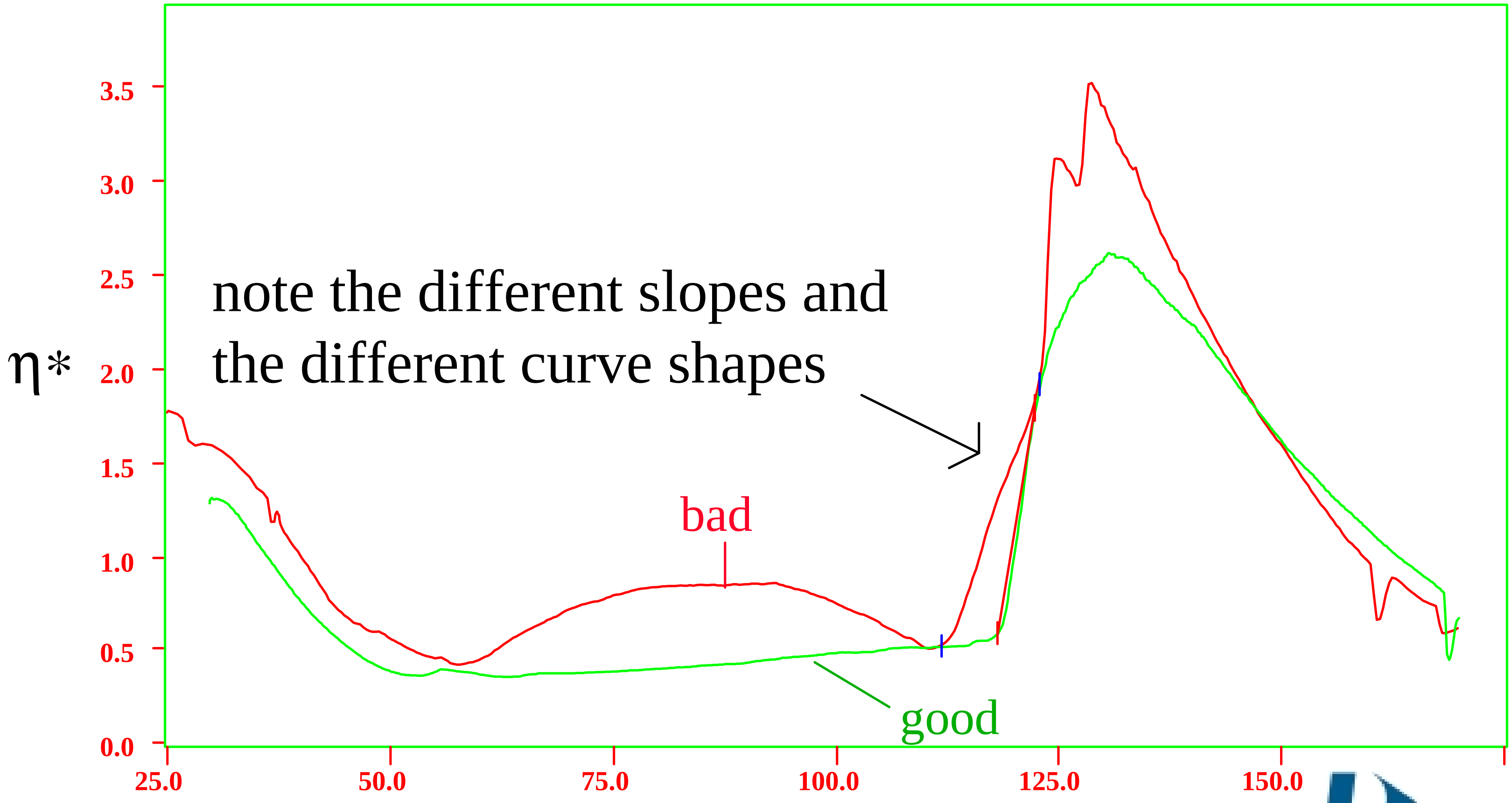
QC can often be done by simply fingerprinting the resin.



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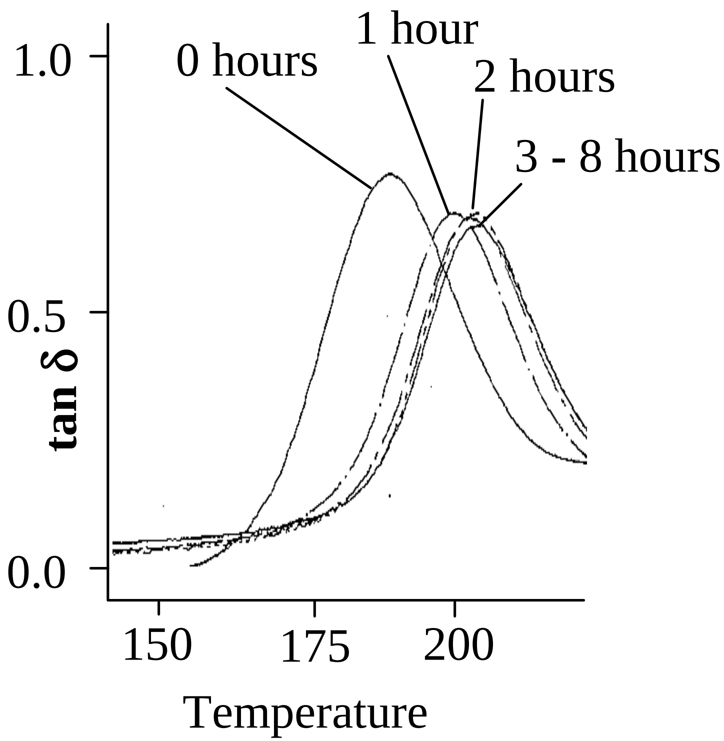
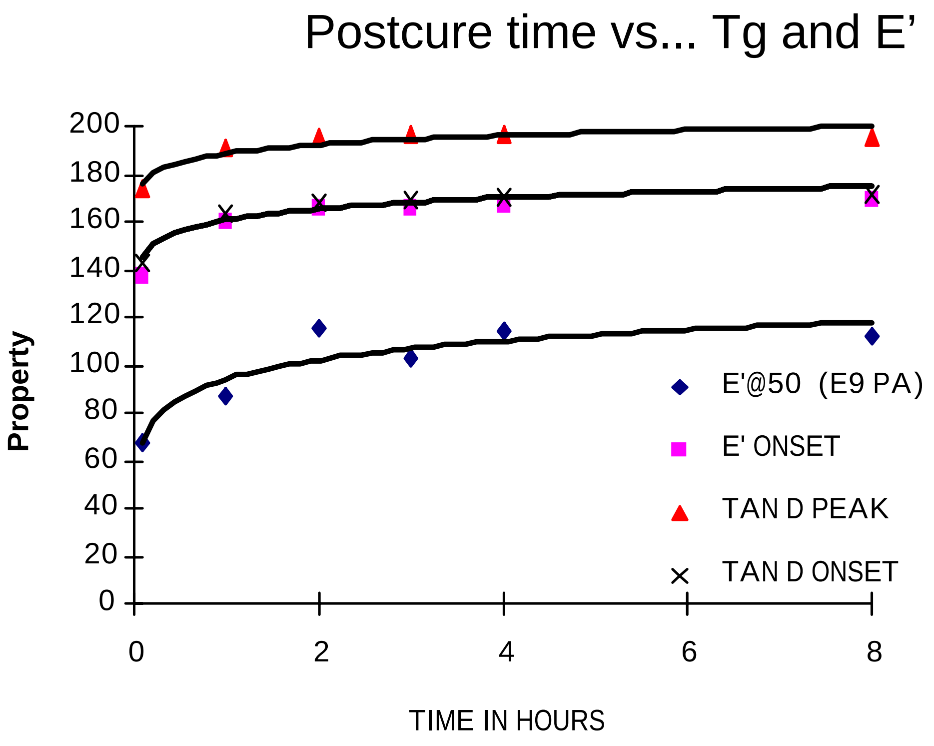
Postcure studies allow process optimization:

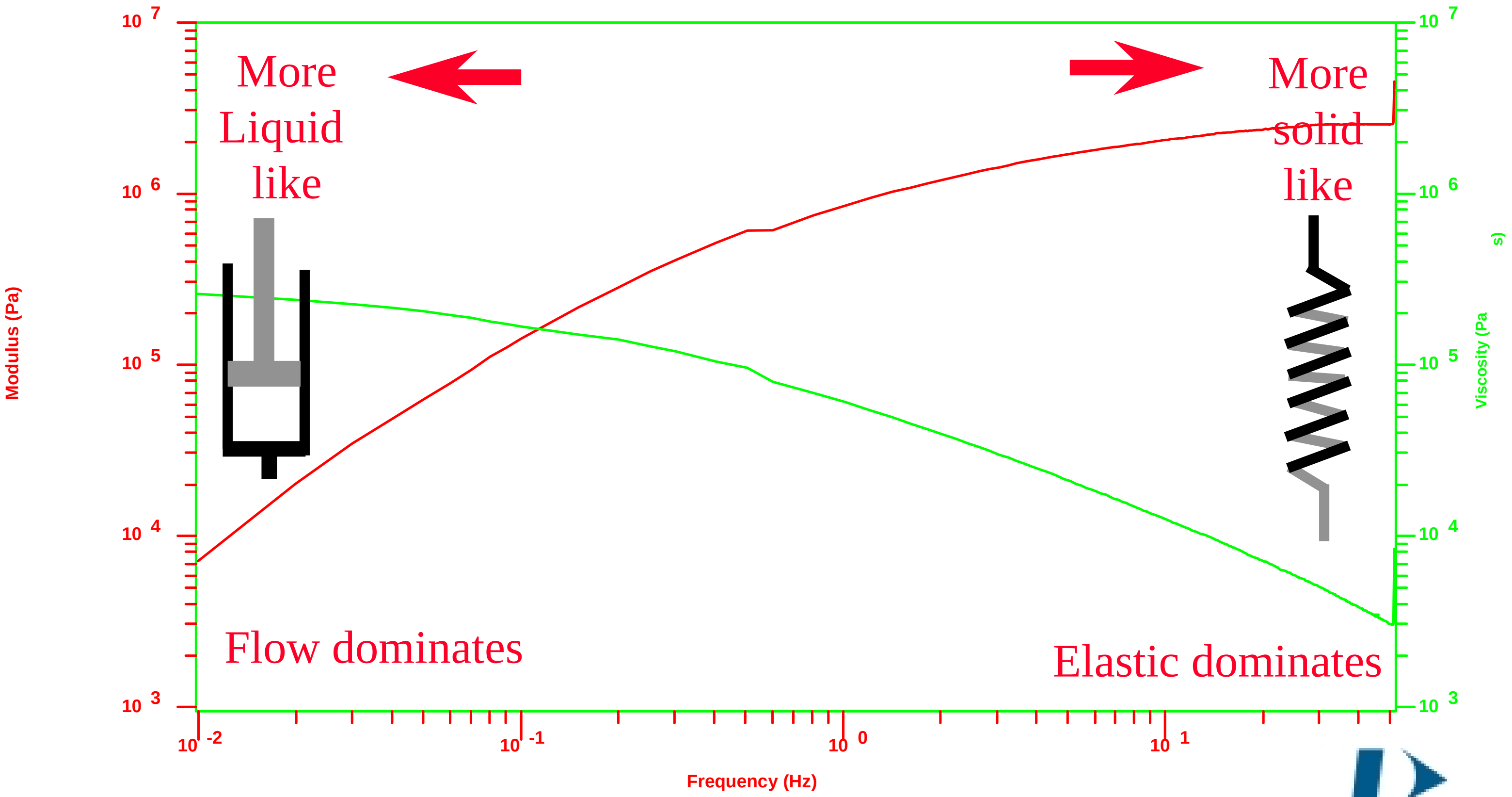




Frequency Scans

- hold temperature constant and vary frequency
- allows one to look at trends in material
- can estimate changes in MW and MWD
- looks at both tack-like and peel-like behavior
- can use data for Time Temperature Superposition to extend frequency range or predict age life.

Frequency determines the type of response



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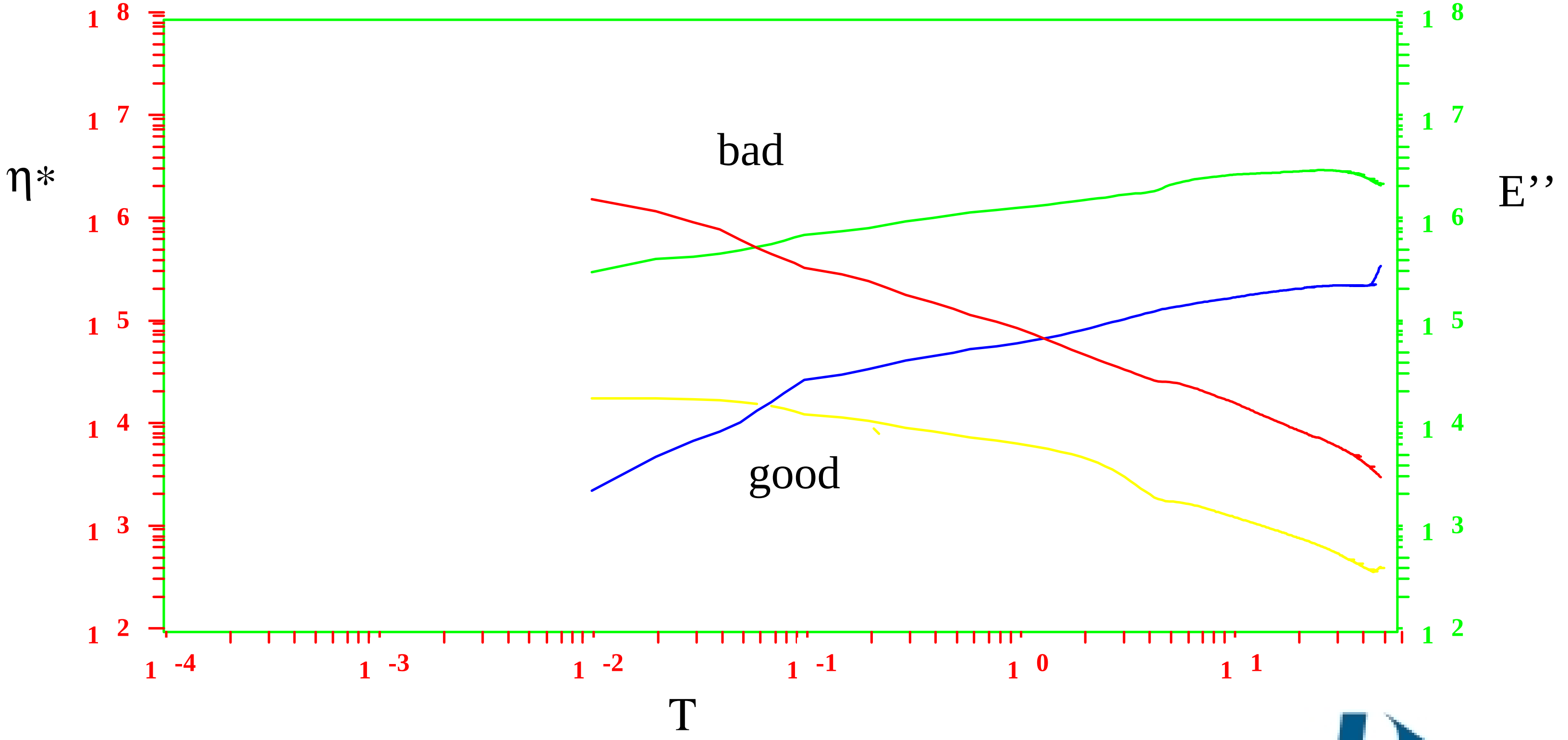
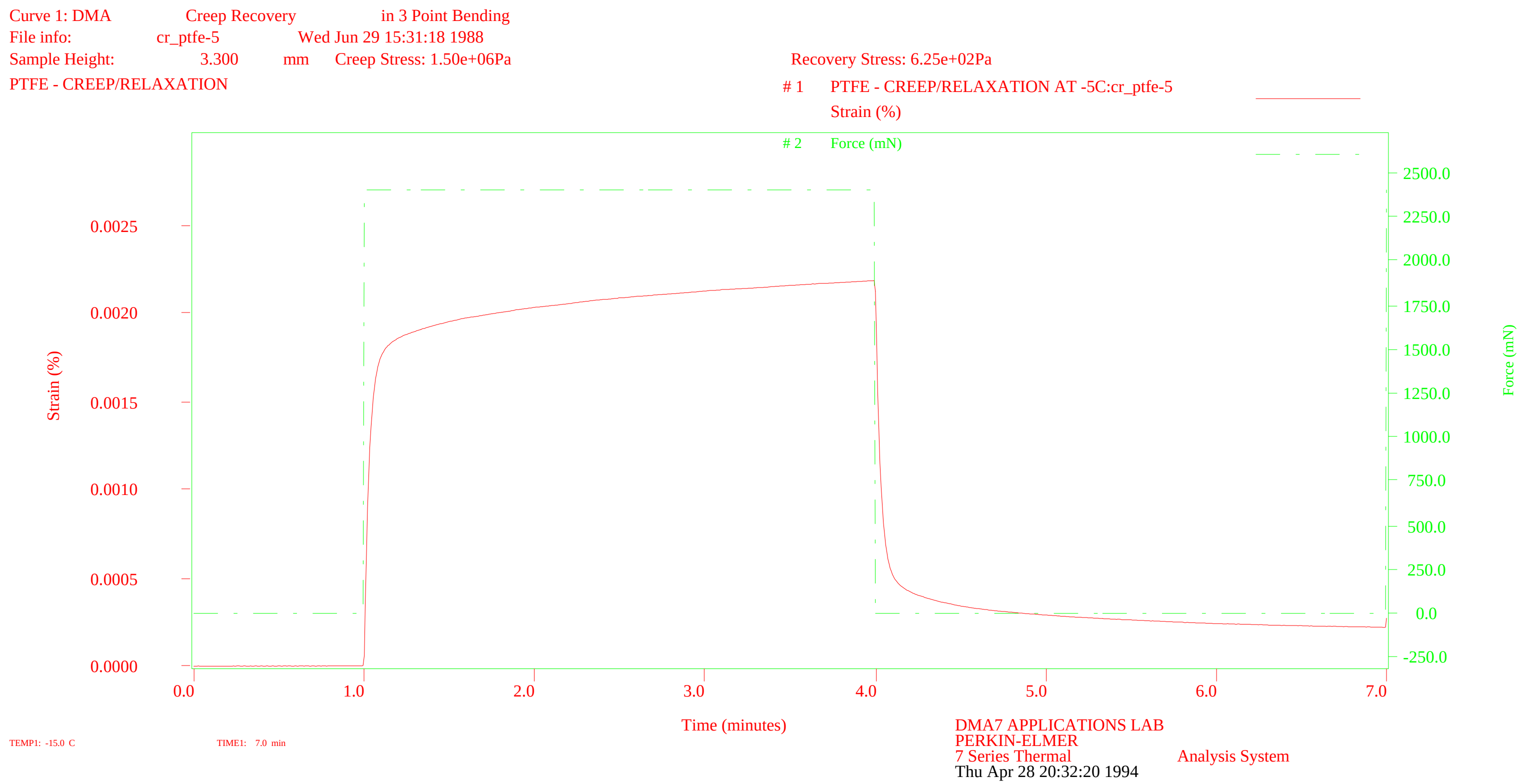
For example, two hot melt adhesives...

show affect of rate (peel vs.... tack)



Creep can look at distortion under load,



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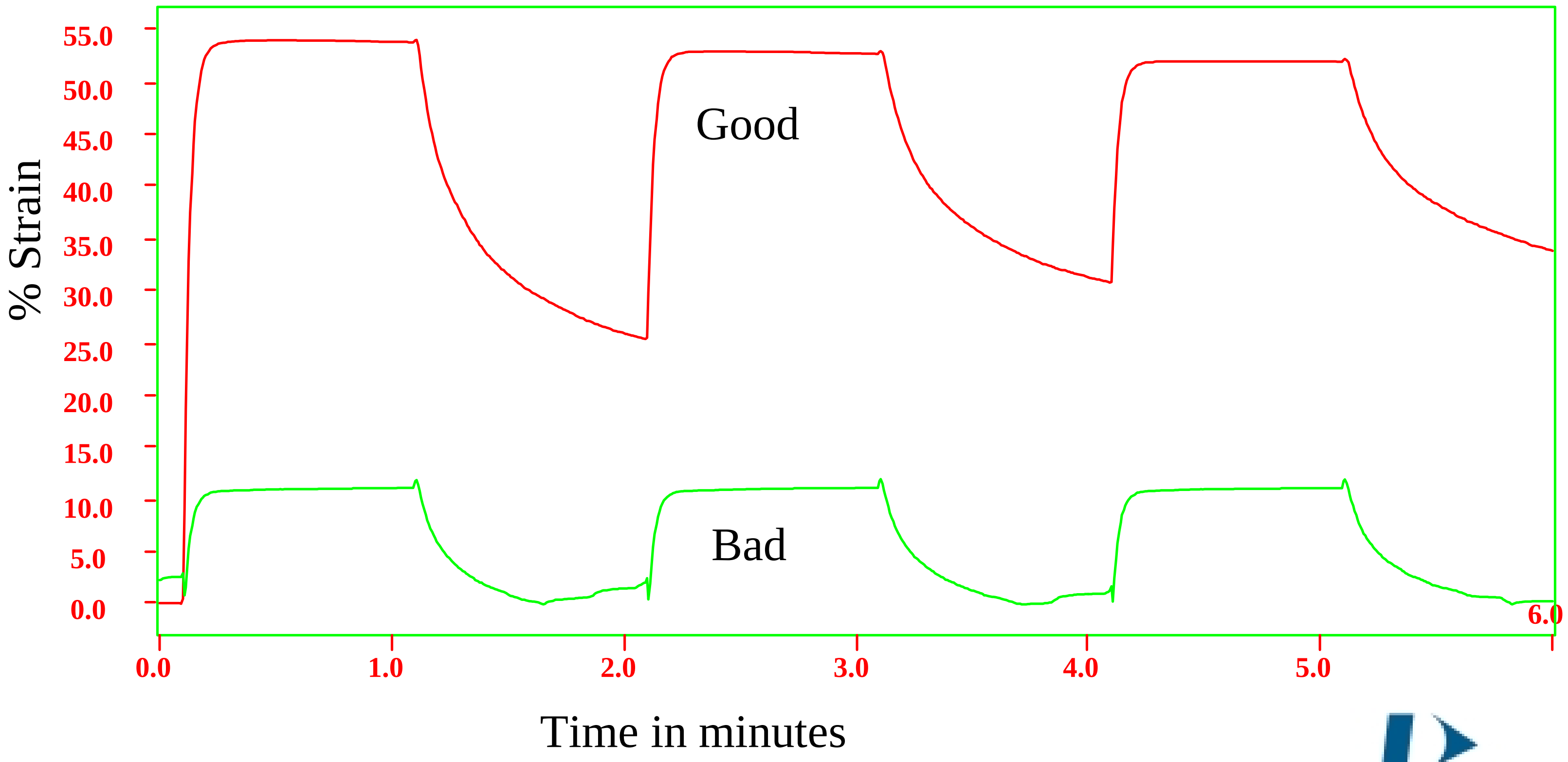
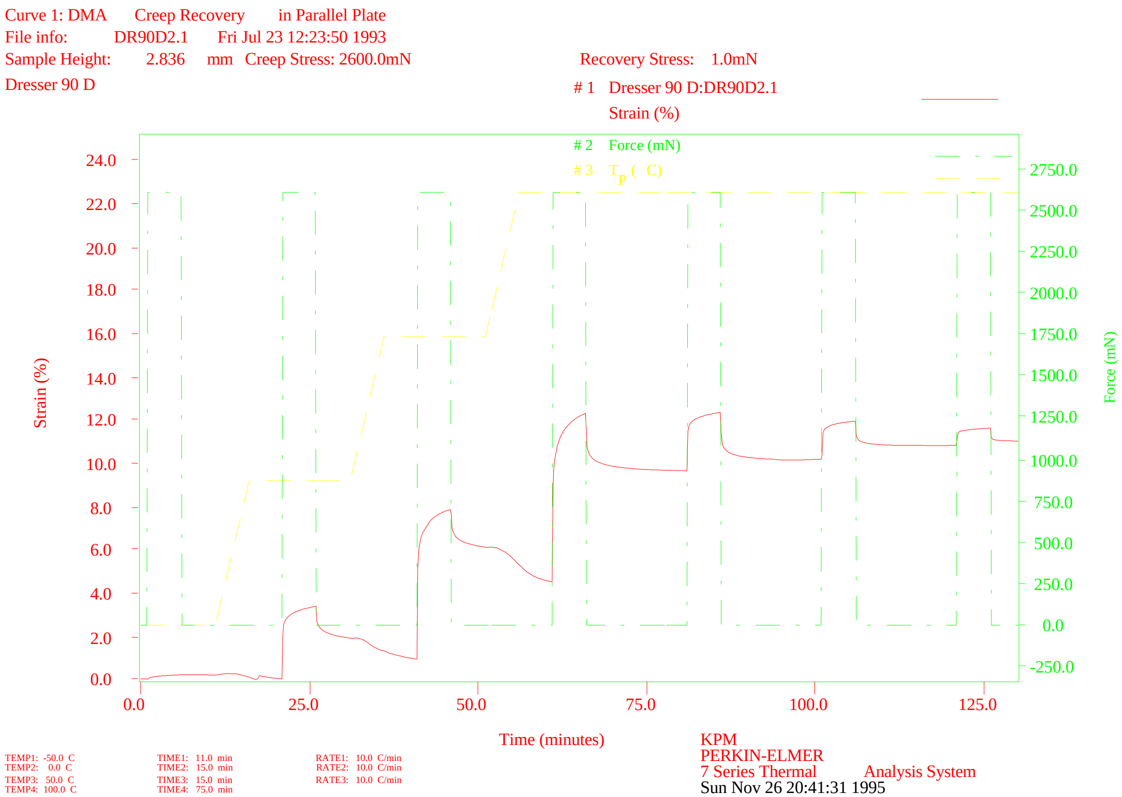
cyclic application of loads,

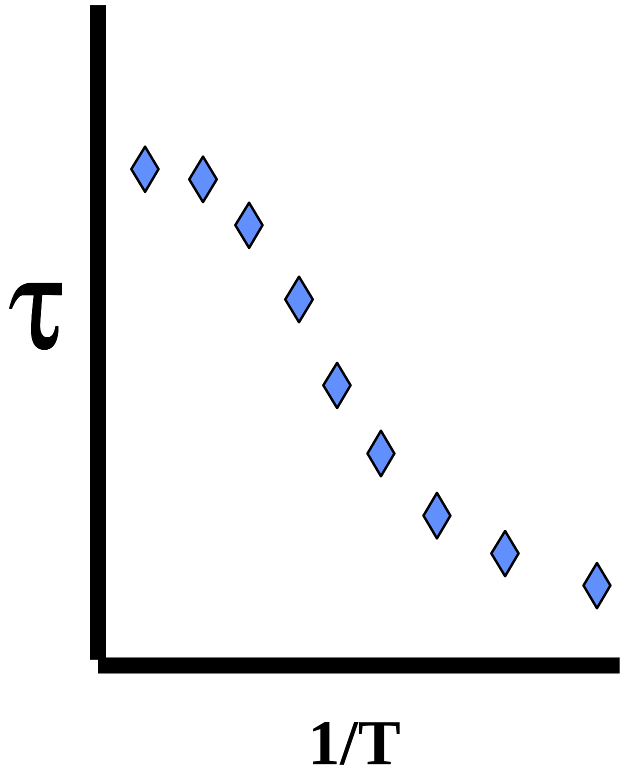
Differences can be seen in good and bad samples and get more apparent with several cycles. Here the bad material is not flowing enough to fill the pores and form a mechanical bond.



and with varying temperatures.



And you can tabulate this stuff graphically...



- The time to 1/e percent recovery is the relaxation.
- This is a measure of how quickly a material recovers. (There is a lot more to this subject.)

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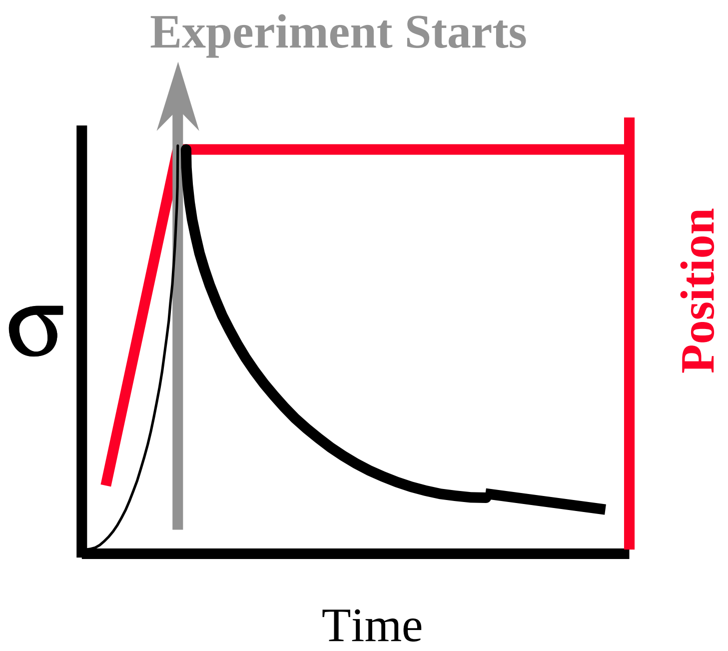
Stress Relaxation

- By exploiting the special controls of the DMA-7e, we can run stress relaxation experiments.
- These look at how the force change for a sample kept at a set distortion as a function of time or temperature.



Sample would be distorted to y length and held.

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Don’t forget the DMA-7e also does Stress Scans

- can do either static or dynamic ramps
- static scans calculate Young’s modulus and stress-strain curves
- dynamic scans give material response to increasing oscillatory forces:
  - get complex viscosity and modulus for each data point
  - can look at changes in elasticity (E’) and lag (phase angle) with increasing stress
- Both methods are fast tests for QC applications after the material has been fully characterized by other DMA modes.

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Specialized Testing is Possible...

The design of the DMA-7e makes it possible to do:

Time-Temperature Superposition (TTS)

DEA/DMA

Tests in Solution

Microscopic DMA

Photo DMA

DMA-?

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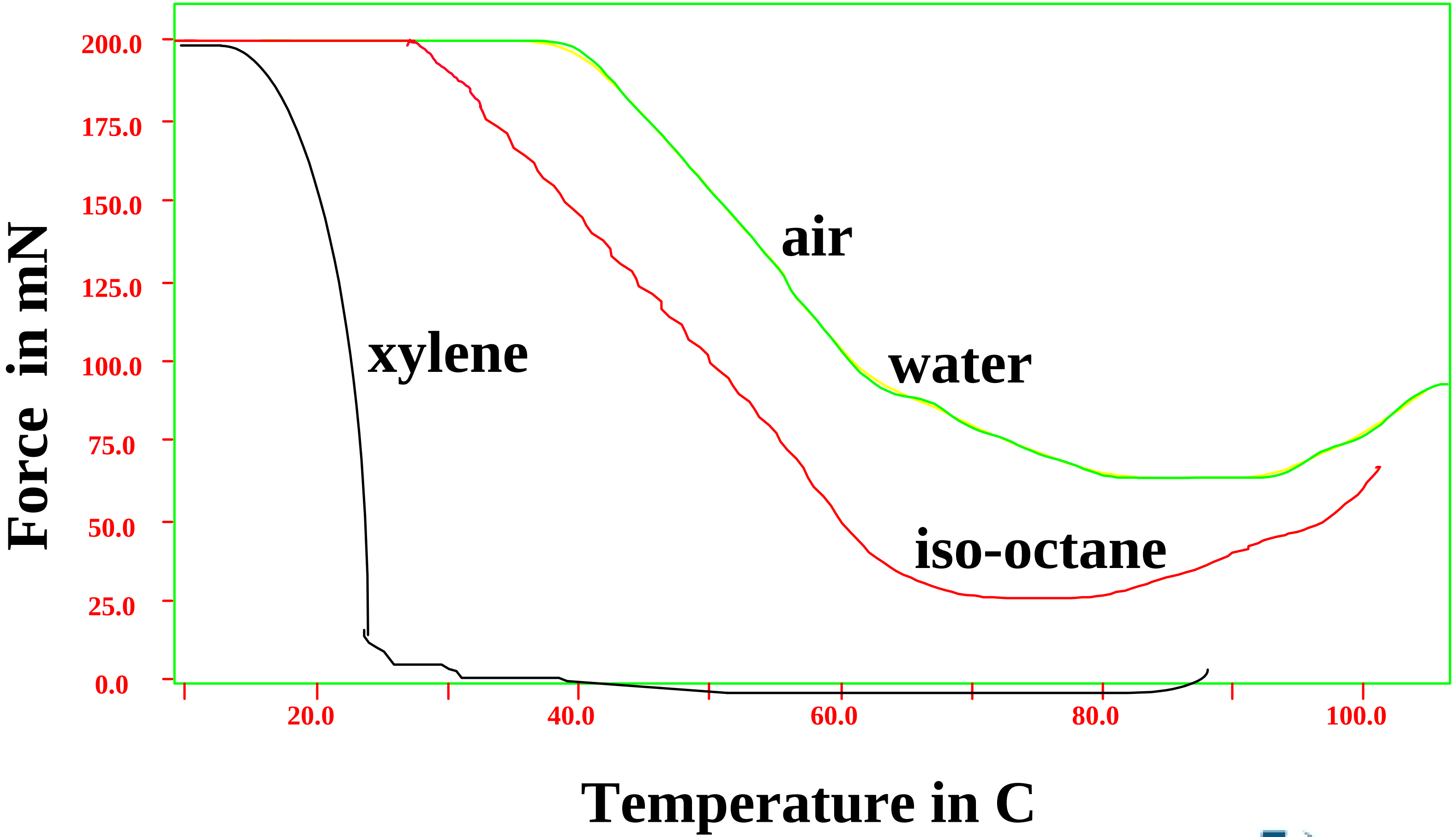
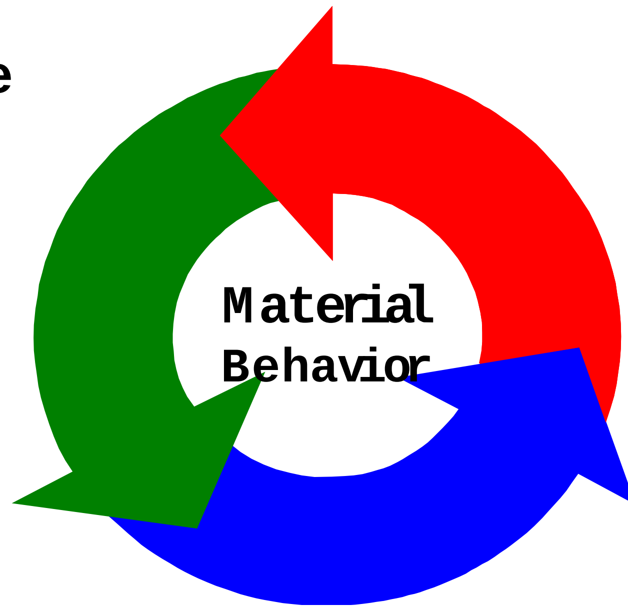
PP fibers in solvent



To Review, DMA ties together...

molecular structure

Molecular weight
MW Distribution
Chain Branching
Cross linking
Entanglements
Phases
Crystallinity
Free Volume
Localized motion
Relaxation Mechanisms



product properties

Dimensional Stability
Impact properties
Long term behavior
Environmental resistance
Temperature performance
Adhesion
Tack
Peel

processing conditions

Stress
Strain
Temperature
Heat History
Frequency
Pressure
Heat set

PerkinElmer™ instruments.

Conclusions

- DMA allows you to preform a wide range of tests from sensitive probes of molecular structure to model studies.
- the DMA-7e allows operation as six different instruments to maximize flexibility.
- Data can be overlayed with DSC, TGA, TMA, and DTA for easier analysis.

PerkinElmer™ instruments.

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