

ARTISAN®
TECHNOLOGY GROUP

Your **definitive** source for quality pre-owned equipment.

Artisan Technology Group
(217) 352-9330 | sales@artisantg.com | artisantg.com

Full-service, independent repair center
with experienced engineers and technicians on staff.

We buy your excess, underutilized, and idle equipment
along with credit for buybacks and trade-ins.

Custom engineering
so your equipment works exactly as you specify.

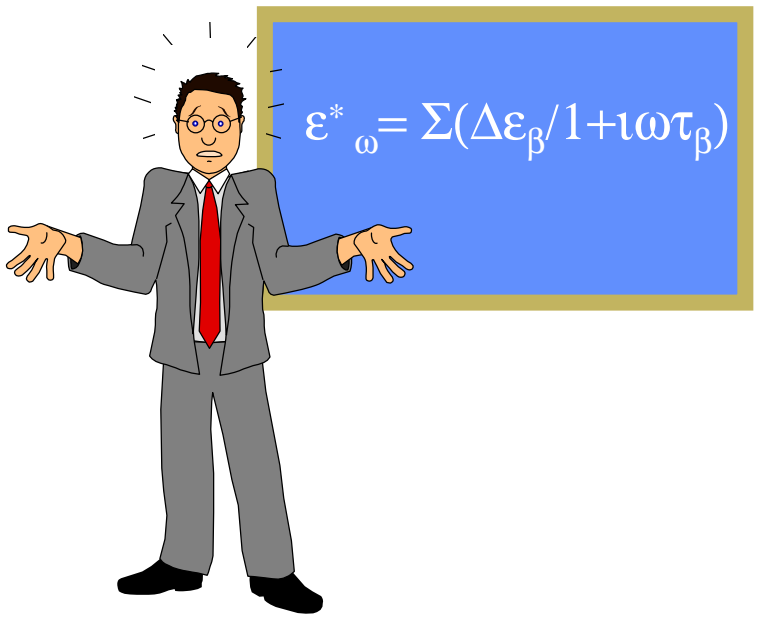
- Critical and expedited services
- In stock / Ready-to-ship
- Leasing / Rentals / Demos
- ITAR-certified secure asset solutions

Expert team | Trust guarantee | 100% satisfaction

All trademarks, brand names, and brands appearing herein are the property of their respective owners.

Visit our website - *Click HERE*

Dynamic Mechanical Analysis (DMA) Basics and Beyond



Dr. Lin Li

Thermal Analysis

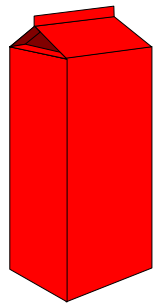
PerkinElmer Inc.

April 2000

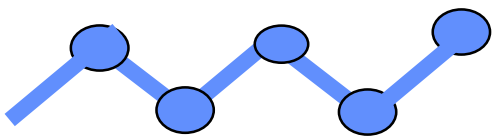
PerkinElmer™ instruments.

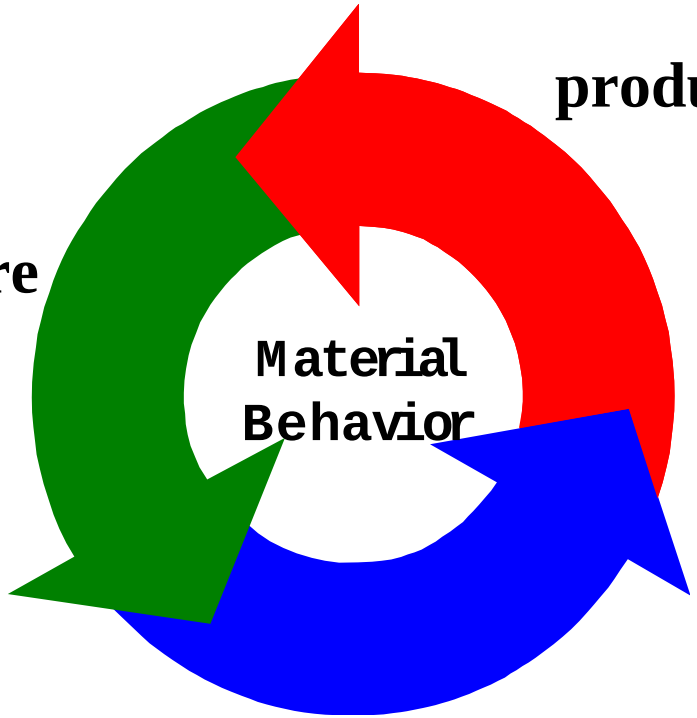
The DMA lets you relate:

product properties

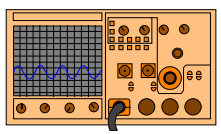


molecular structure





processing conditions

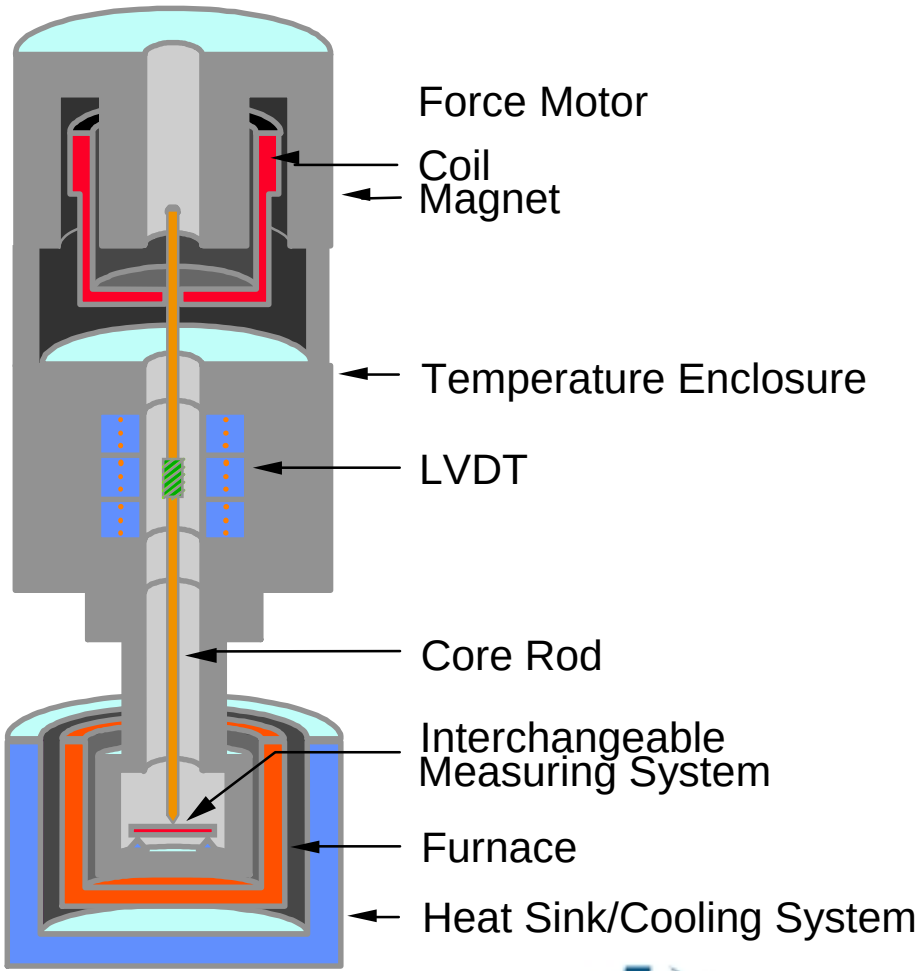


PerkinElmer™
instruments.

DMA Structure in general

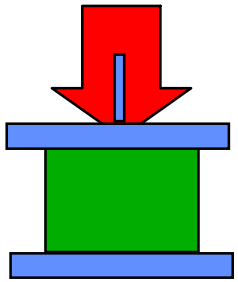
How the DMA works:

- 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.

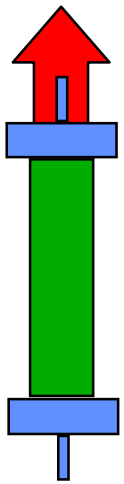


PerkinElmer™
instruments.

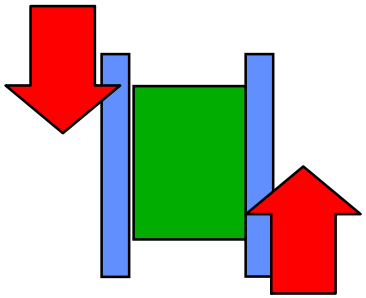
Outstanding Flexibility 1: Multiple Geometries



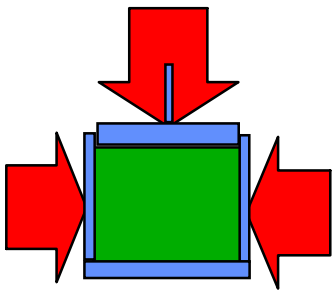
Compressive



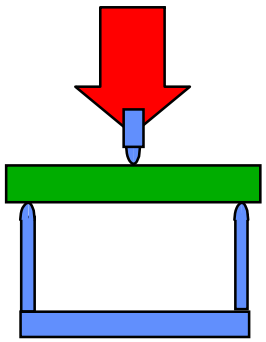
Extension



Shear



Cup & Plate

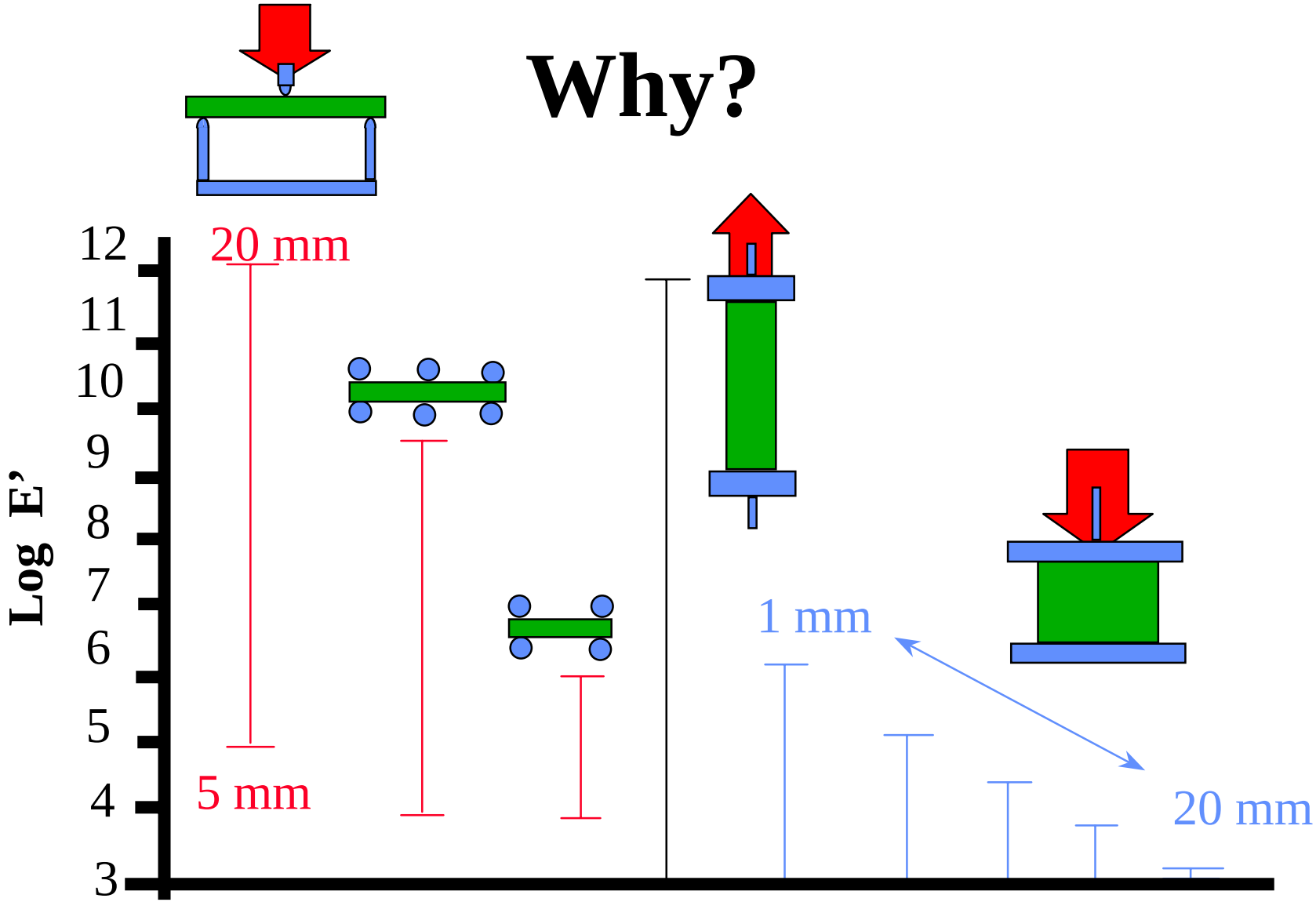


Flexure

- 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*

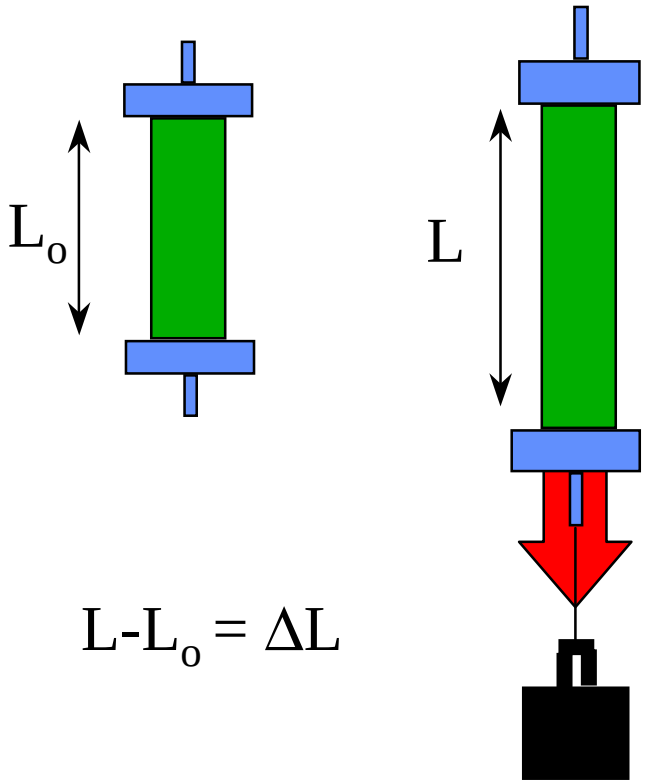
PerkinElmer™ instruments.

Why?



PerkinElmer™
instruments.

Stress Causes Strain...



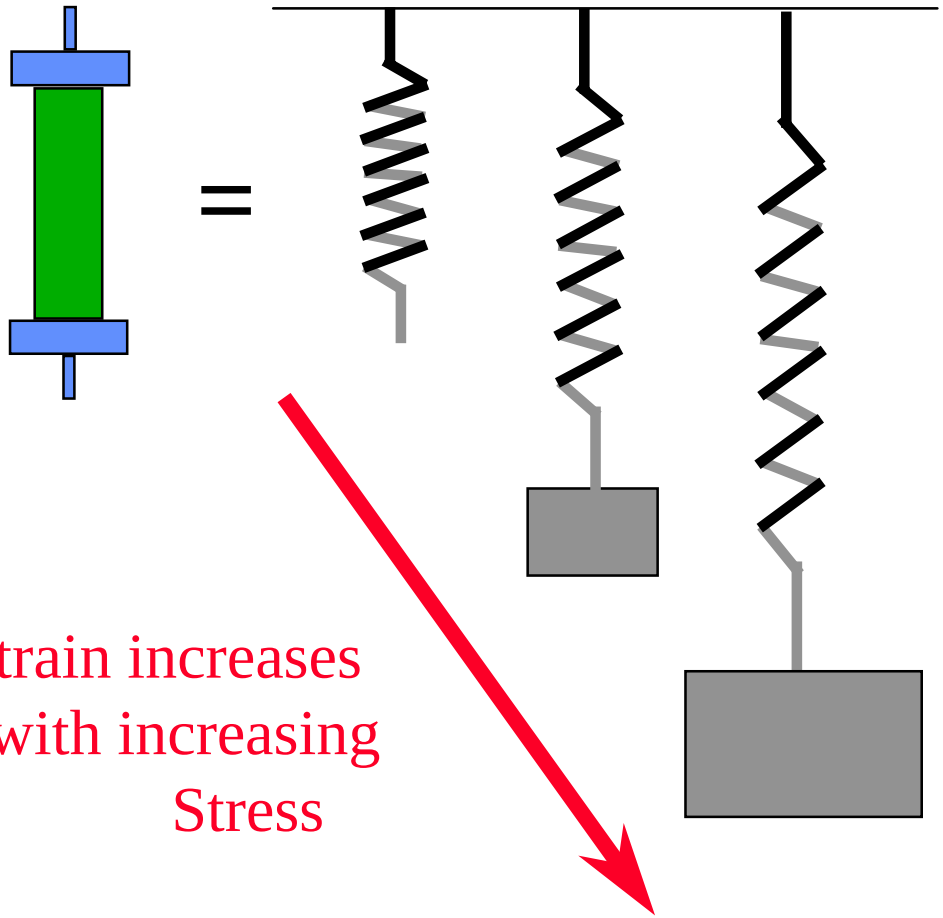
$L - L_o = \Delta L$

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	$\varepsilon = 1/2\{1-(L_o/L)^2\}$

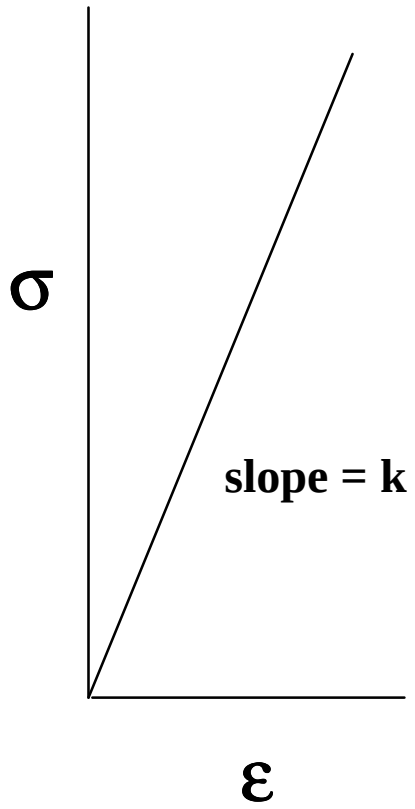
The different definitions of tensile strain become equivalent at very small deformations.

PerkinElmer™ instruments.

The Elastic Limit: Hooke's Law

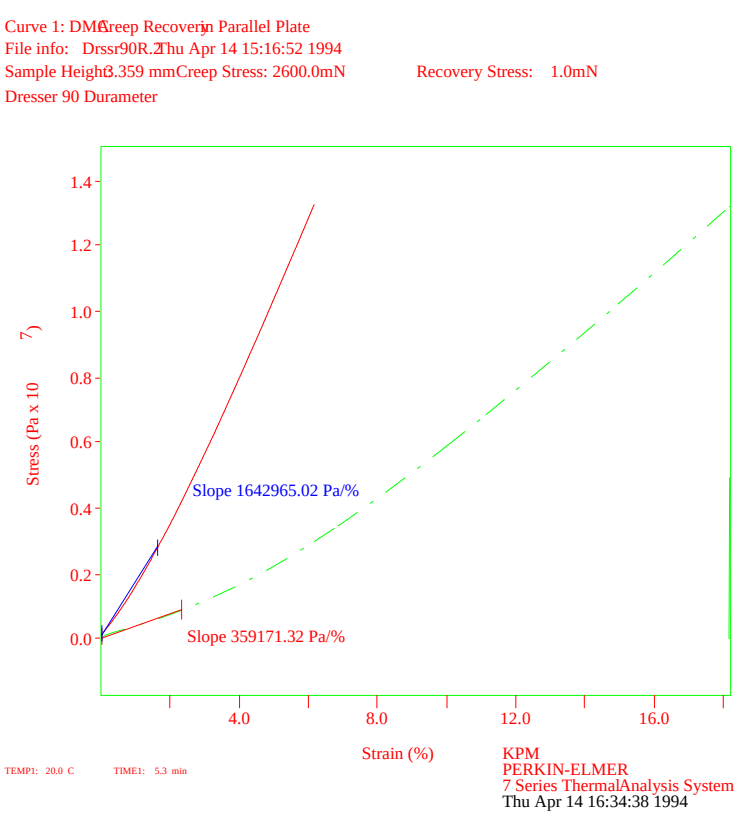


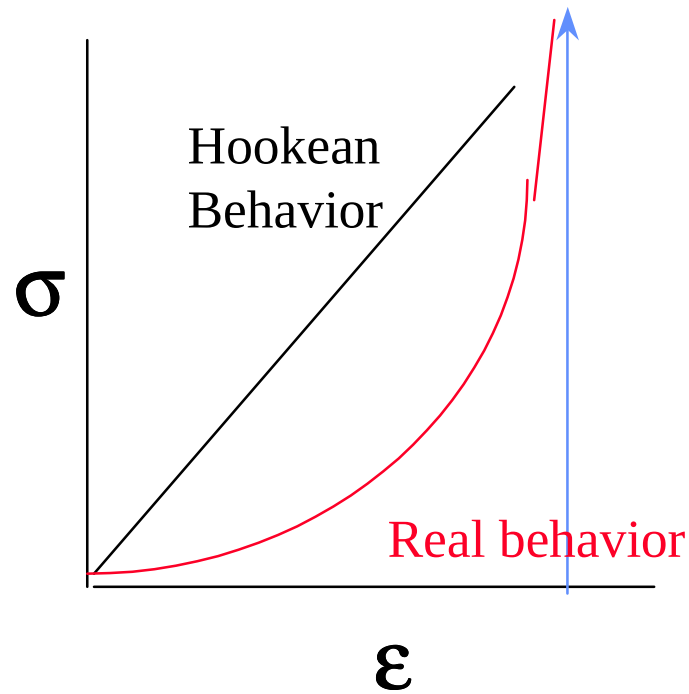
Strain increases with increasing Stress



PerkinElmer™ instruments.

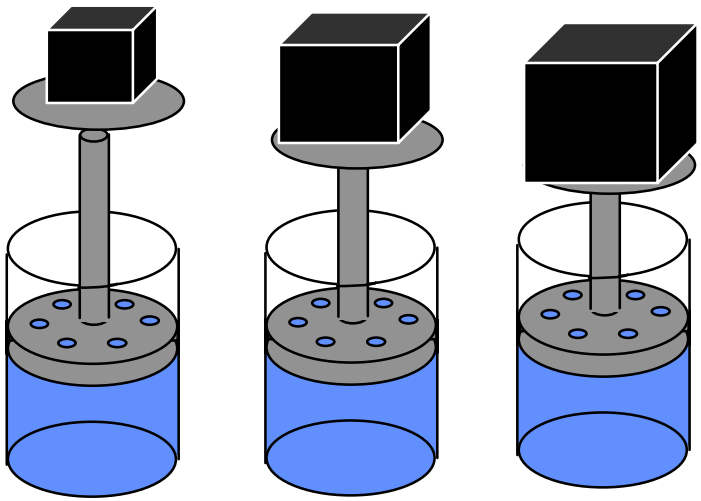
Real vs... Hookean Stress-Strain Curves

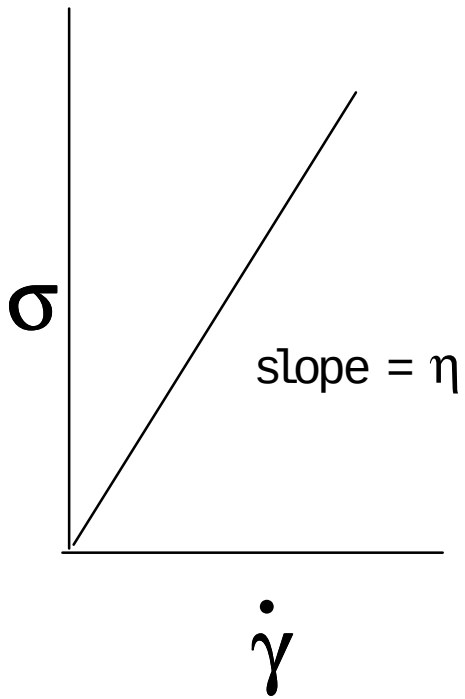




PerkinElmer™ instruments.

The Viscous Limit: Newtonian Behavior

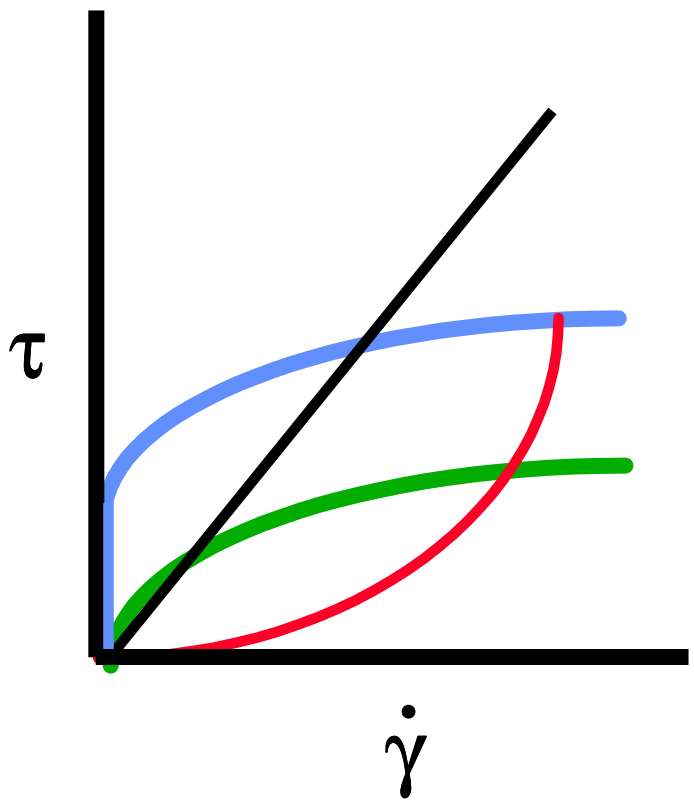




The speed at which the fluid flows through the holes (the strain rate) increases with stress!!!

PerkinElmer™ instruments.

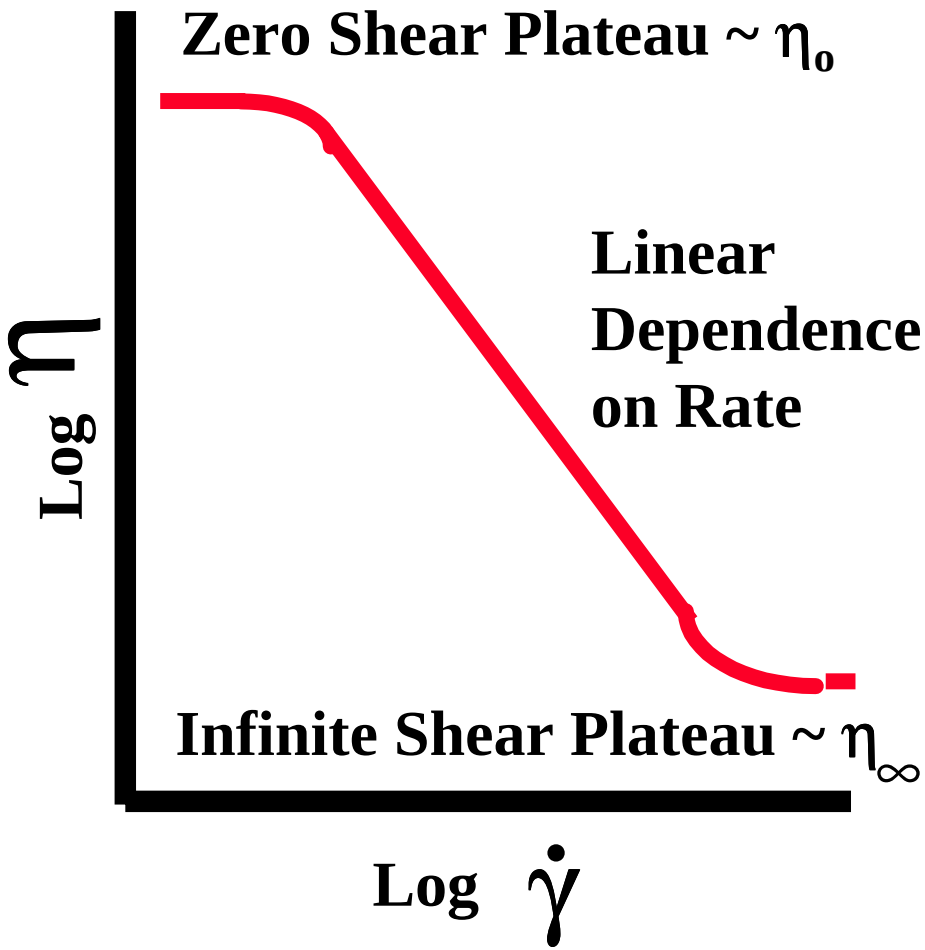
Viscosity Effects



- 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.

PerkinElmer™ instruments.

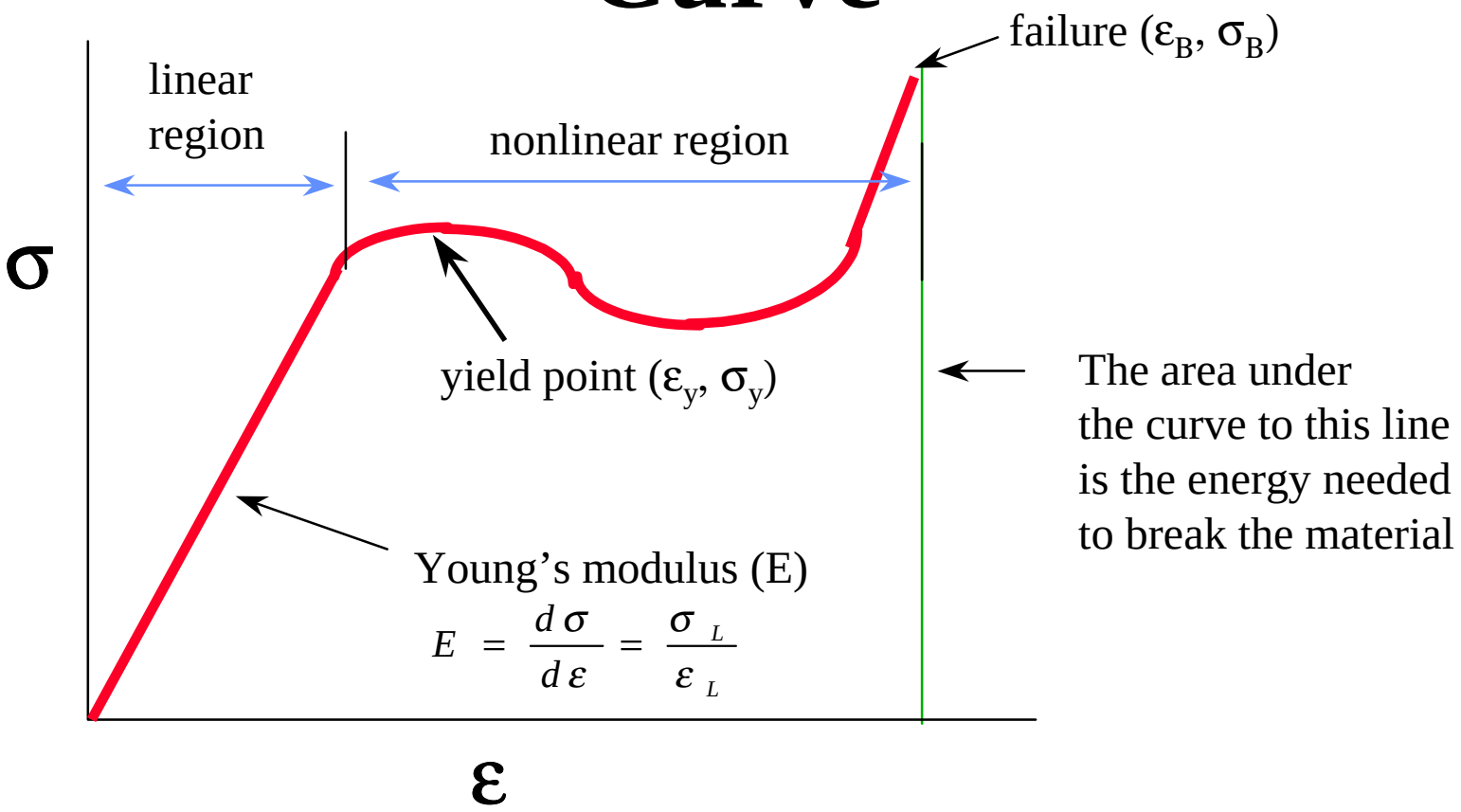
Polymers are Non-Newtonian Fluids!!!



- 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.

PerkinElmer™ instruments.

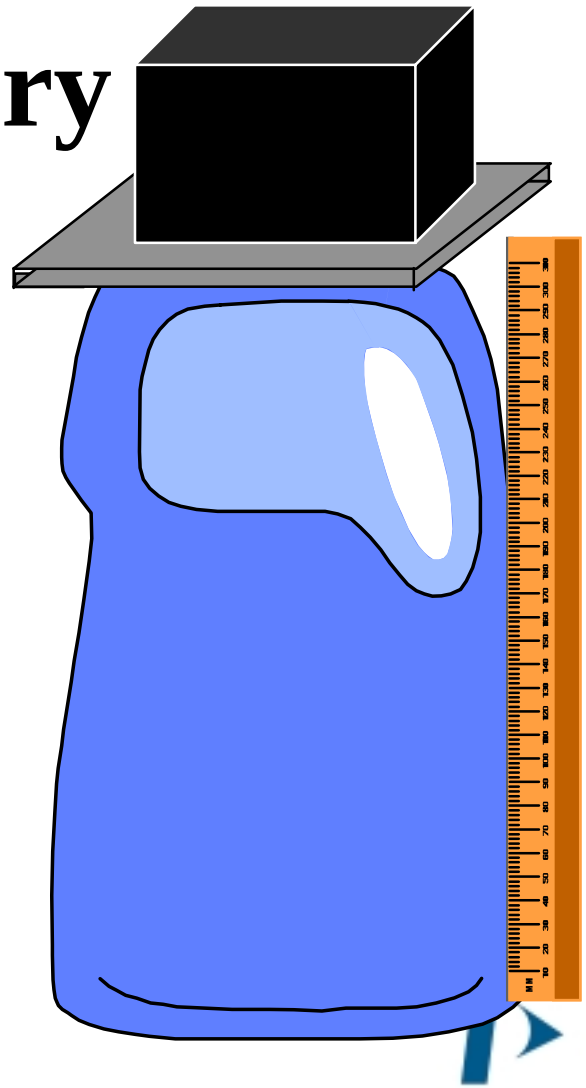
Analyzing a Stress-Strain Curve



PerkinElmer™ instruments.

Under Continuos Loads: Creep Recovery

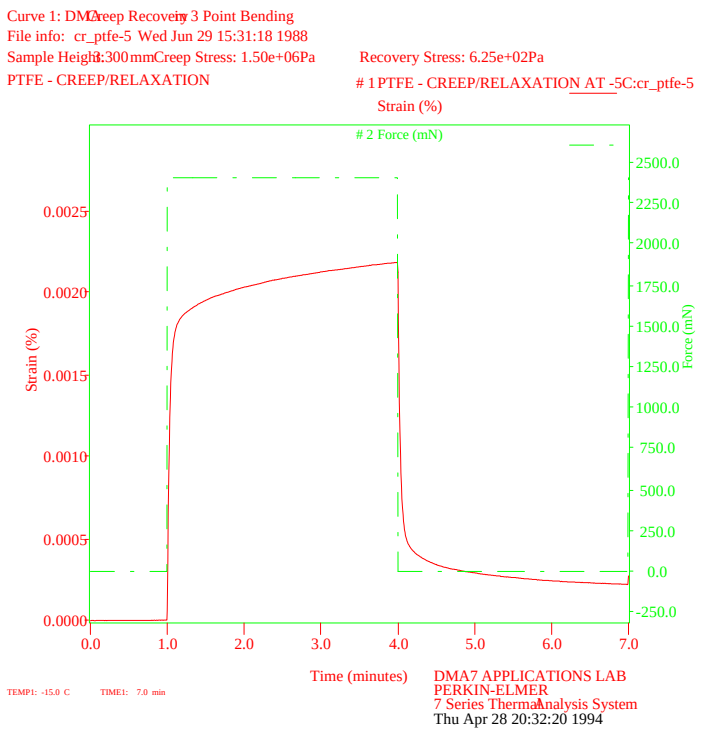
- Applying a constant load for long times and removing it from a sample.
- Allows one to see the distortion under constant load **and** also how well it recovers.



PerkinElmer™ instruments.

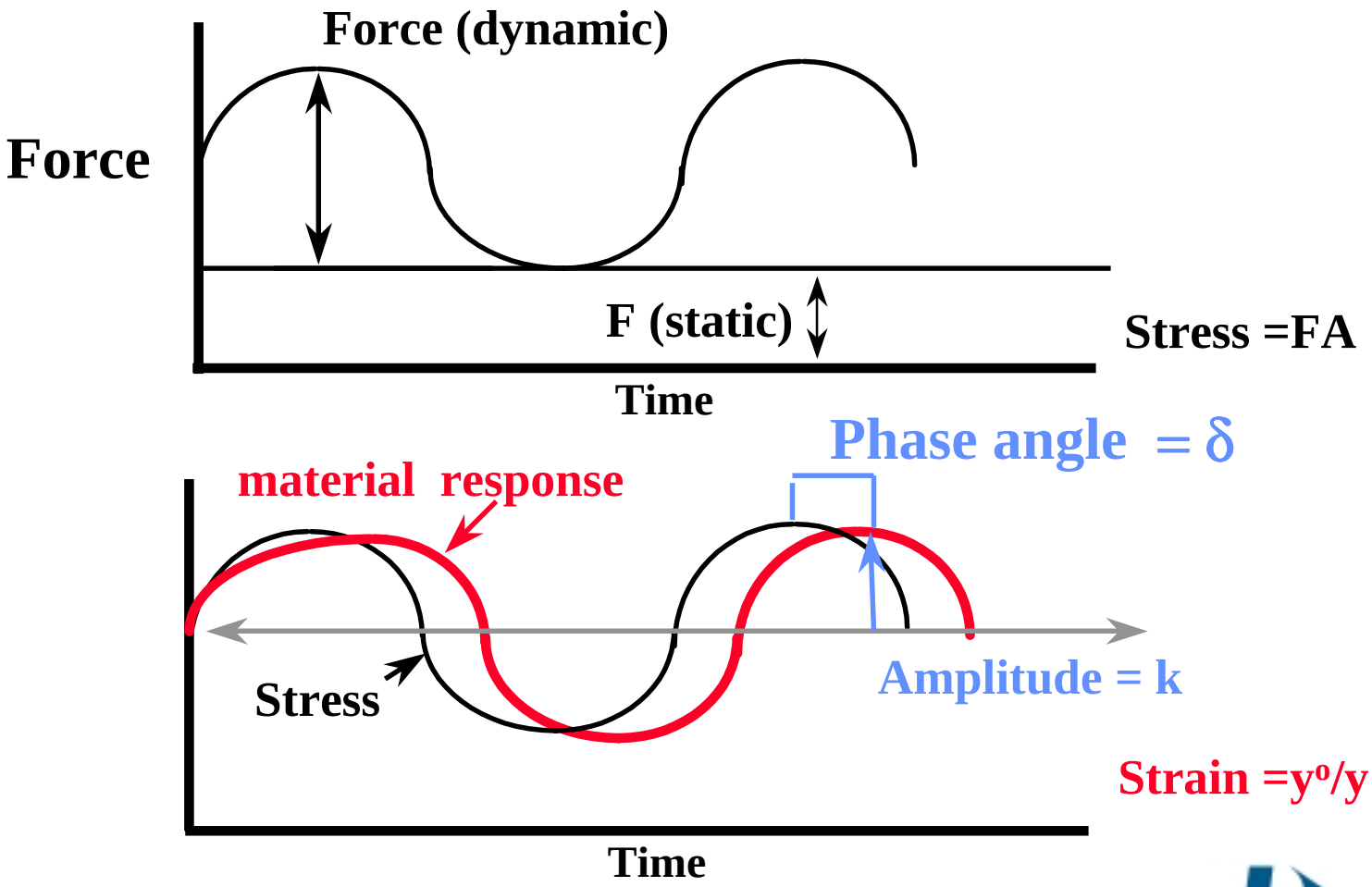
Creep is a fundamental engineering test.

- 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.



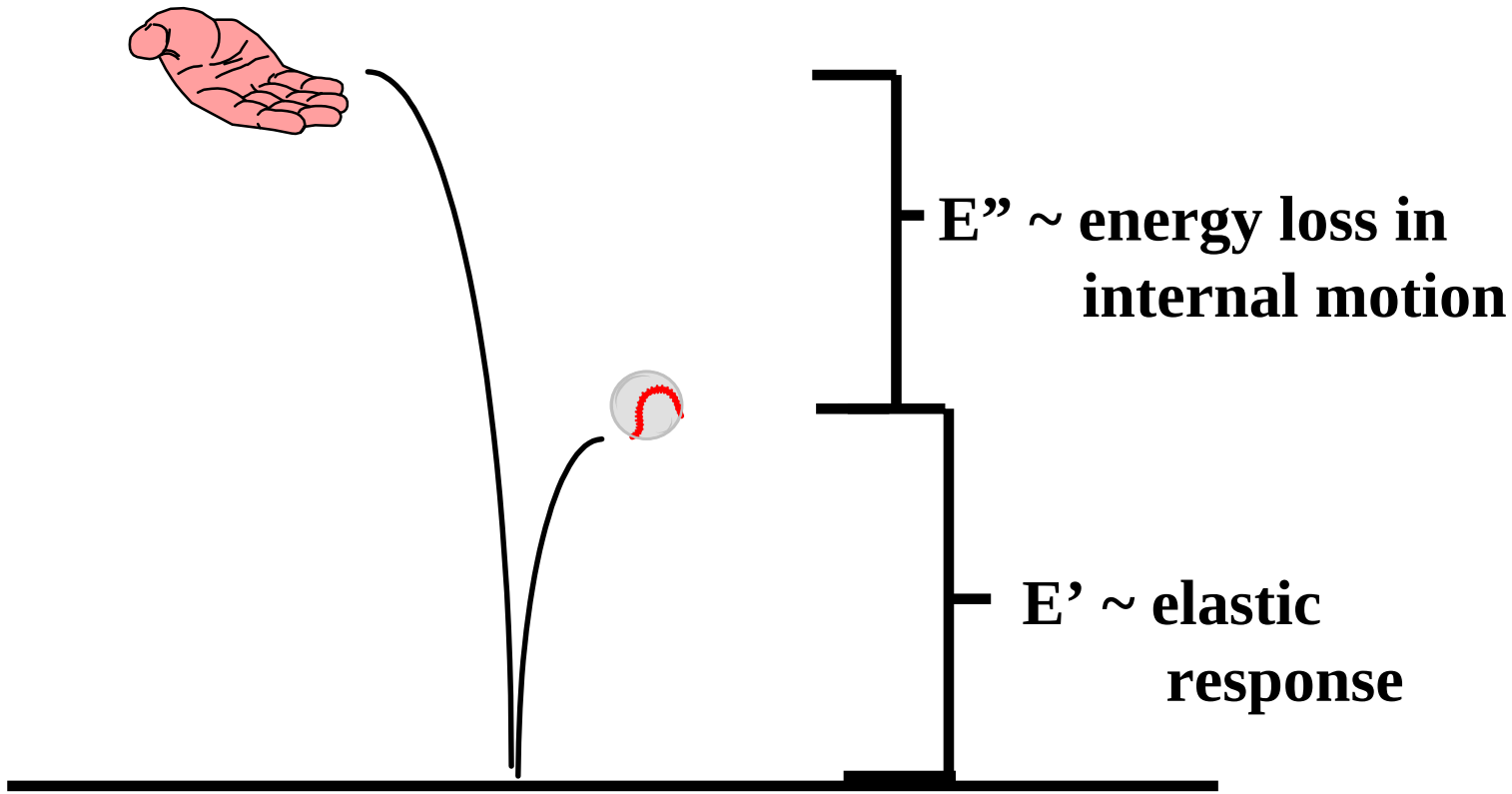
PerkinElmer™ instruments.

Dynamic Stress



PerkinElmer™
instruments.

Why? Let's bounce a ball.



PerkinElmer™ instruments.

All this is calculated from δ and k:

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

$$\text{Tan } \delta = E''/E'$$

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

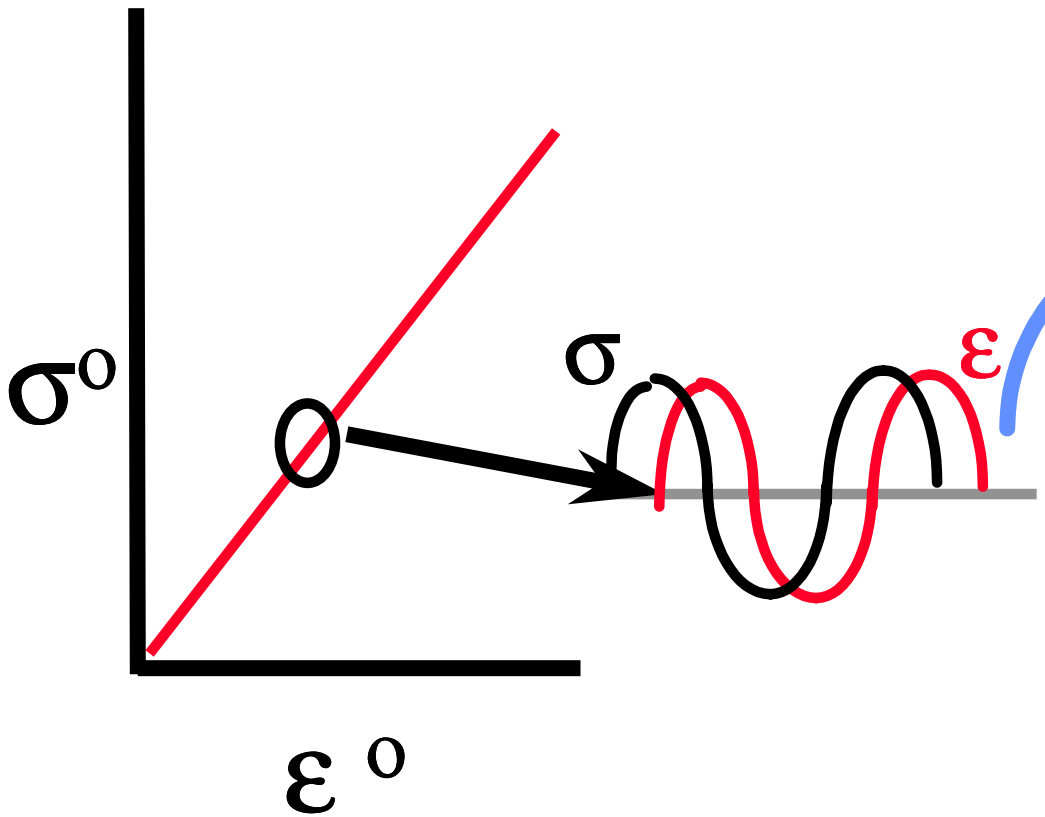
$$G^* = E^*/2(1+\nu)$$

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

PerkinElmer™ instruments.

To apply this to materials...

Dynamic Stress Scan



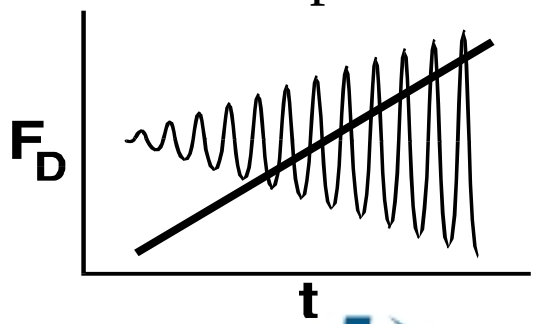
Since each part of the ramp has a sine wave stress associated with it, we get:

tan δ

E*, E', E"

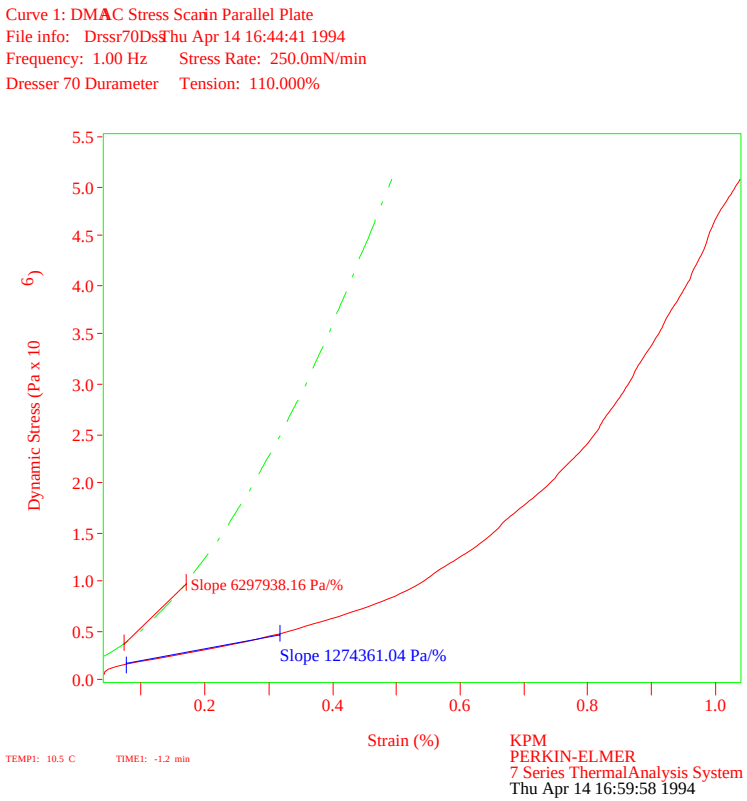
η

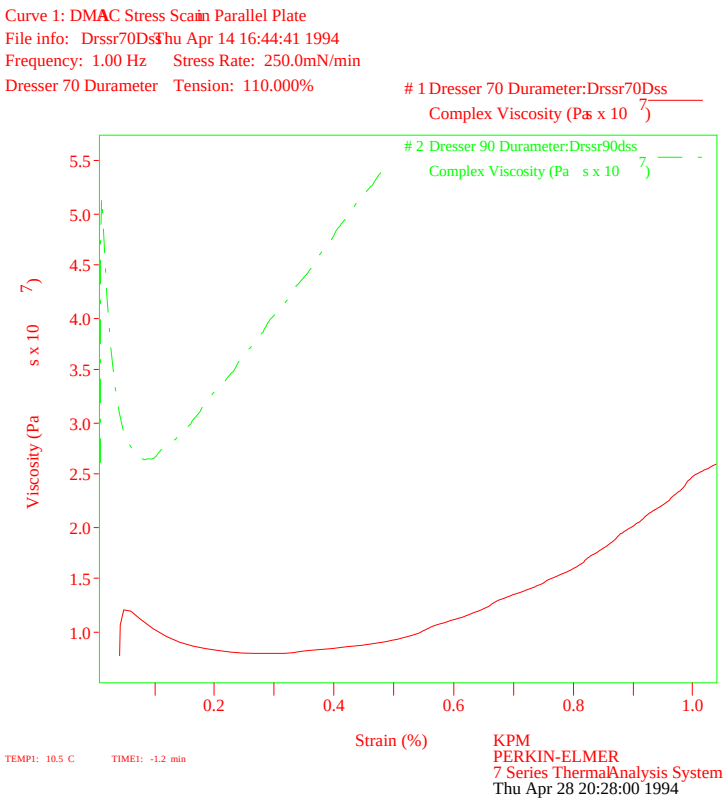
for each data point!!



PerkinElmer™ instruments.

For example, DSS Curves

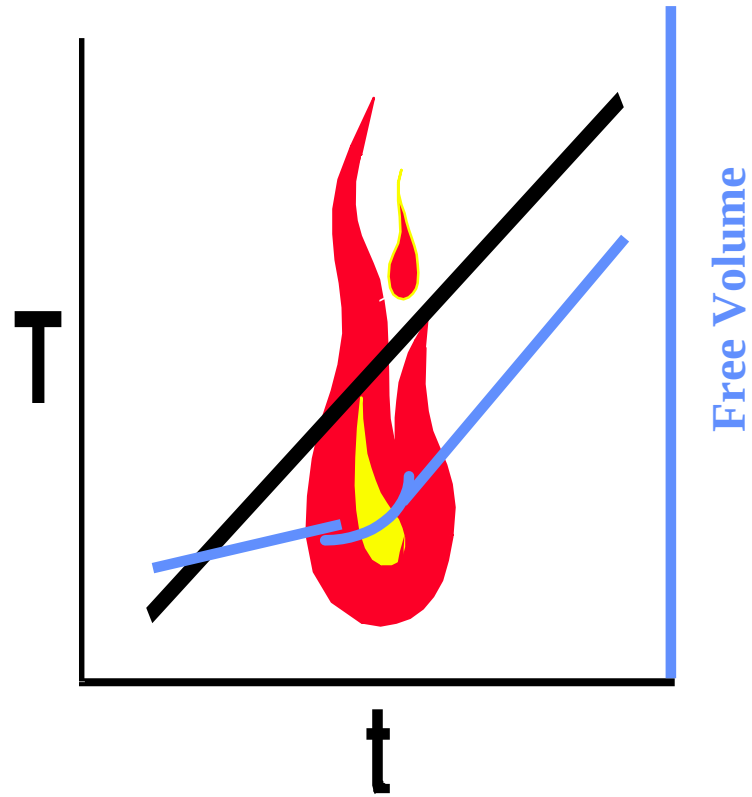




PerkinElmer™ instruments.

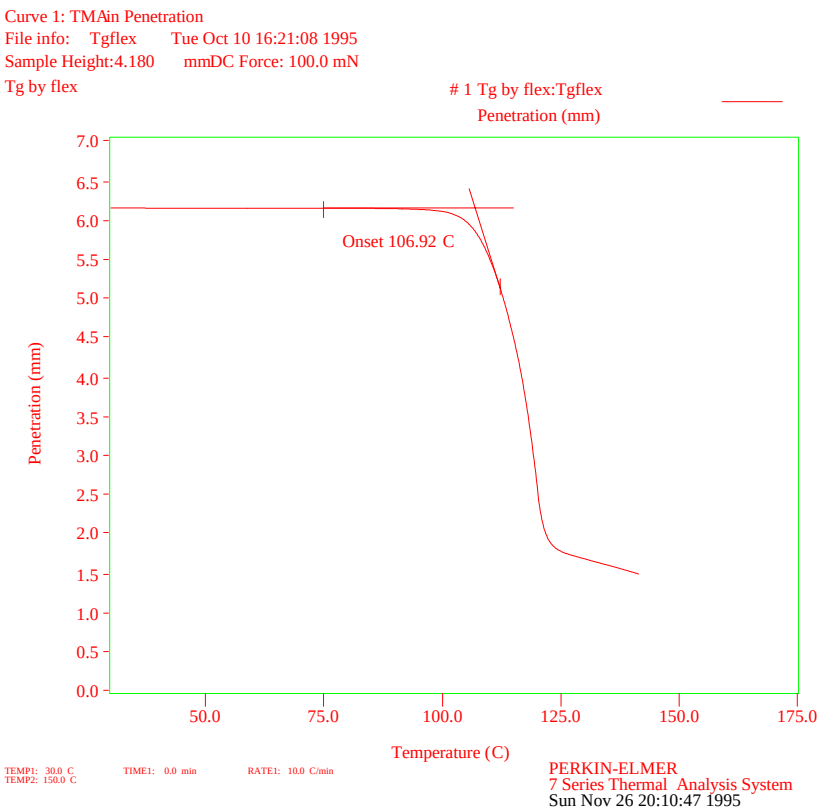
Now, let's induce temperature as a variable.

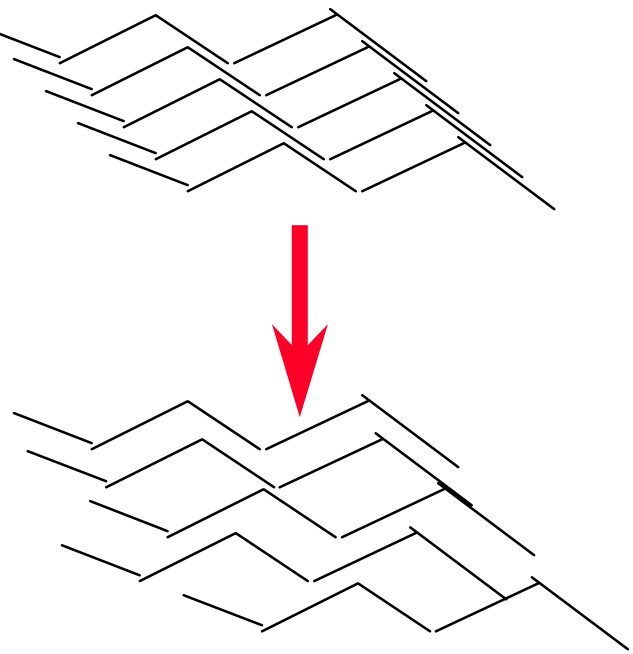
- We can heat the material under minimal load at a calibrated rate.
- This allows the material to change with temperature.
- These changes can be described in terms of free volume or relaxation times.



PerkinElmer™
instruments.

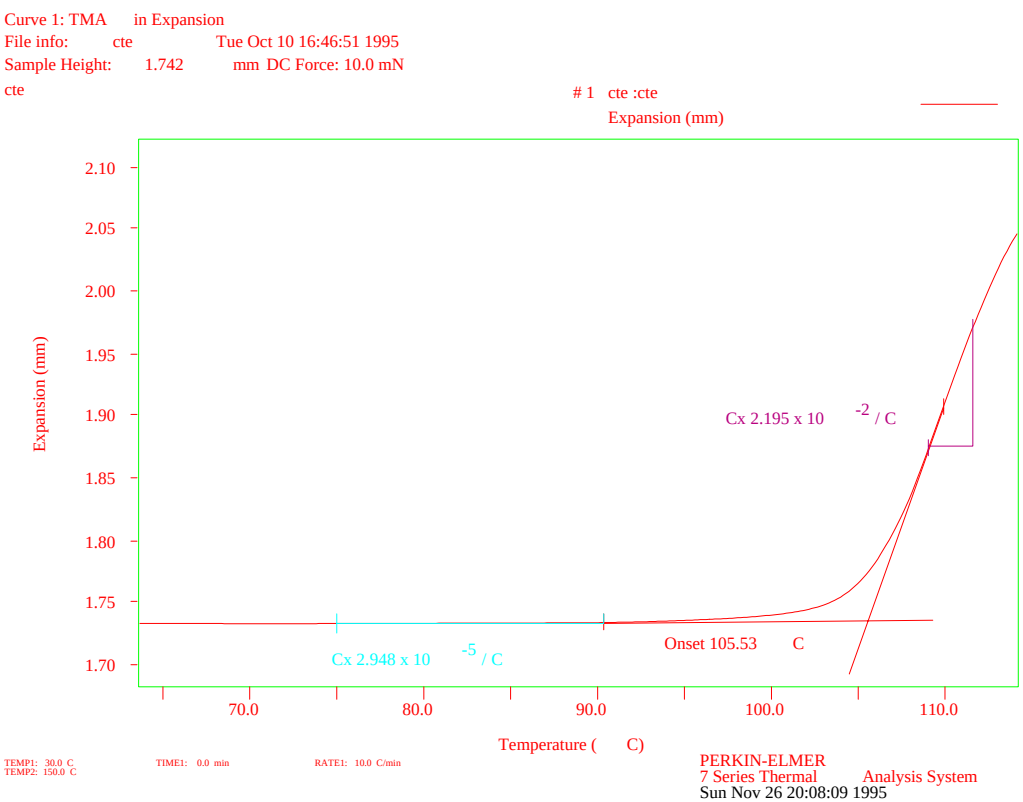
Thermomechanical Analysis as a starting Point.

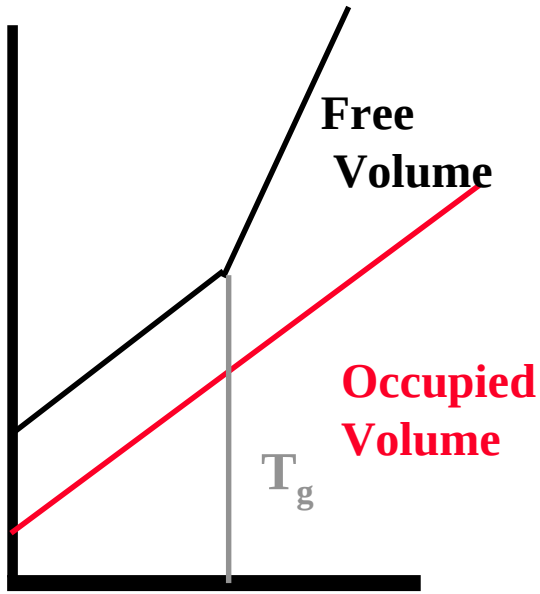




PerkinElmer™ instruments.

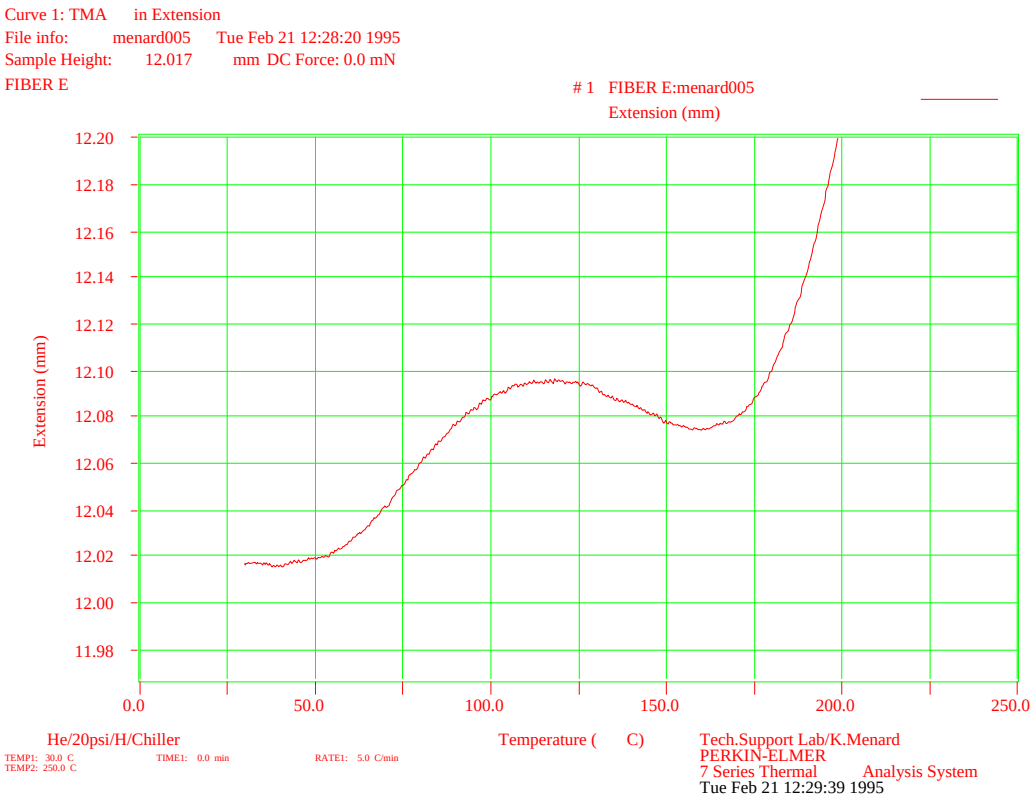
TMA - It's all free volume.





PerkinElmer™ instruments.

And it’s not just Tg.



(the traditional way to do heat set)

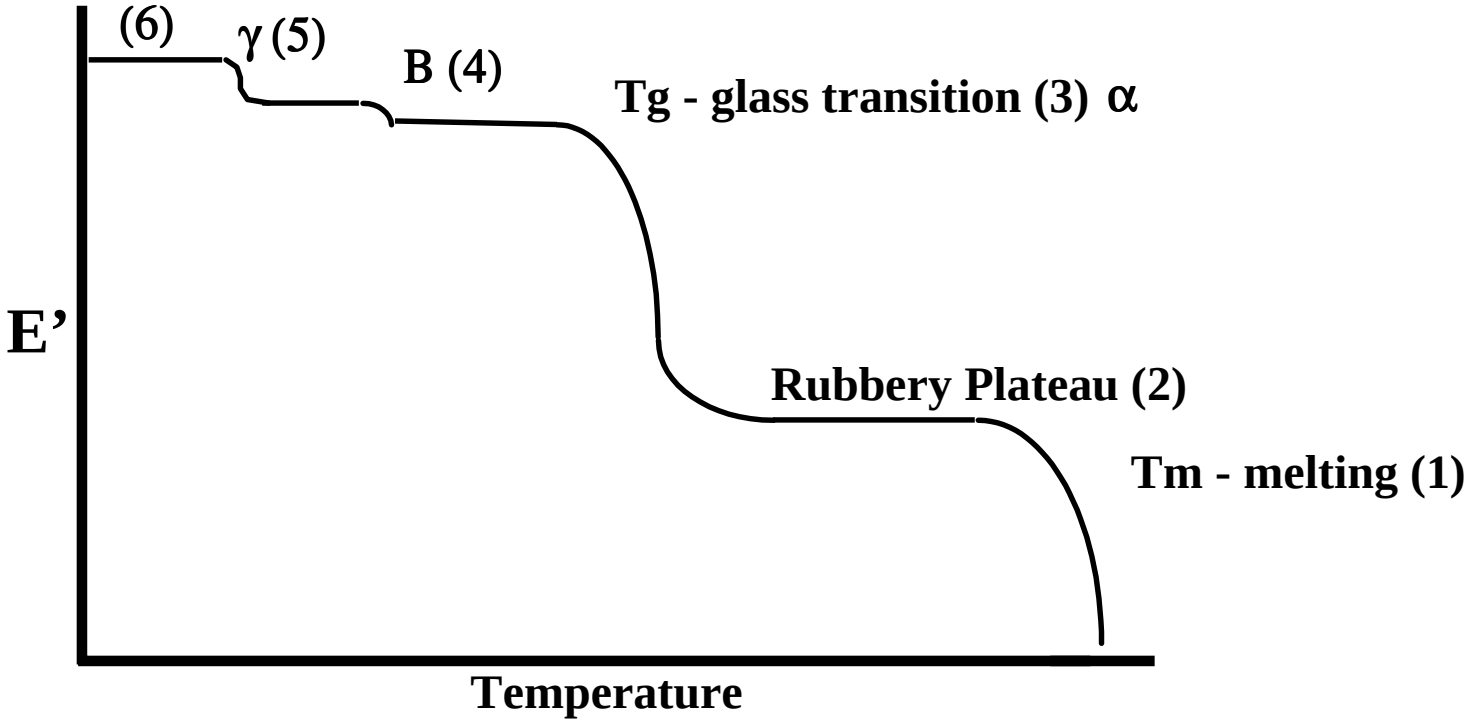
PerkinElmer™ instruments.

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**

PerkinElmer™
instruments.

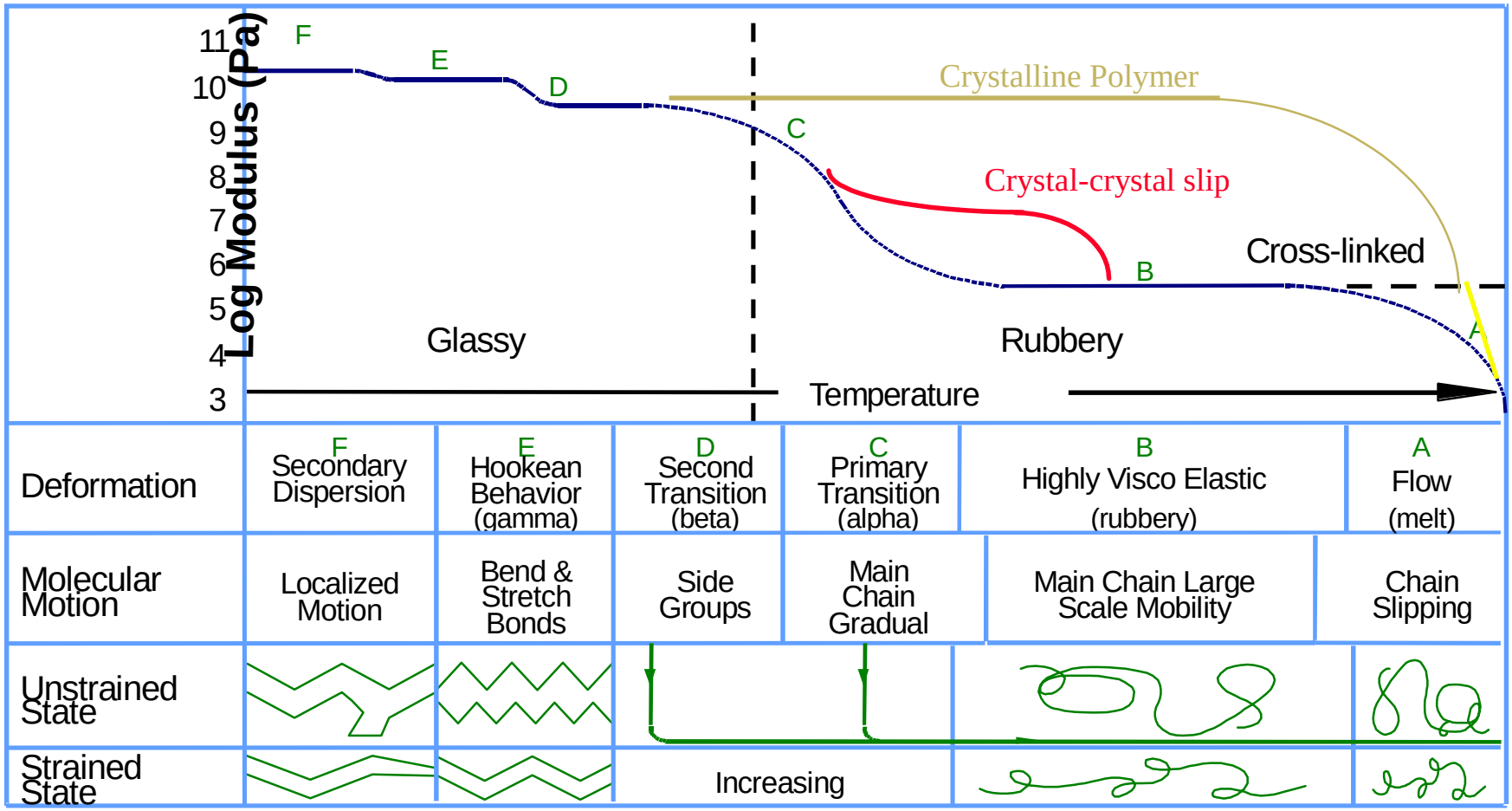
Idealized Multi-Event DMA Scan



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

PerkinElmer™ instruments.

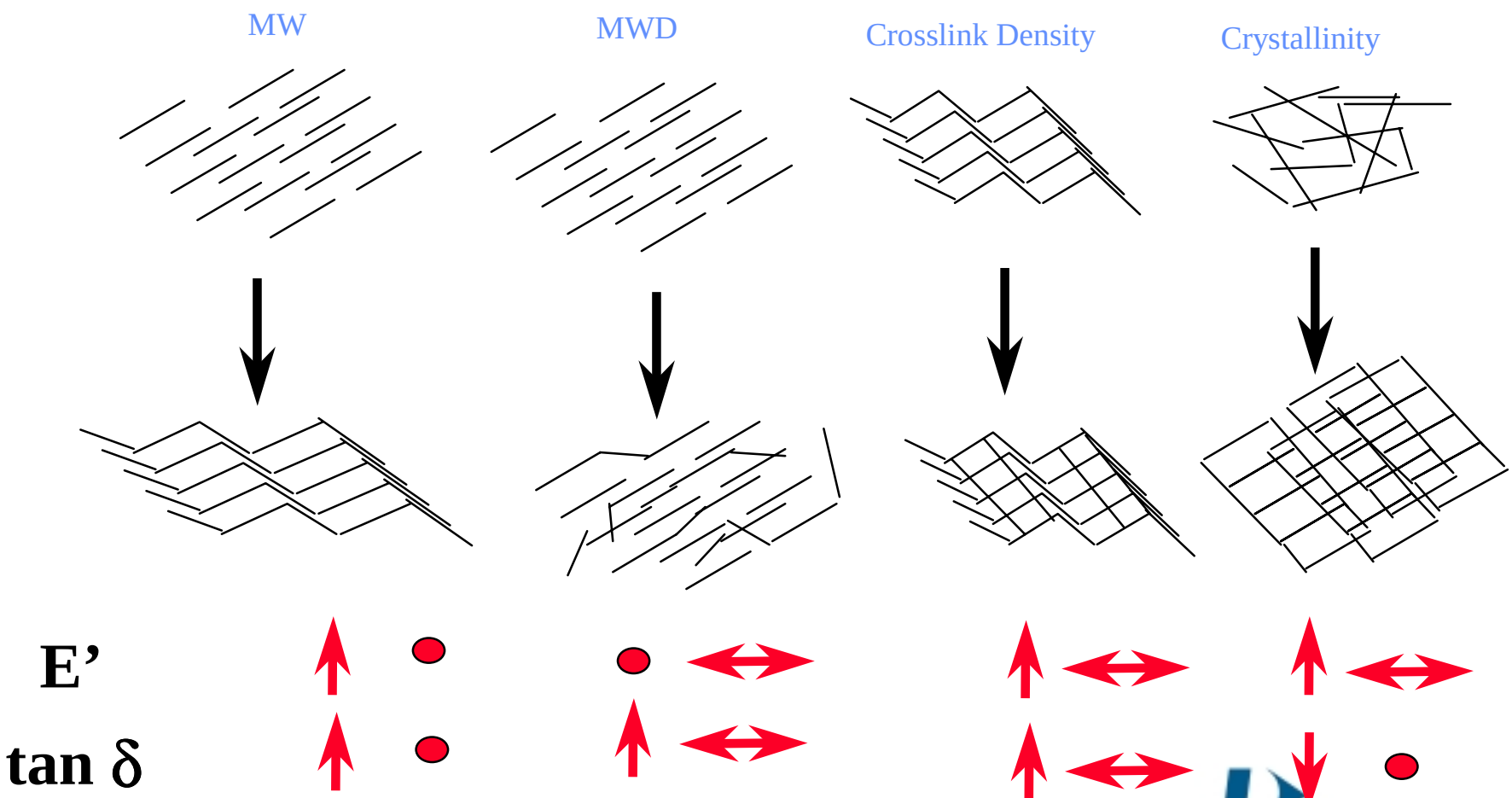
In more detail...



R. Seymour, 1971

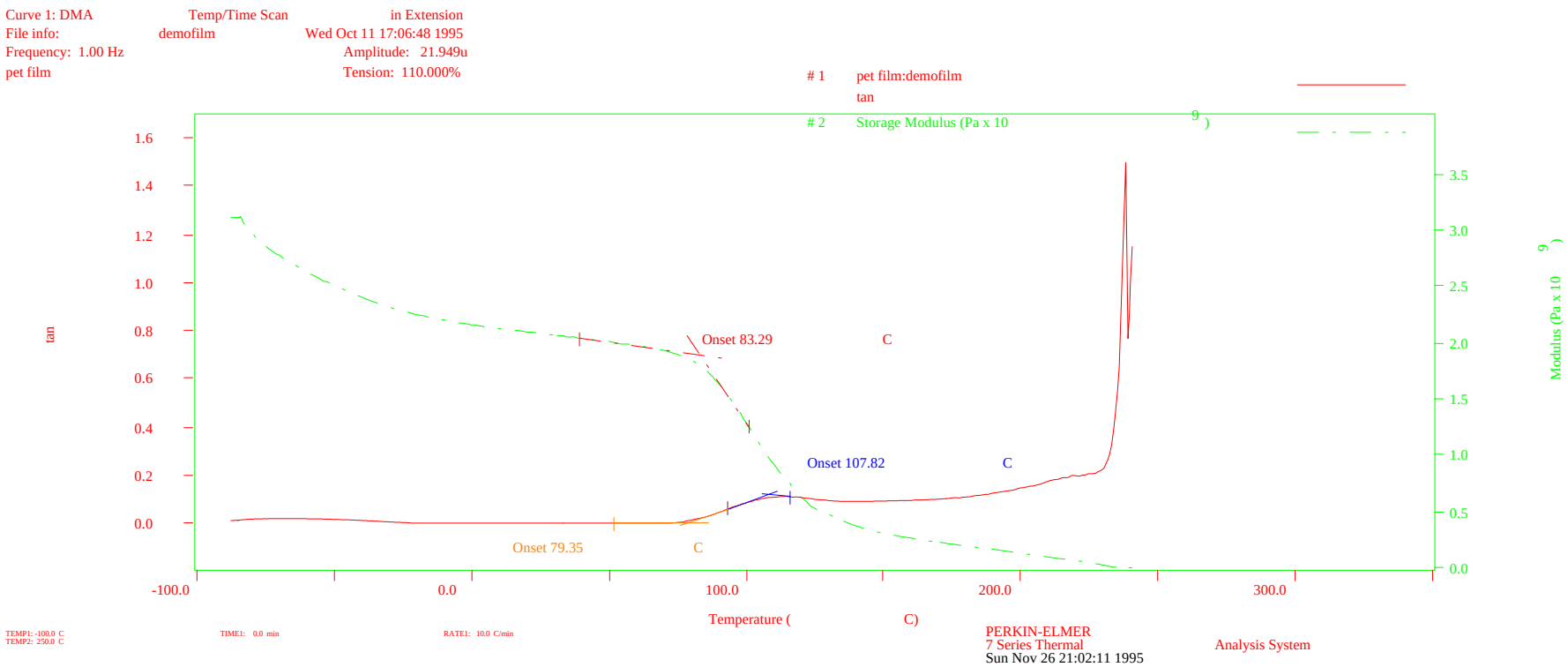
PerkinElmer™ instruments.

Common changes show as:

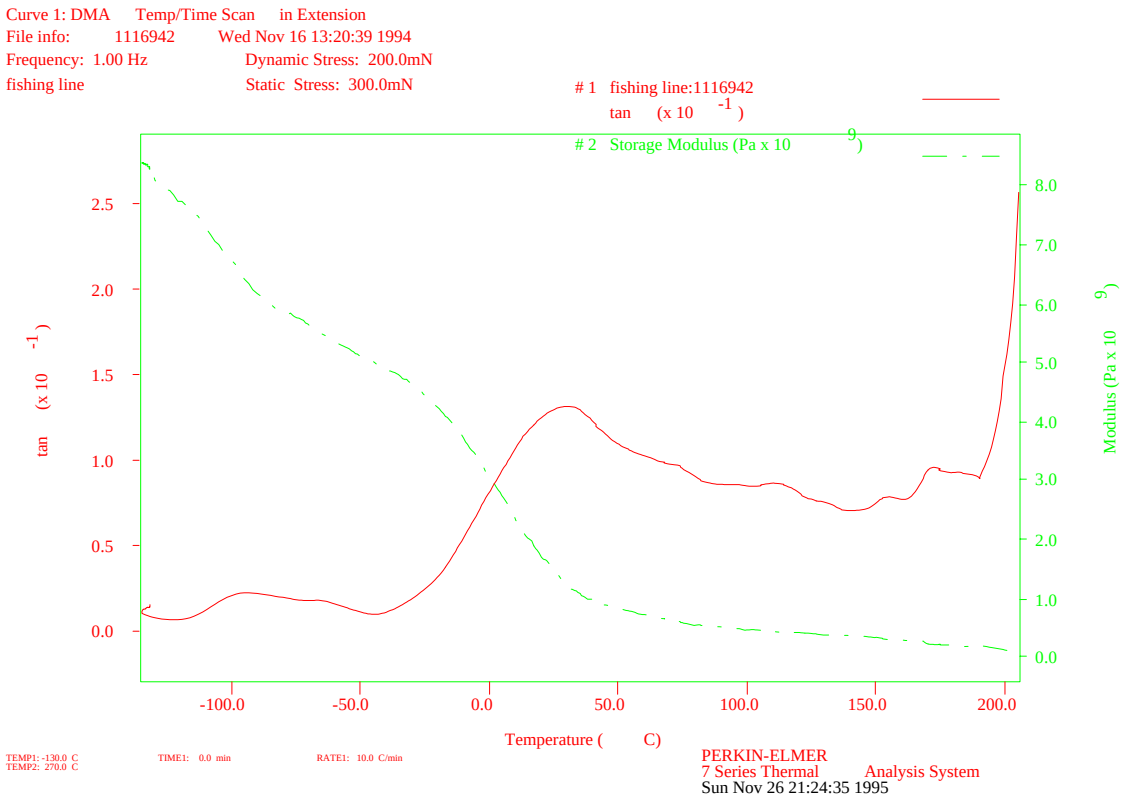


PerkinElmer™
instruments.

Tg are easily seen, as in PET Film



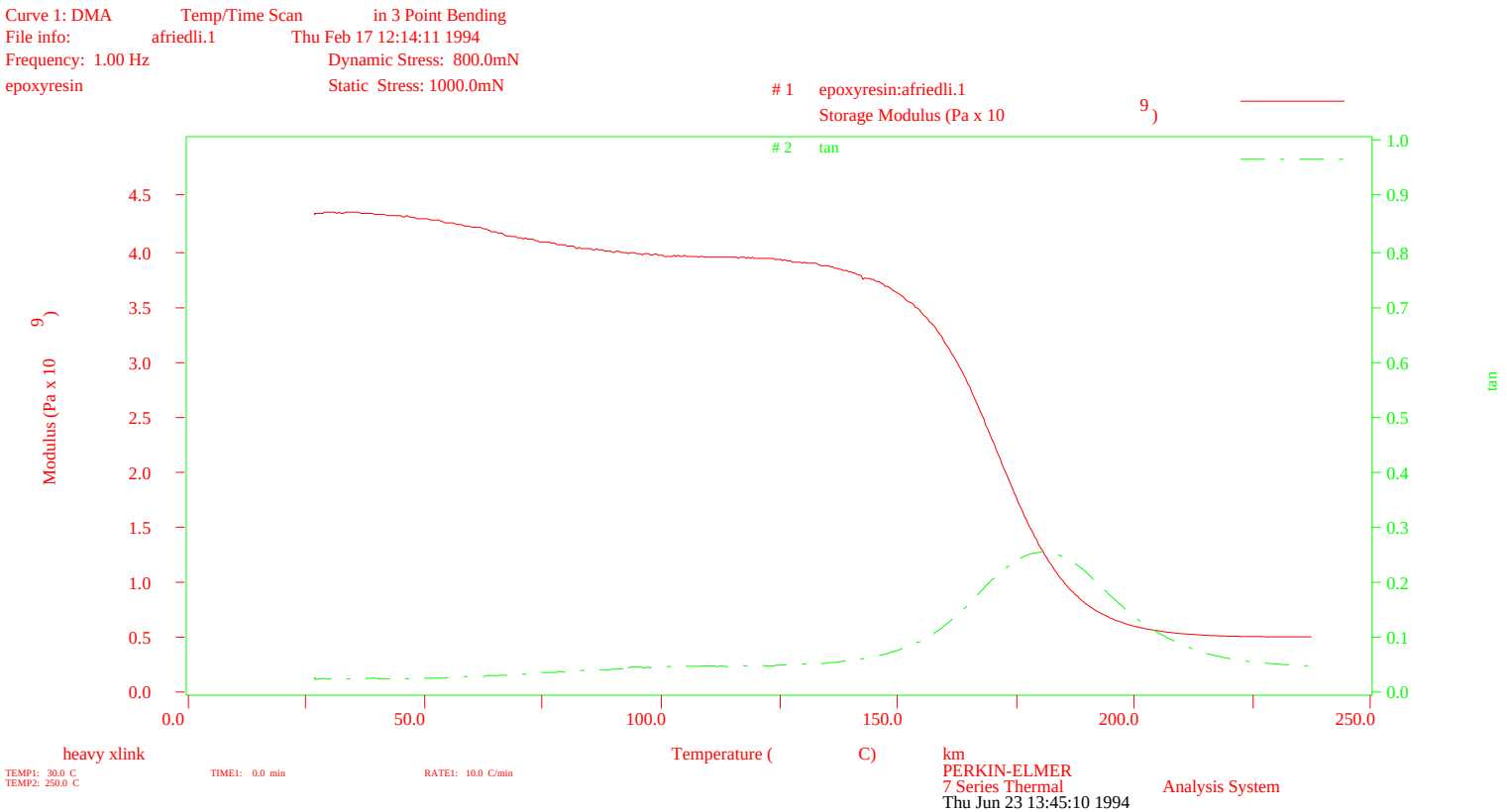
or in PP fishing line.



Sample prep can be minimal if only temperatures are needed.

PerkinElmer™ instruments.

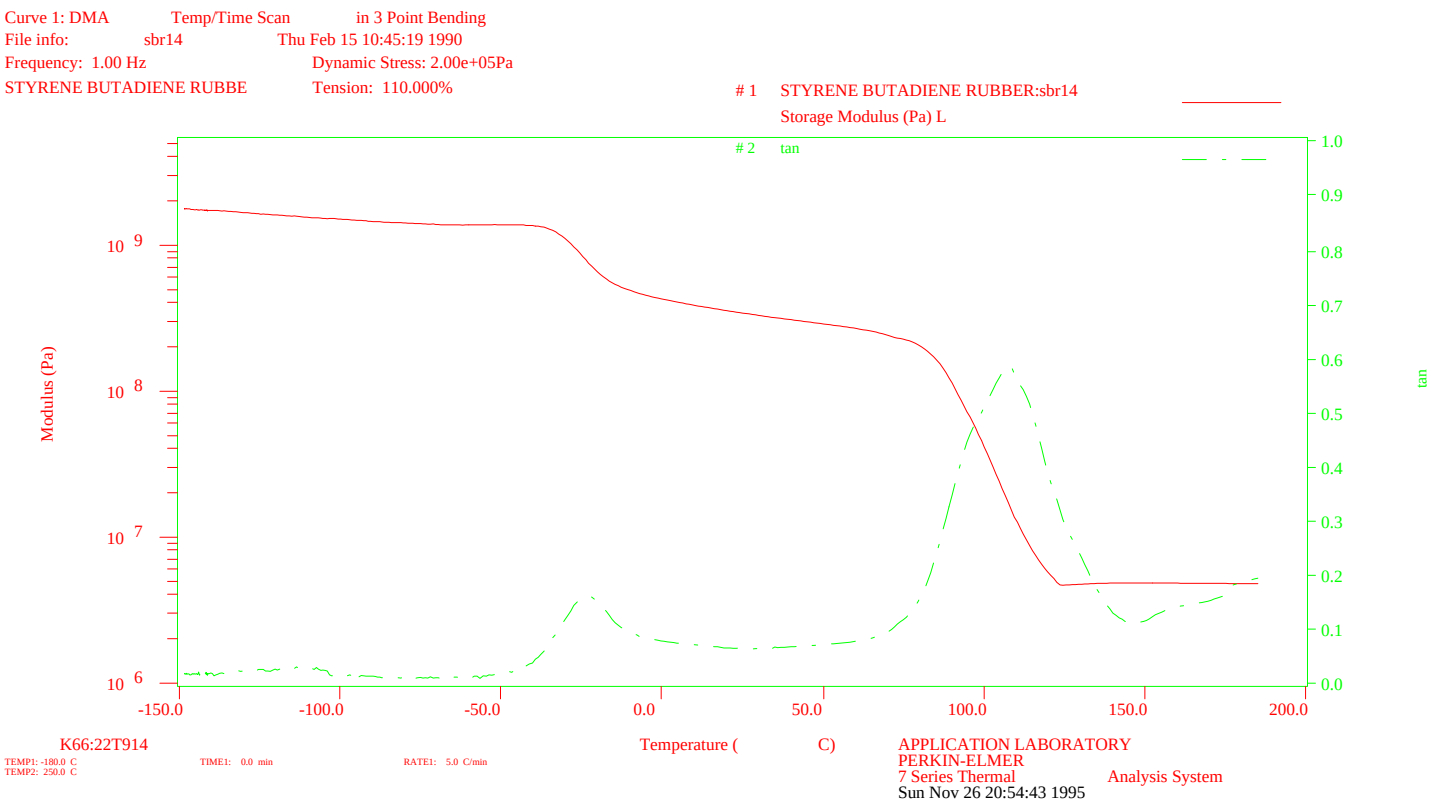
Transitions are clearly seen in highly crosslinked samples



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

PerkinElmer™ instruments.

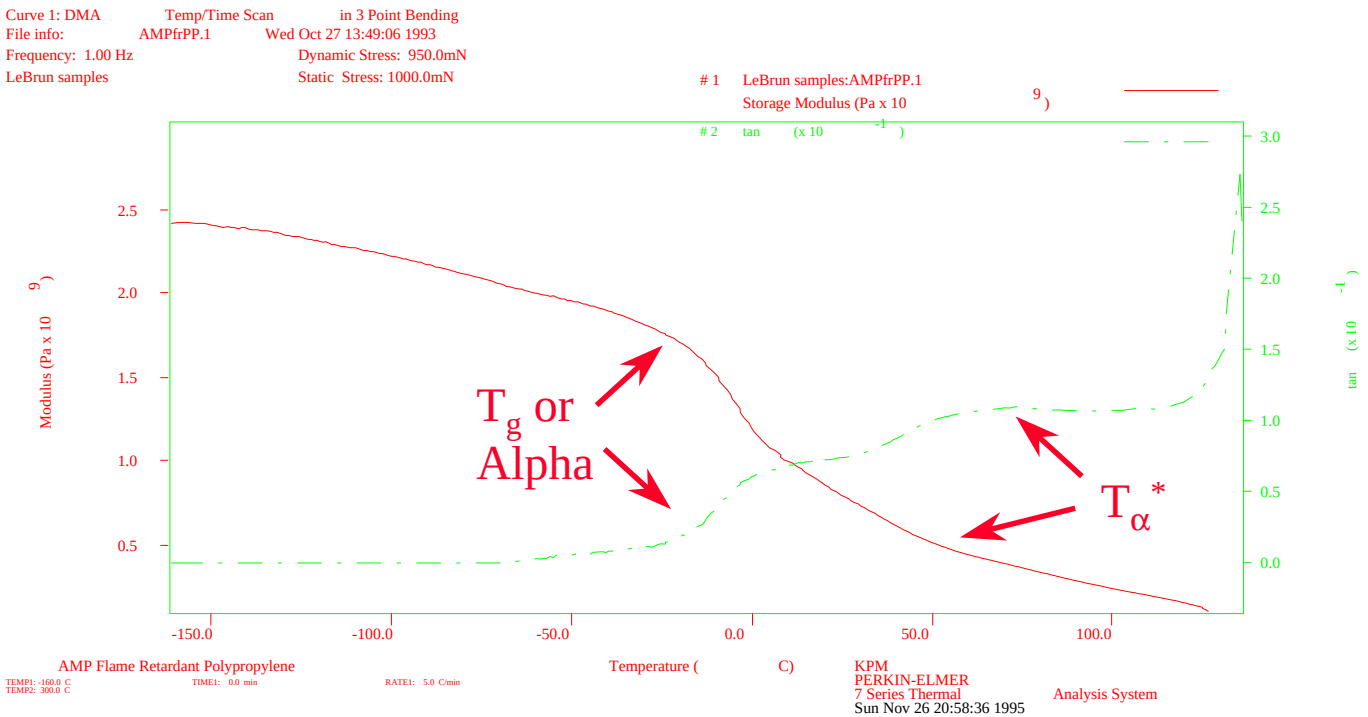
as well as in blends.



PerkinElmer™ instruments.

It’s not always so simple:

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



PerkinElmer™ instruments.

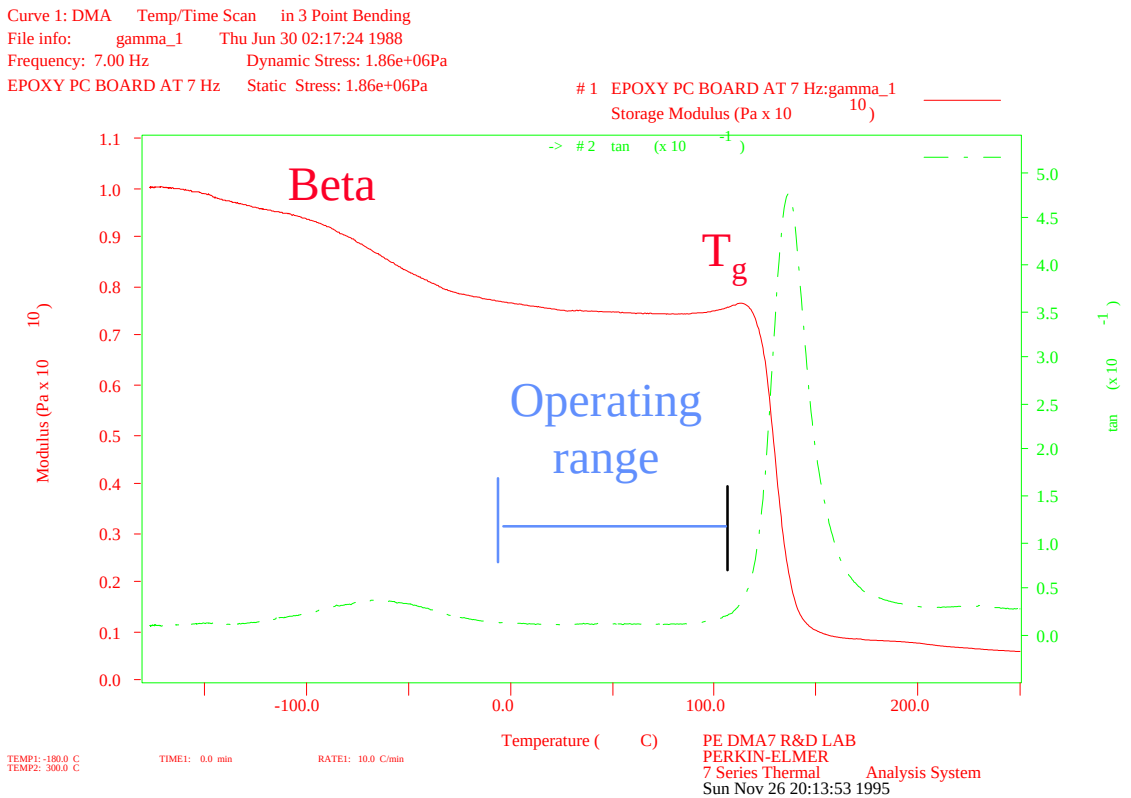
Higher Order Transitions affect toughness



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

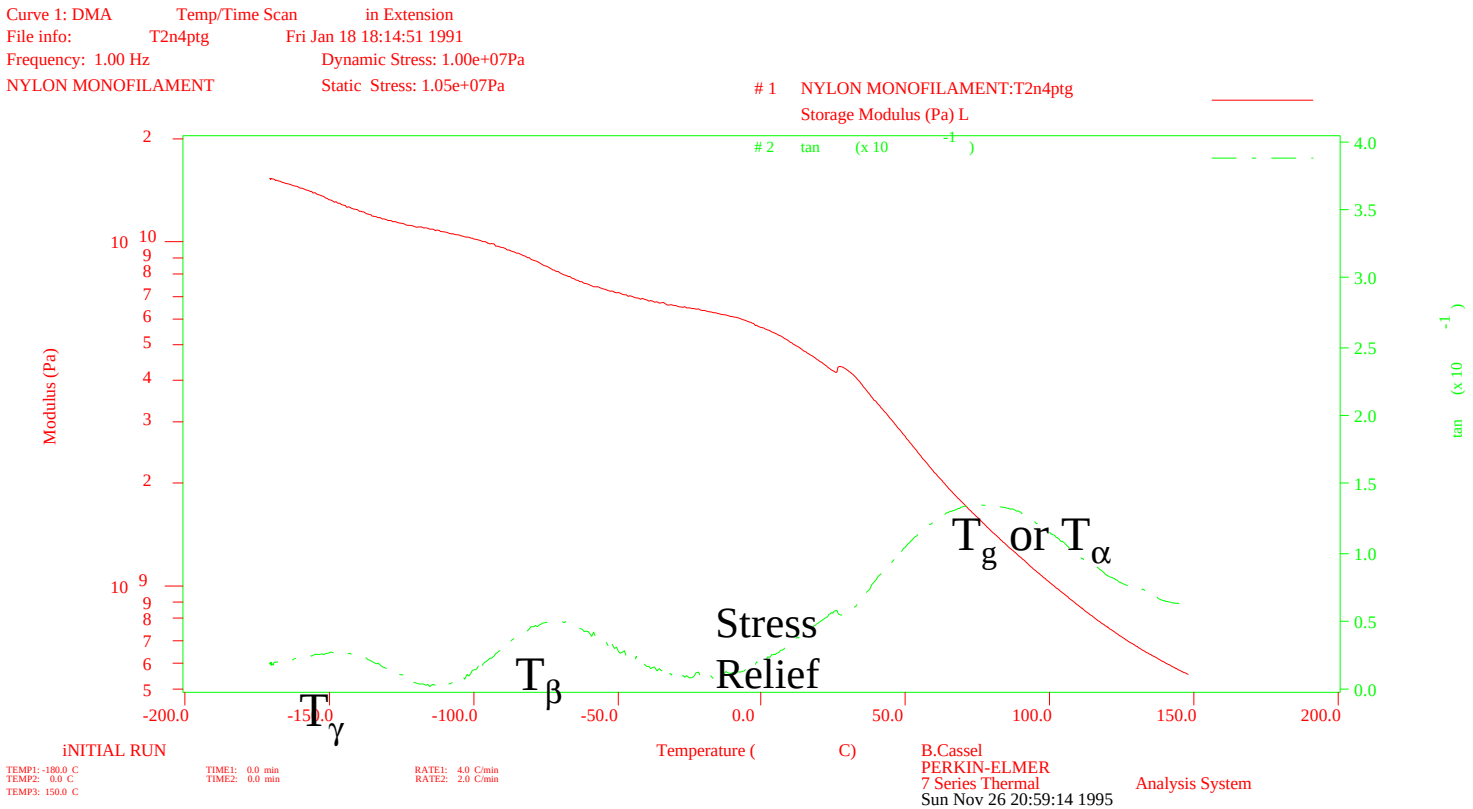
PerkinElmer™ instruments.

...and also define operating range.



PerkinElmer™ instruments.

It can get complex...



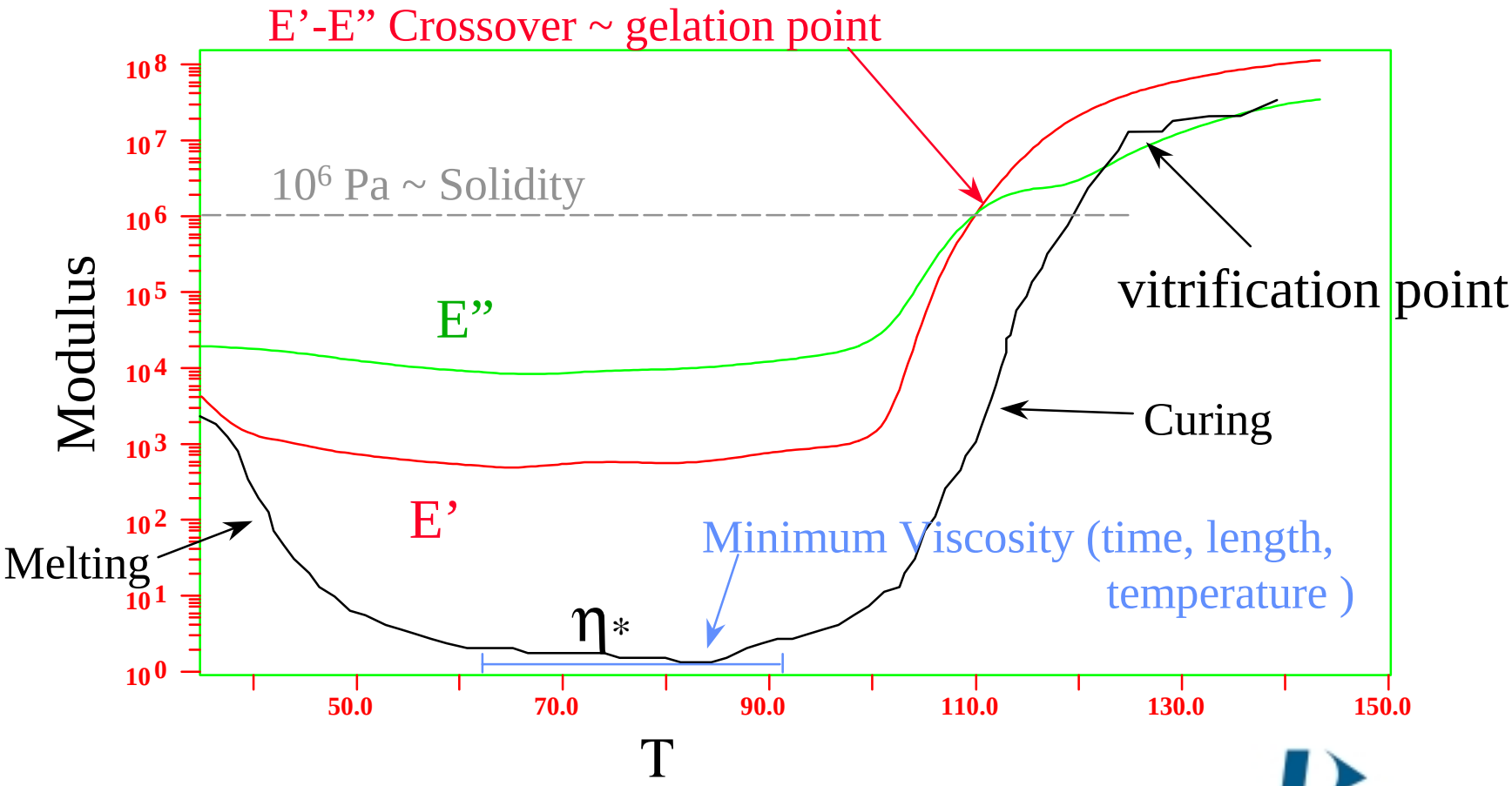
PerkinElmer™ instruments.

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

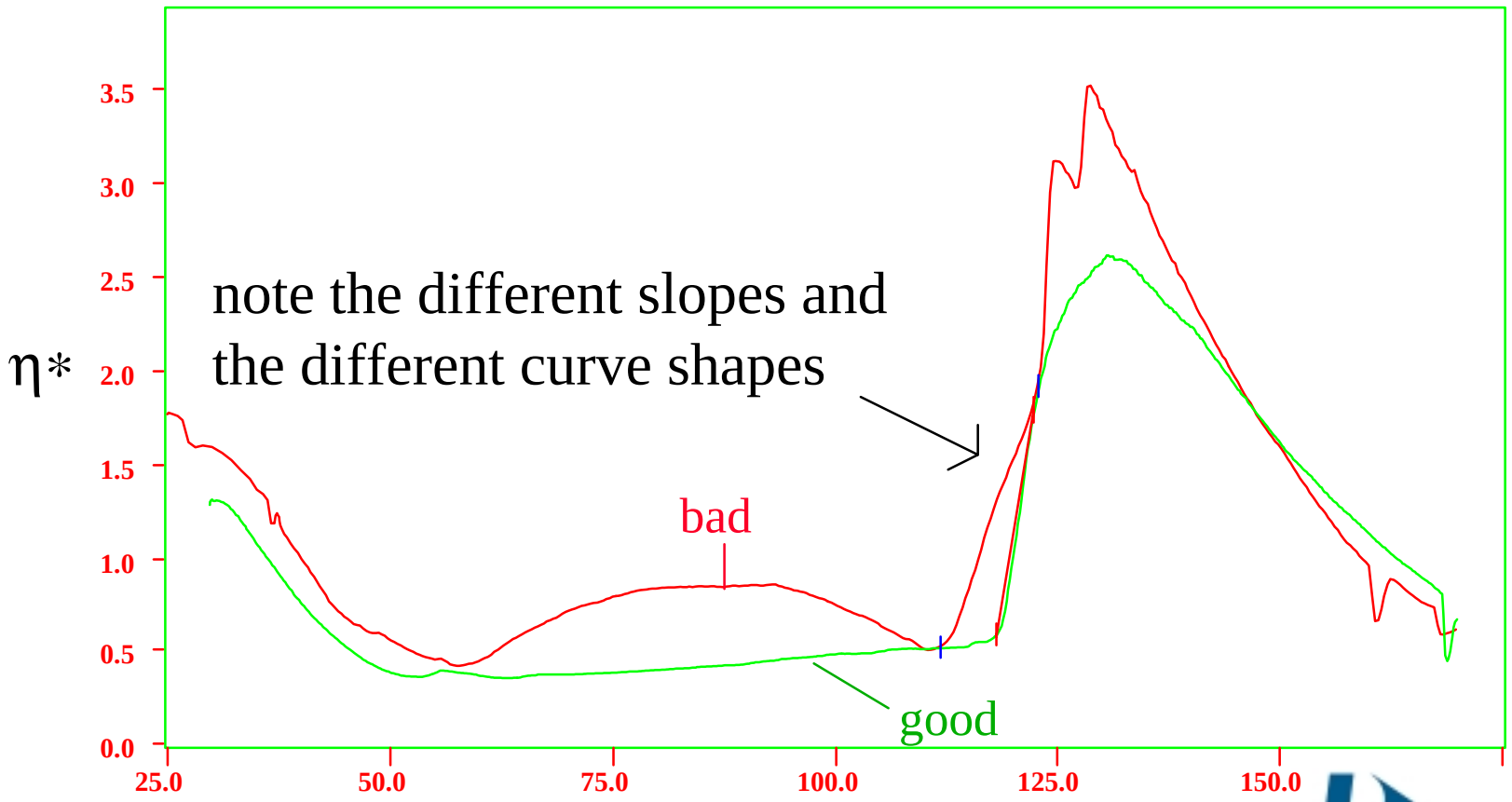
PerkinElmer™
instruments.

Analysis of a Cure by DMA



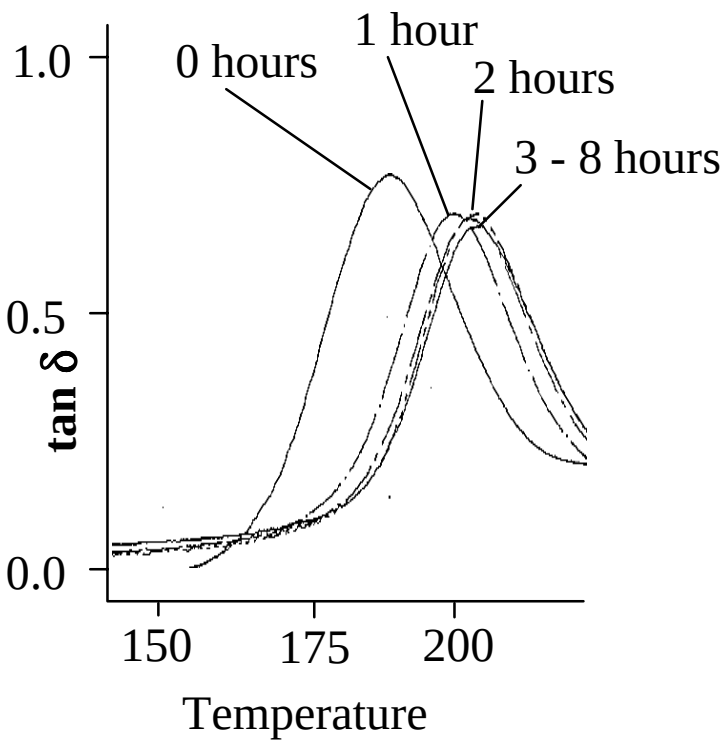
PerkinElmer™ instruments.

QC can often be done by simply fingerprinting the resin.

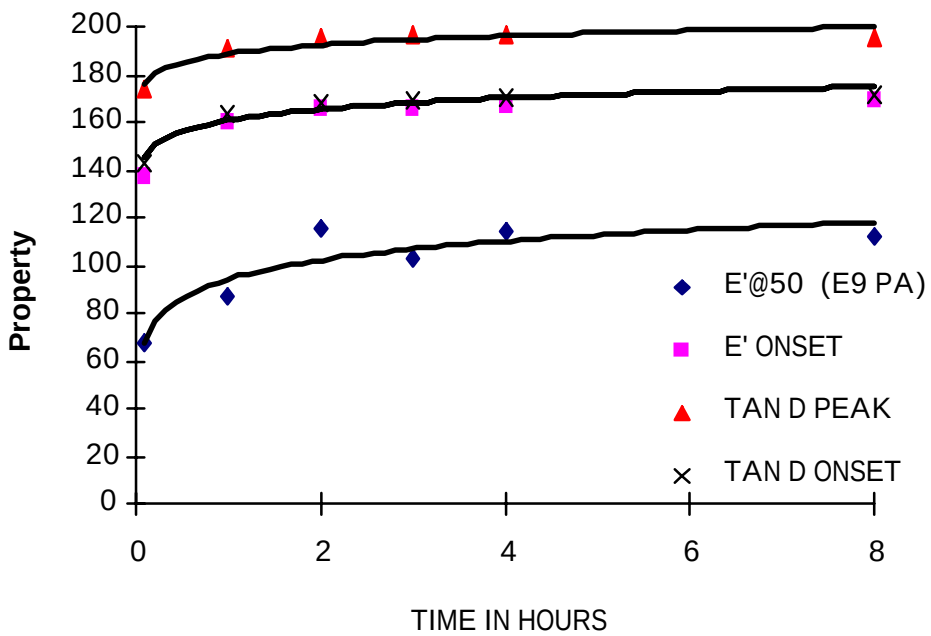


PerkinElmer™
instruments.

Postcure studies allow process optimization:



Postcure time vs... Tg and E'



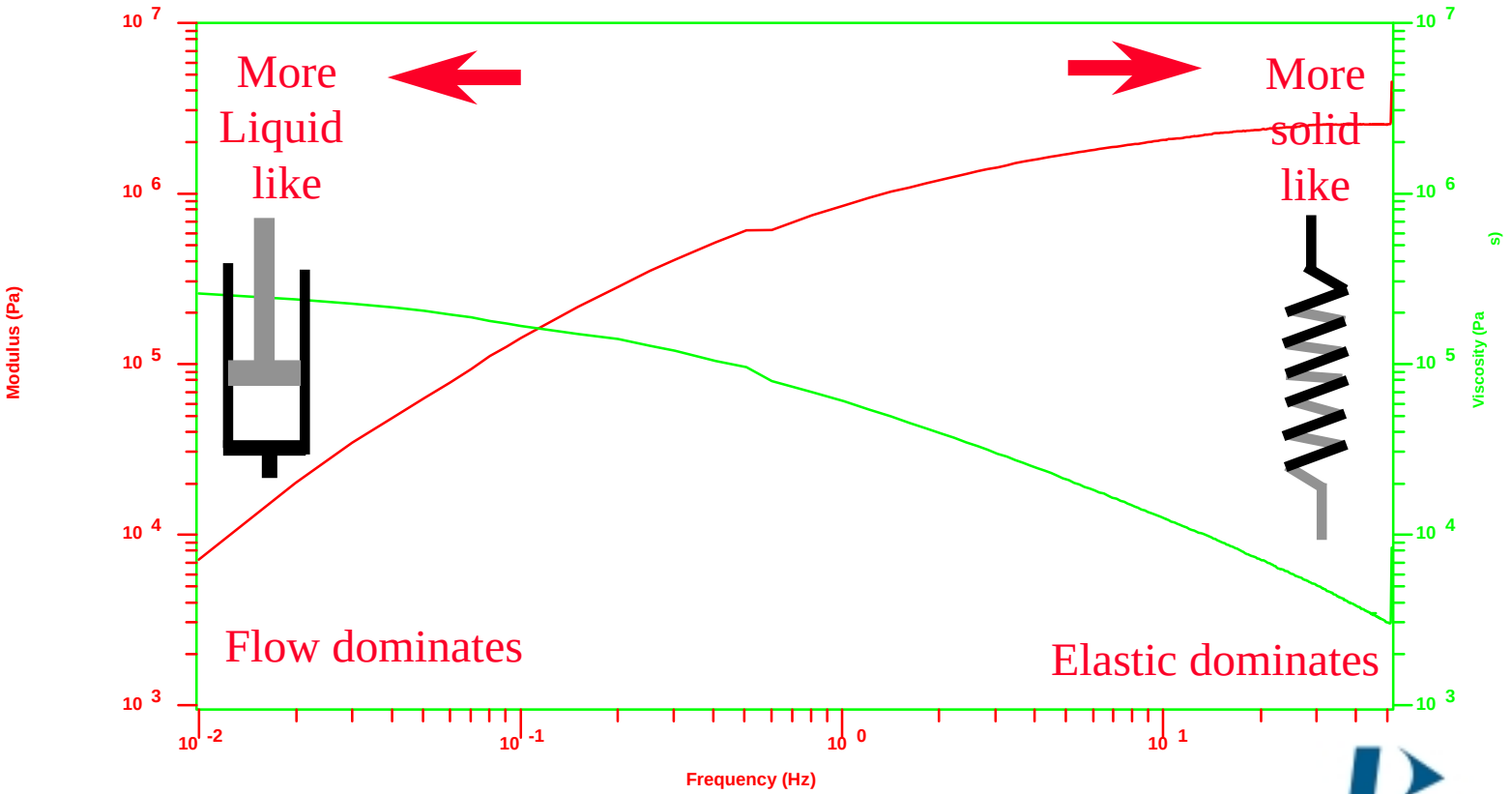
PerkinElmer™ instruments.

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.**

PerkinElmer™
instruments.

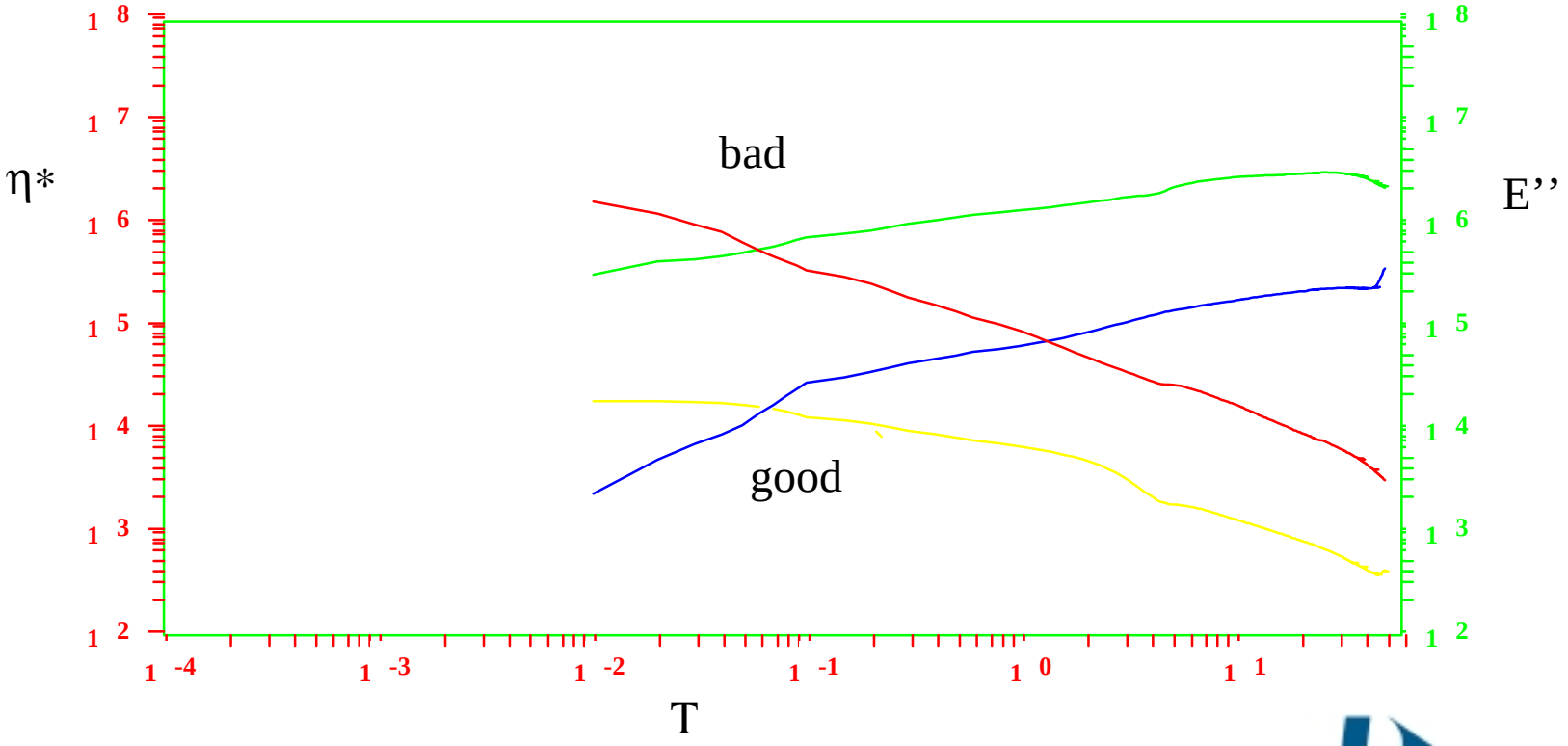
Frequency determines the type of response



PerkinElmer™ instruments.

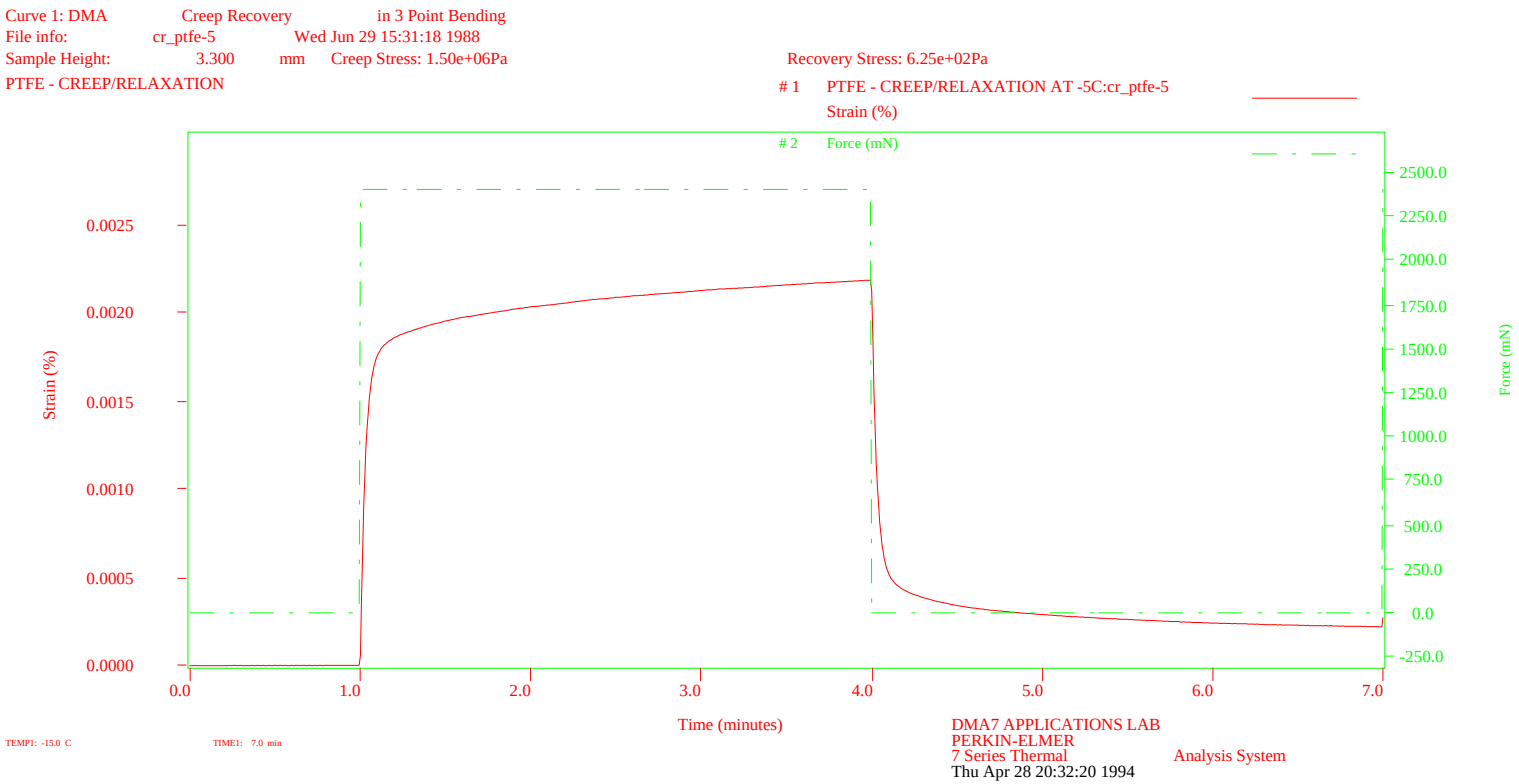
For example, two hot melt adhesives...

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



PerkinElmer™
instruments.

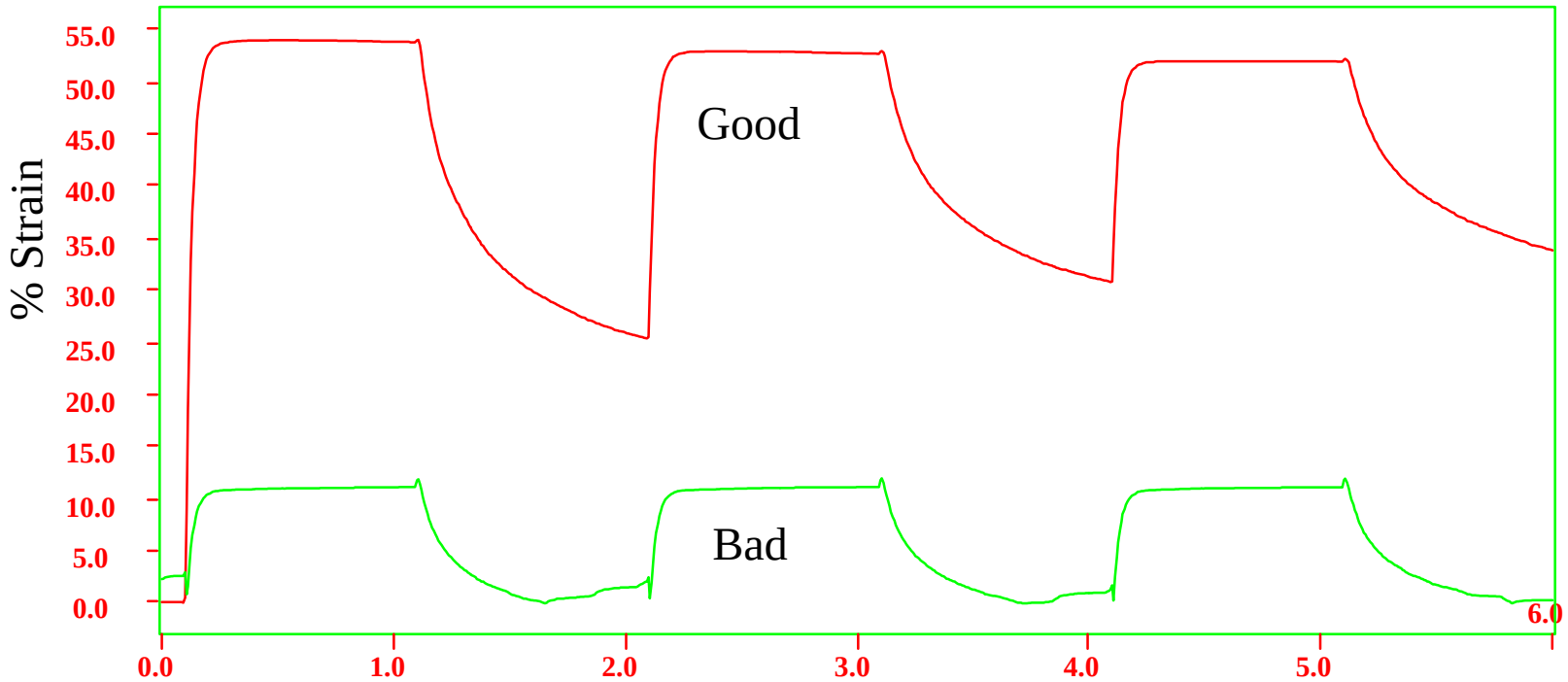
Creep can look at distortion under load,



PerkinElmer™ instruments.

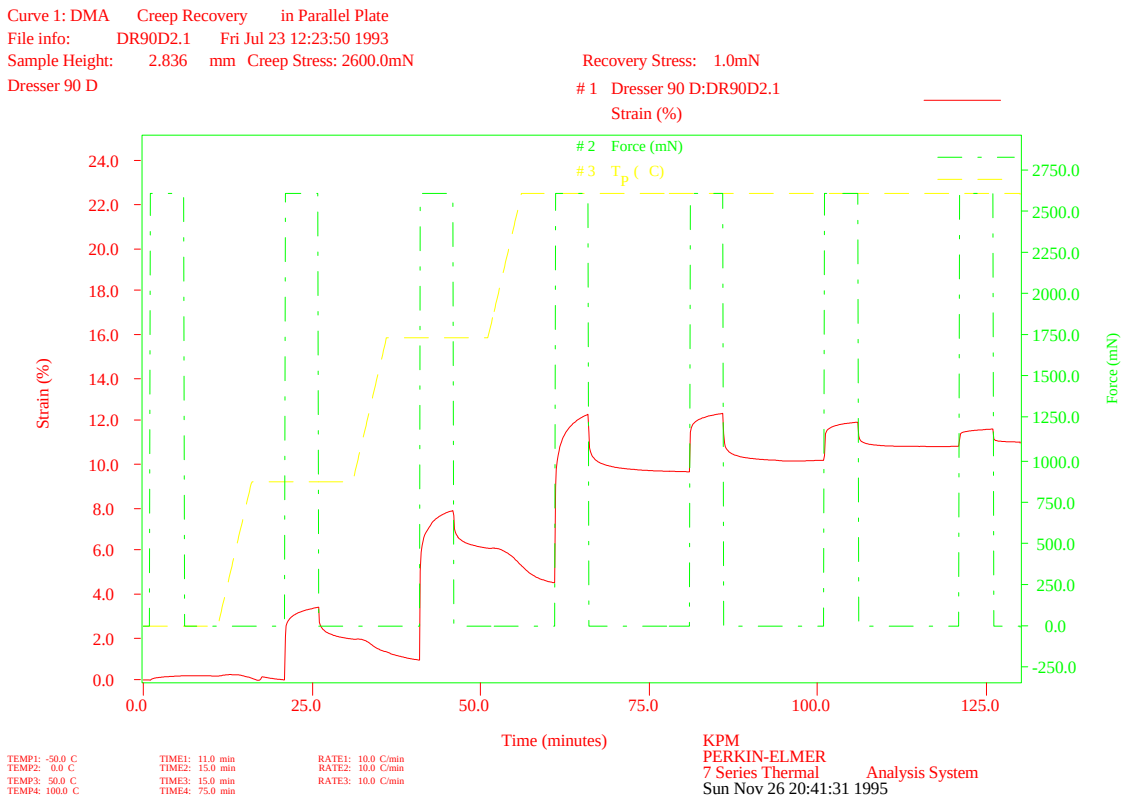
cyclic application of loads,

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.



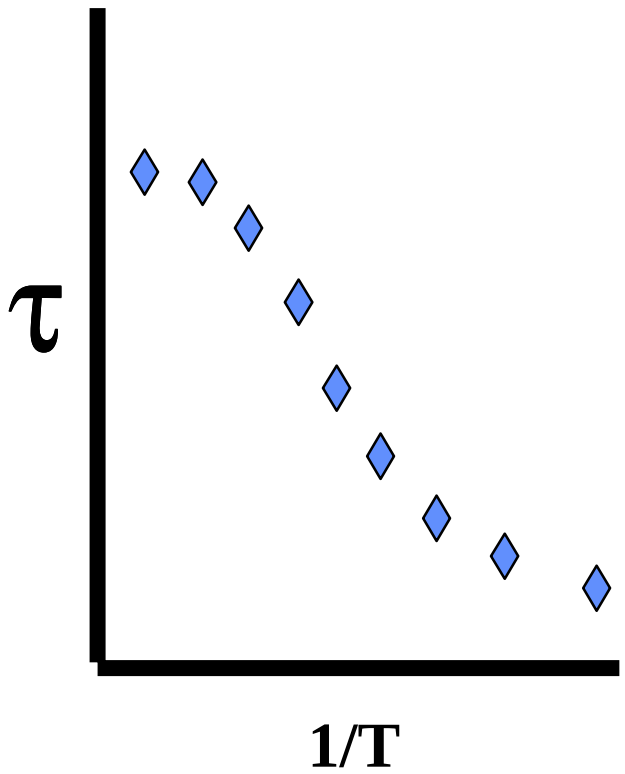
PerkinElmer™ instruments.

and with varying temperatures.



PerkinElmer™ instruments.

And you can tabulate this stuff graphically...

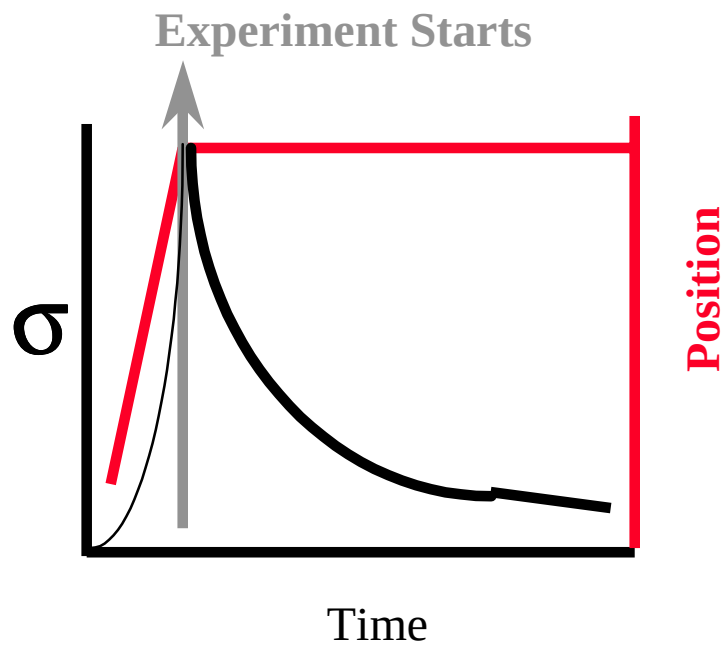


- The time to 1/e percent recovery is the relaxation.
- This is a measure of how quickly a material recovers. (There is a lot more to this subject.)

PerkinElmer™ instruments.

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.

PerkinElmer™
instruments.

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.**

PerkinElmer™
instruments.

Specialized Testing is Possible...

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

Time-Temperature Superposition (TTS)

DEA/DMA

Tests in Solution

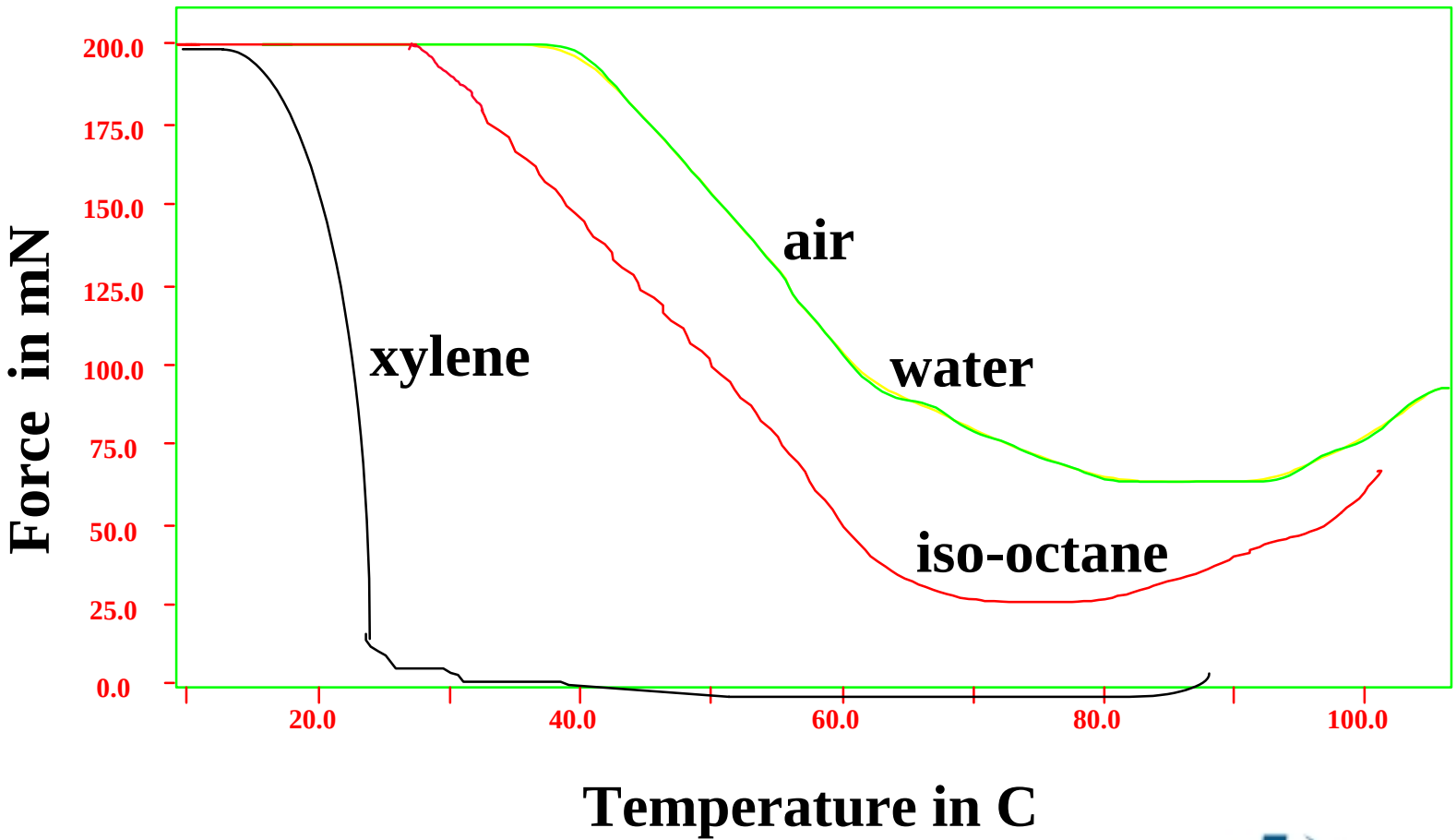
Microscopic DMA

Photo DMA

DMA-?

PerkinElmer™ instruments.

PP fibers in solvent

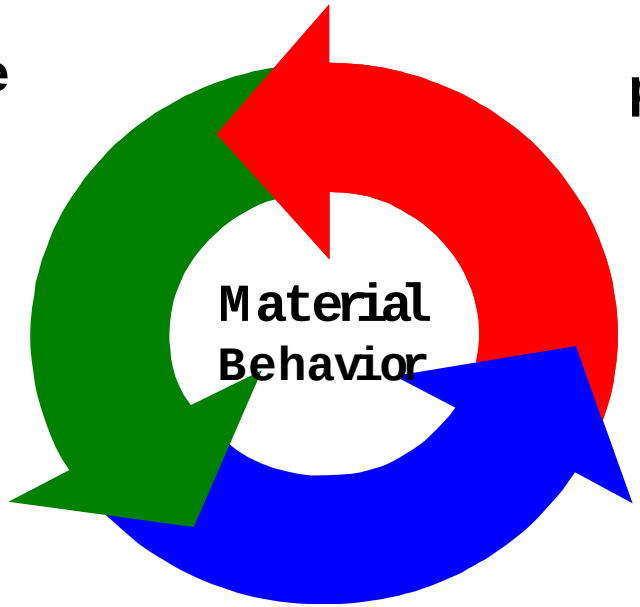


PerkinElmer™
instruments.

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.

References: Books

- Menard, DMA: Introduction to the Technique, Its Applications and Theory, CRC Press, 1999.
- Brostow et a., Failure of Plastics, Hanser, 1986.
- Ferry, Viscoelastic Properties of Polymers, Wiley, 1980.
- Gordon et al., Computer Programs for Rheologists, Hanser, 1995.
- Gol'dman, Prediction of Deformation Properties of Polymeric and Composite Materials,, ACS, 1994.
- Mascosko, Rheology, VCH, 1993.
- Matsouka, Relaxation Phenomena in Polymers, Hanser, 1993.
- McCrum et al, Anelastic and Dielectric Properties of Polymeric Solids, Dover, 1992 (reprint of 1967 edition).
- Nielsen et al., Mechanical Properties of Polymers and Composites, Dekker, 1994.
- Sperling, Introduction to Physical Polymer Science, Academic Press, 1994.
- Ward et al., Introduction to Mechanical Properties of Solid Polymers, Wiley, 1993.

PerkinElmer™ instruments.

Artisan Technology Group is an independent supplier of quality pre-owned equipment

Gold-standard solutions

Extend the life of your critical industrial, commercial, and military systems with our superior service and support.

We buy equipment

Planning to upgrade your current equipment? Have surplus equipment taking up shelf space? We'll give it a new home.

Learn more!

Visit us at **artisantg.com** for more info on price quotes, drivers, technical specifications, manuals, and documentation.

Artisan Scientific Corporation dba Artisan Technology Group is not an affiliate, representative, or authorized distributor for any manufacturer listed herein.

We're here to make your life easier. How can we help you today?

(217) 352-9330 | sales@artisantg.com | artisantg.com

ARTISAN® TECHNOLOGY GROUP