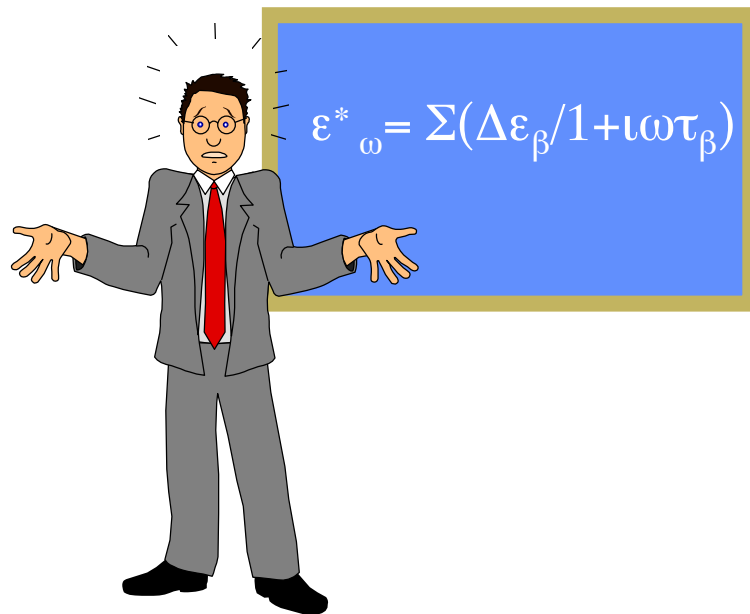
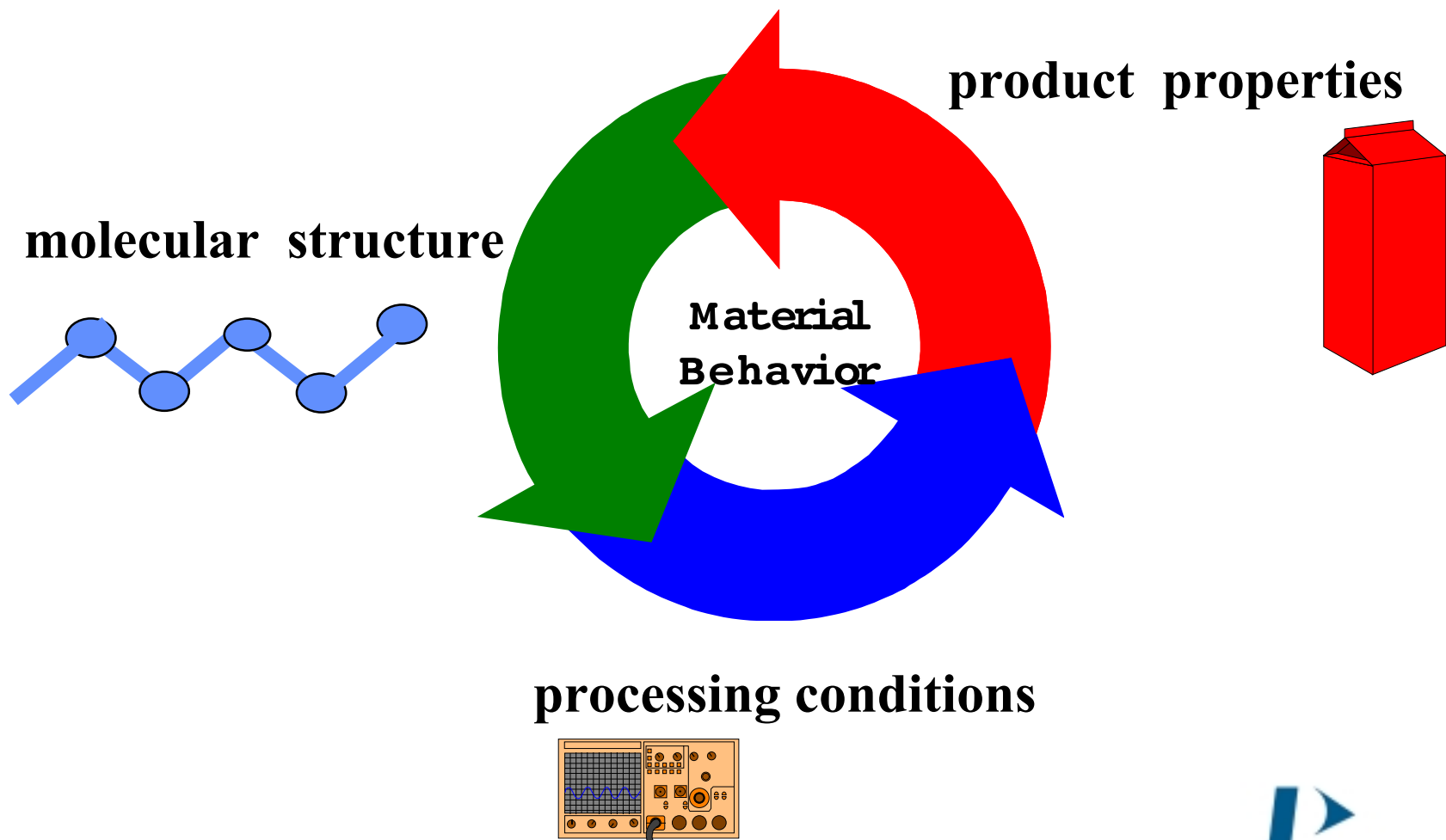


Dynamic Mechanical Analysis (DMA) Basics and Beyond



Dr. Lin Li
Thermal Analysis
PerkinElmer Inc.
April 2000

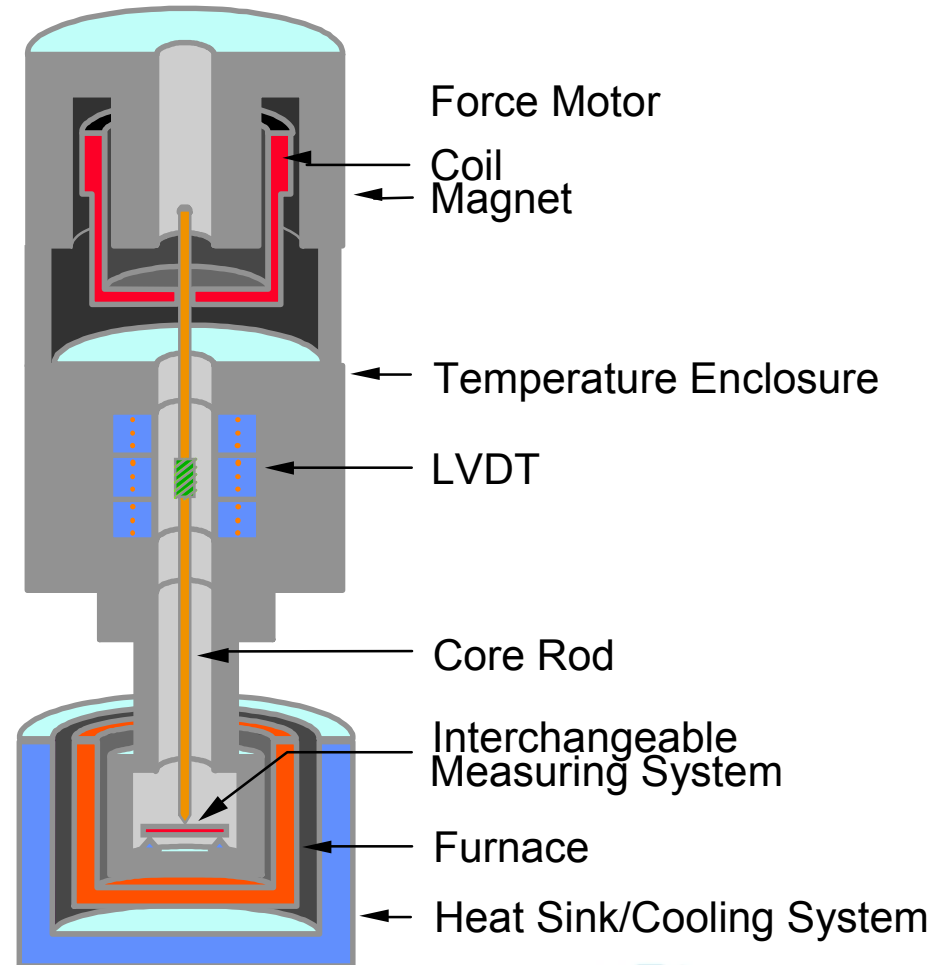
The DMA lets you relate:



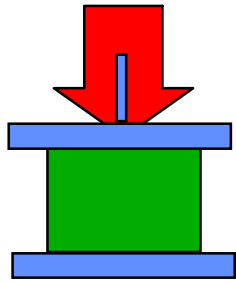
DMA Structure in general

How the DMA works:

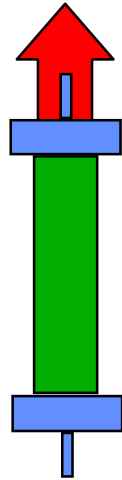
- Constant inputs and outputs function as in the TMA
- A sine wave current is added to the force coil
- The resultant sine wave voltage of the LVDT is compared to the sine wave force
- The amplitude of the LVDT is related to the storage modulus, E' via the spring constant, k .
- The phase lag, δ , is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



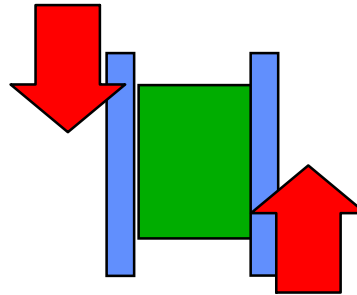
Outstanding Flexibility 1: Multiple Geometries



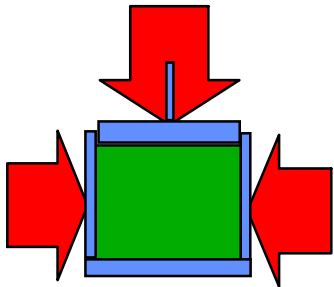
Compressive



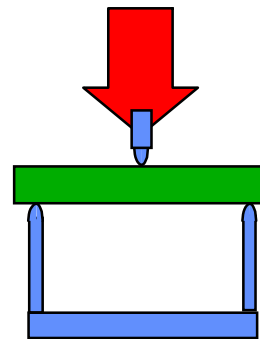
Extension



Shear



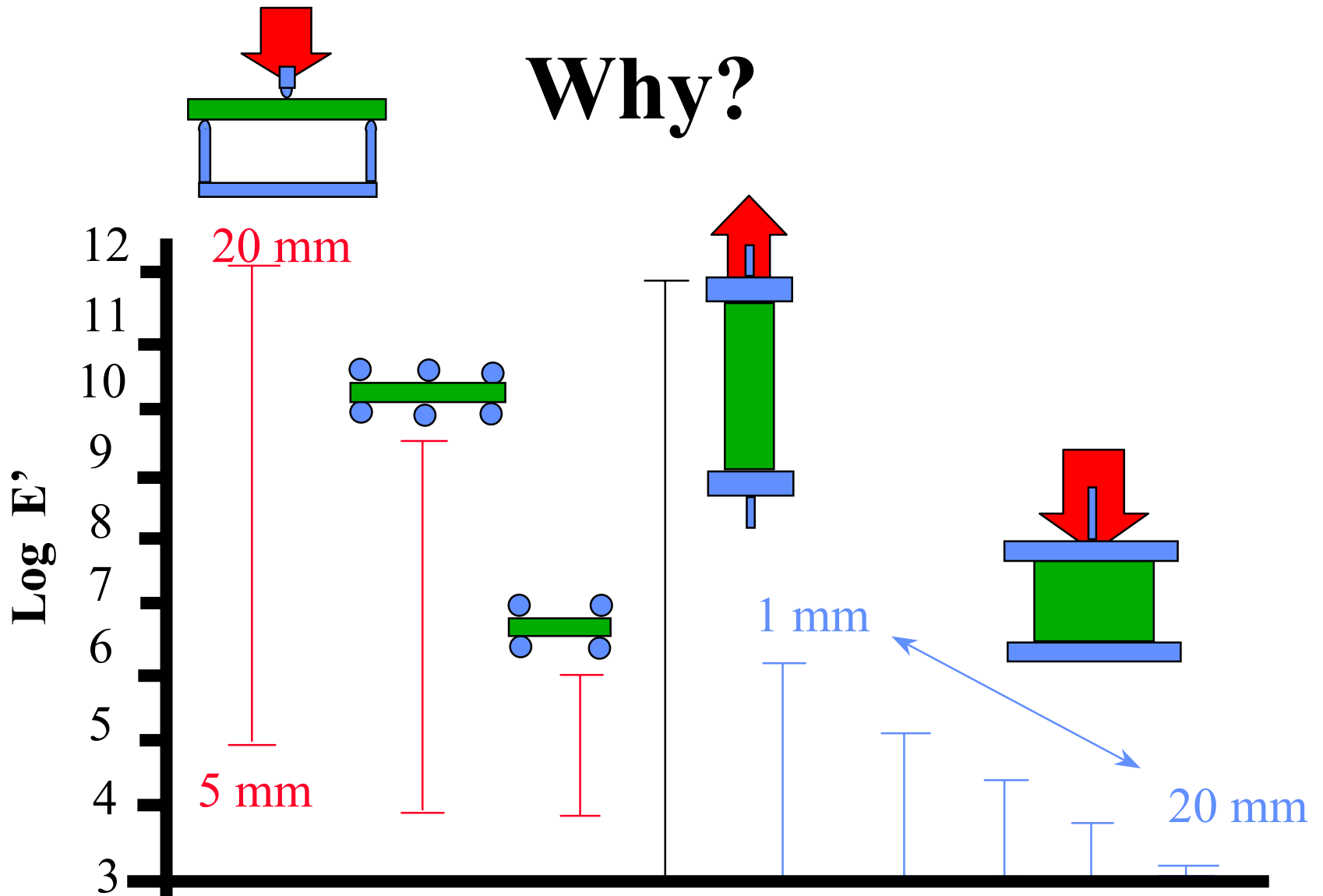
Cup & Plate



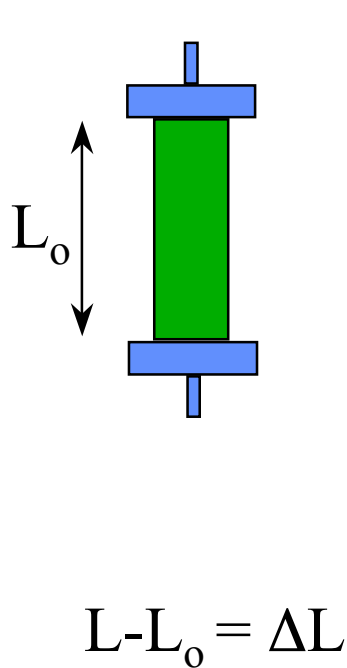
Flexure

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

Why?



Stress Causes Strain...



Cauchy or
Engineering Strain

$$\epsilon = \Delta L / L_0$$

Henchy or
True Strain

$$\epsilon = \ln (\Delta L / L_0)$$

Kinetic Theory
of Rubber Strain

$$\epsilon = 1/3 \{L / L_0 - (L_0 / L)^2\}$$

Kirchhoff Strain

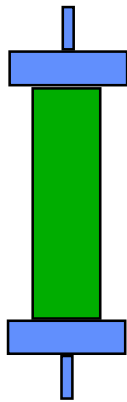
$$\epsilon = 1/2 \{ (L / L_0)^2 - 1 \}$$

Murnaghan Strain

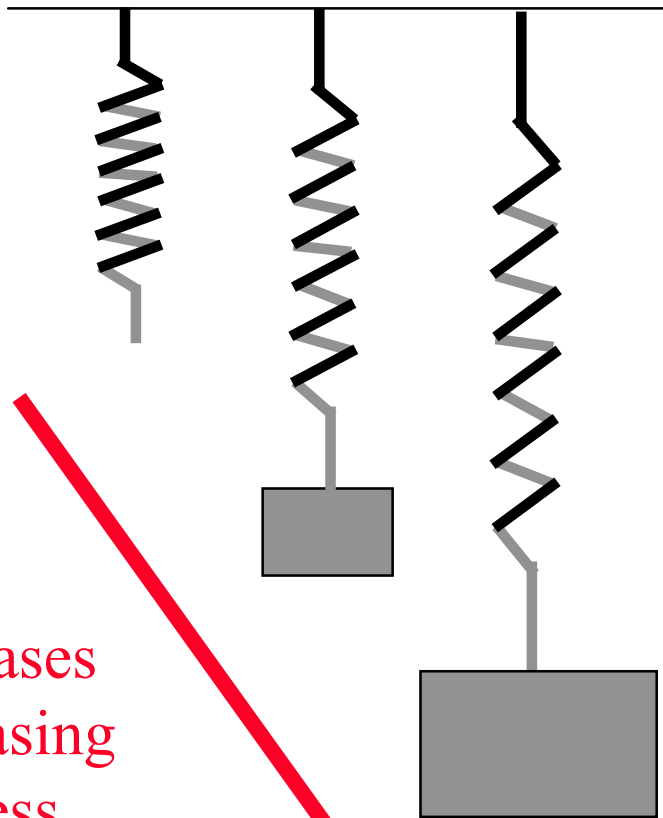
$$\epsilon = 1/2 \{ 1 - (L_0 / L)^2 \}$$

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

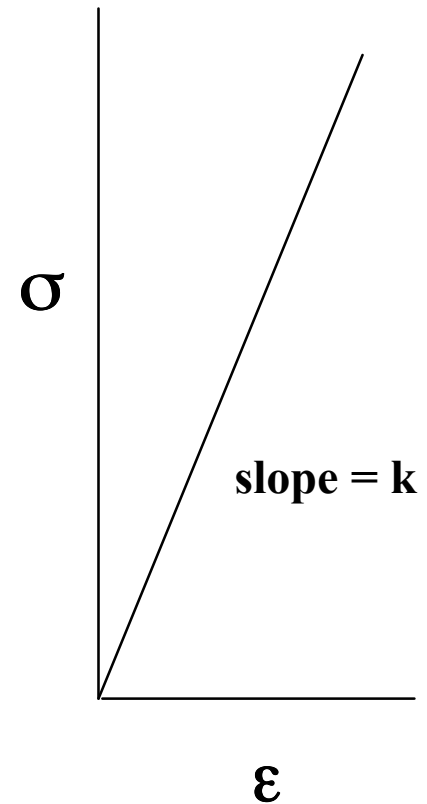
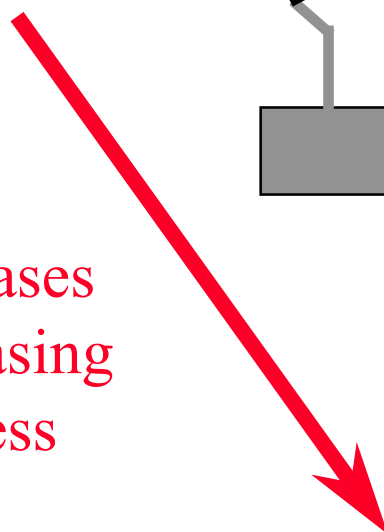
The Elastic Limit: Hooke's Law



=

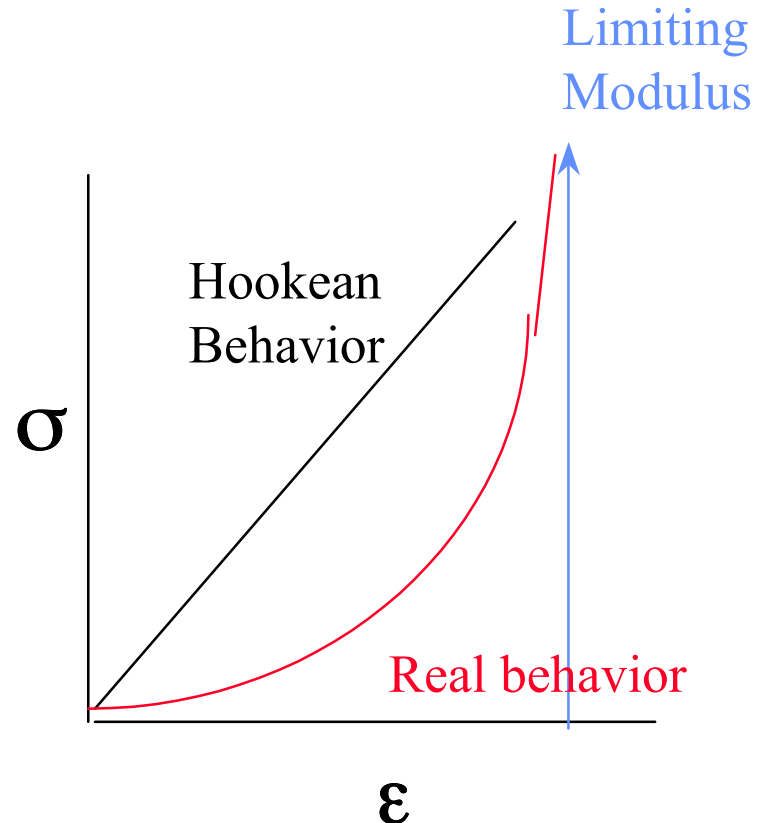
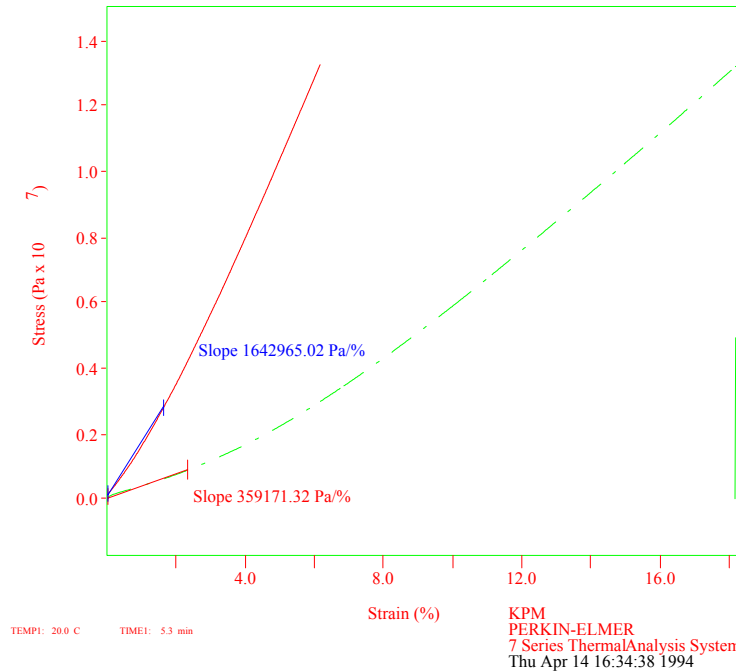


Strain increases
with increasing
Stress

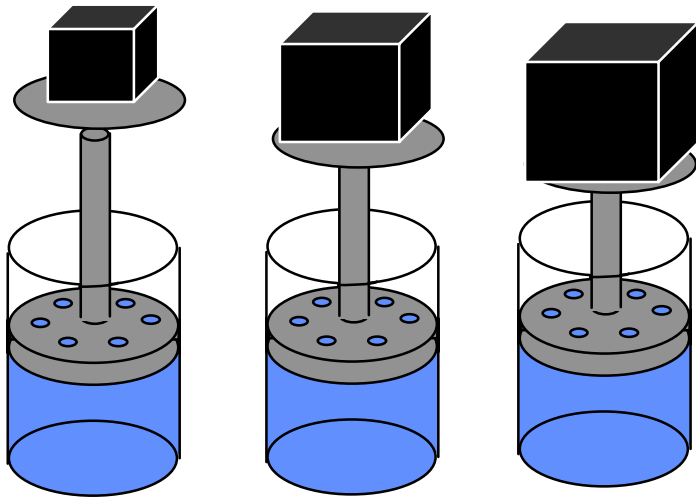


Real vs... Hookean Stress-Strain Curves

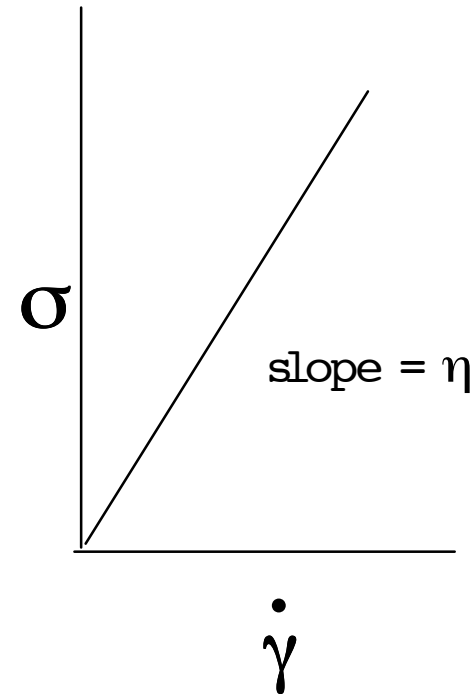
Curve 1: DMCreep Recovery Parallel Plate
 File info: Drrsr90R.2Thu Apr 14 15:16:52 1994
 Sample Height: 3.359 mm Creep Stress: 2600.0mN
 Dresser 90 Durameter
 Recovery Stress: 1.0mN



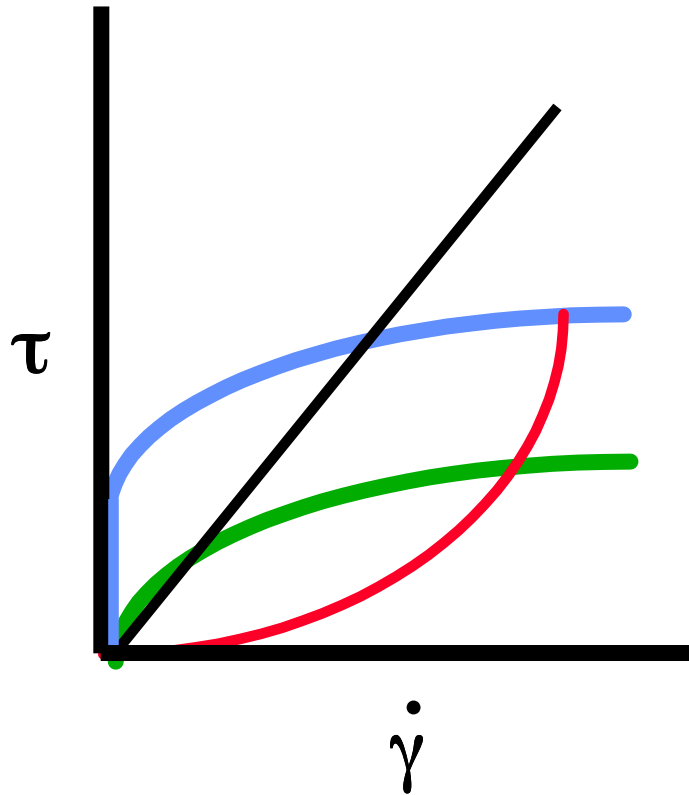
The Viscous Limit: Newtonian Behavior



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

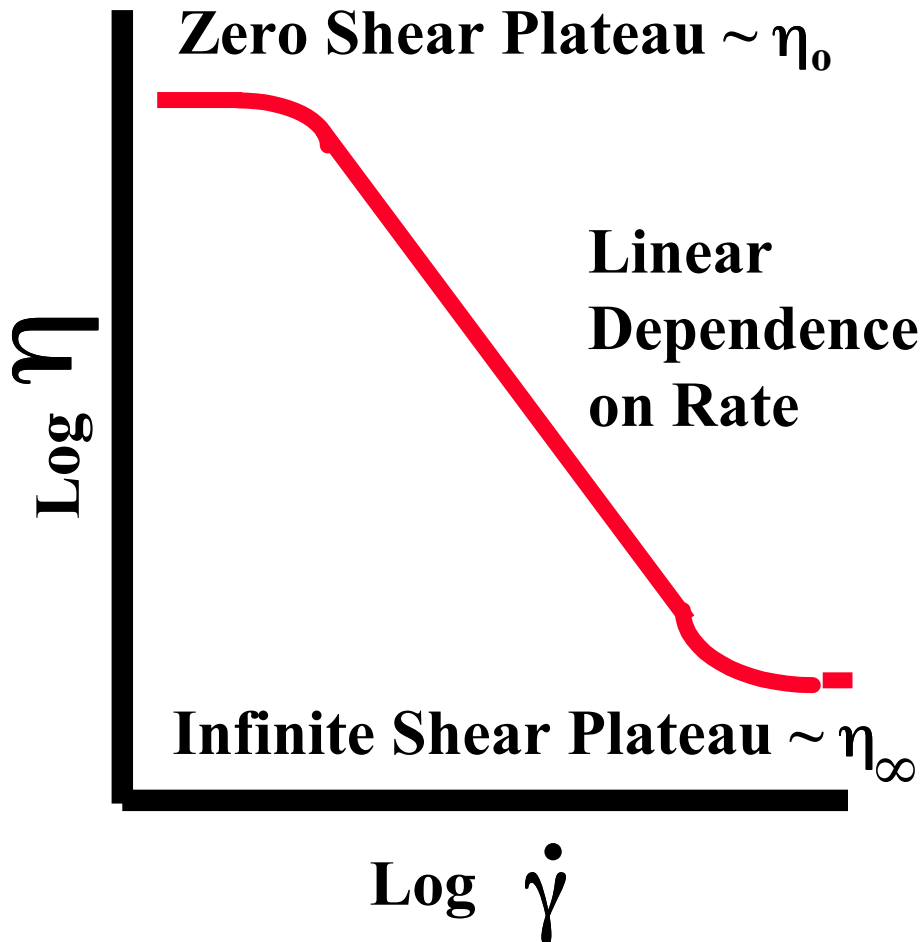


Viscosity Effects



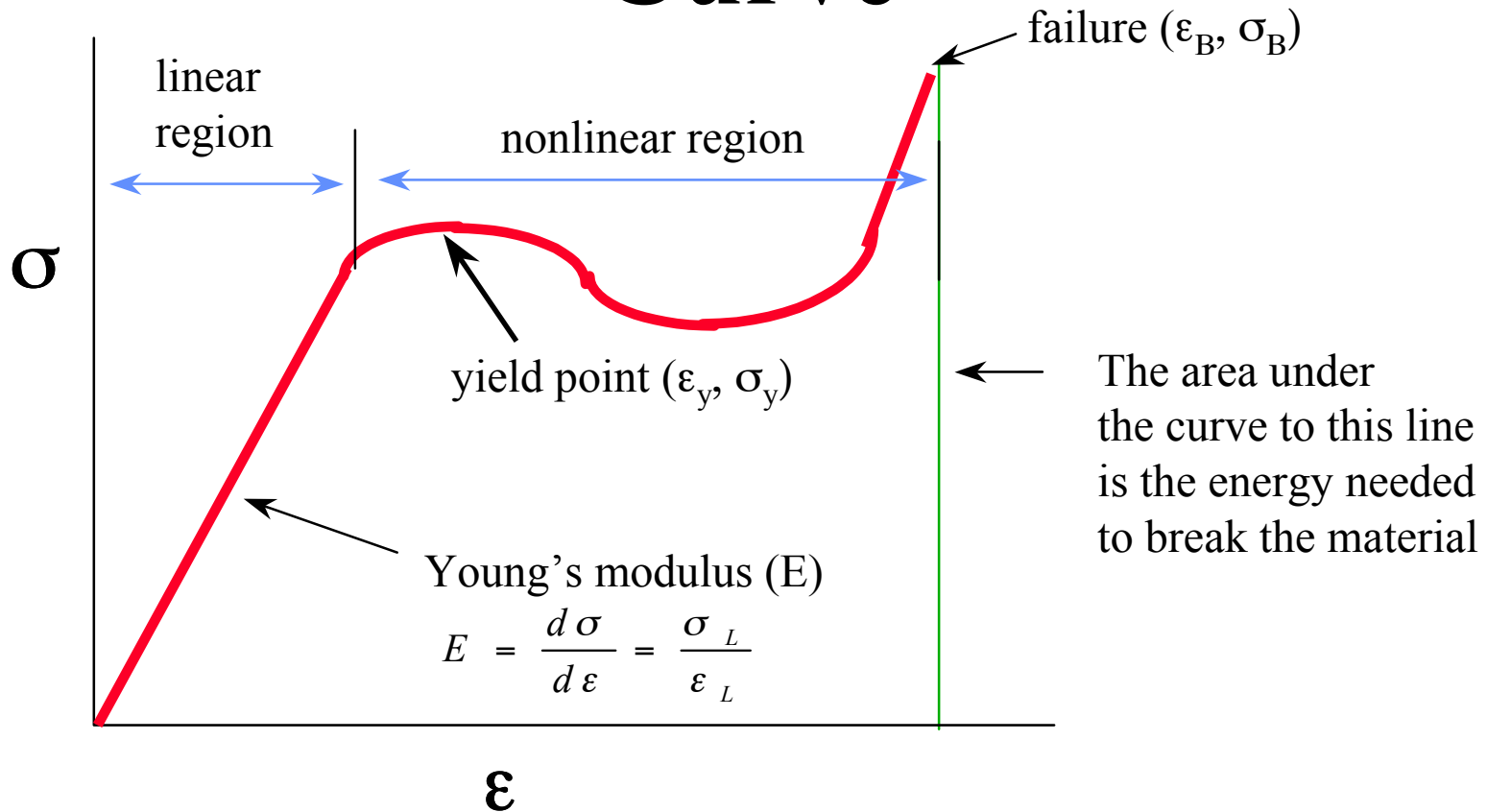
- Newtonian behavior is linear and the viscosity is independent of rate.
- Pseudoplastic fluids get thinner as shear increases.
- Dilatant Fluids increase their viscosity as shear rates increase.
- Plastic Fluids have a yield point with pseudoplastic behavior.
- Thixotropic and rheopectic fluids show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

Polymers are Non-Newtonian Fluids!!!



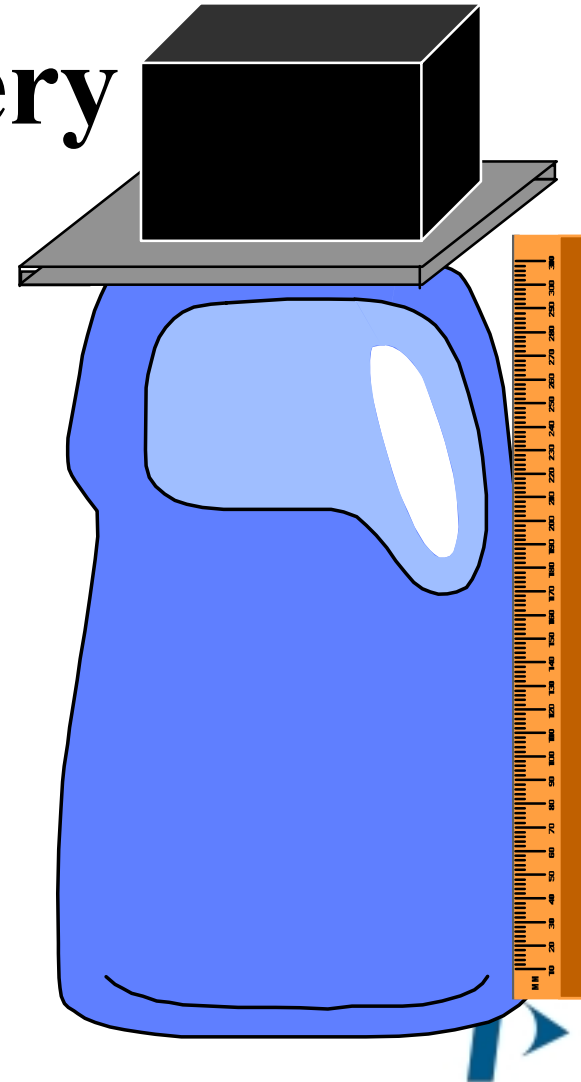
- At low shear rates, the viscosity is controlled by MW. The material shows Newtonian behavior
- Viscosity shows a linear dependence on rate above the η_0 region.
- At high rates, the material can no longer shear thin and a second plateau is reached.

Analyzing a Stress-Strain Curve



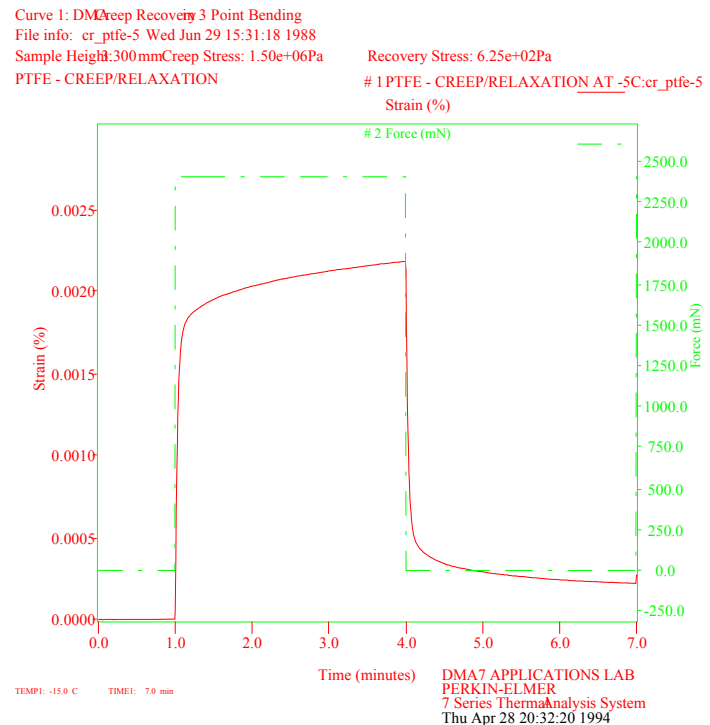
Under Continuous Loads: Creep Recovery

- 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.

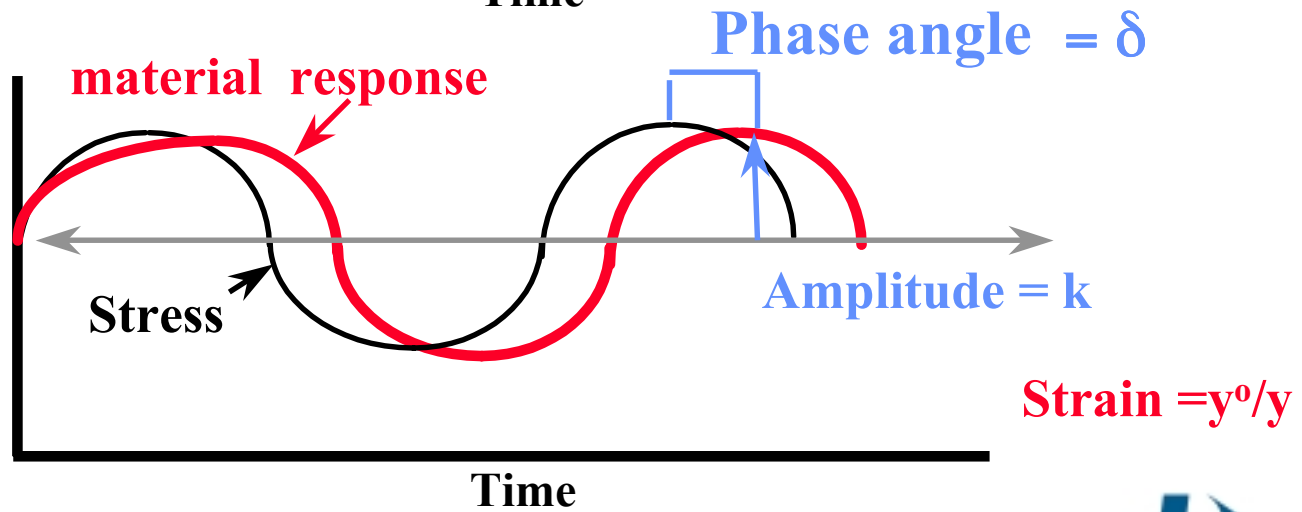
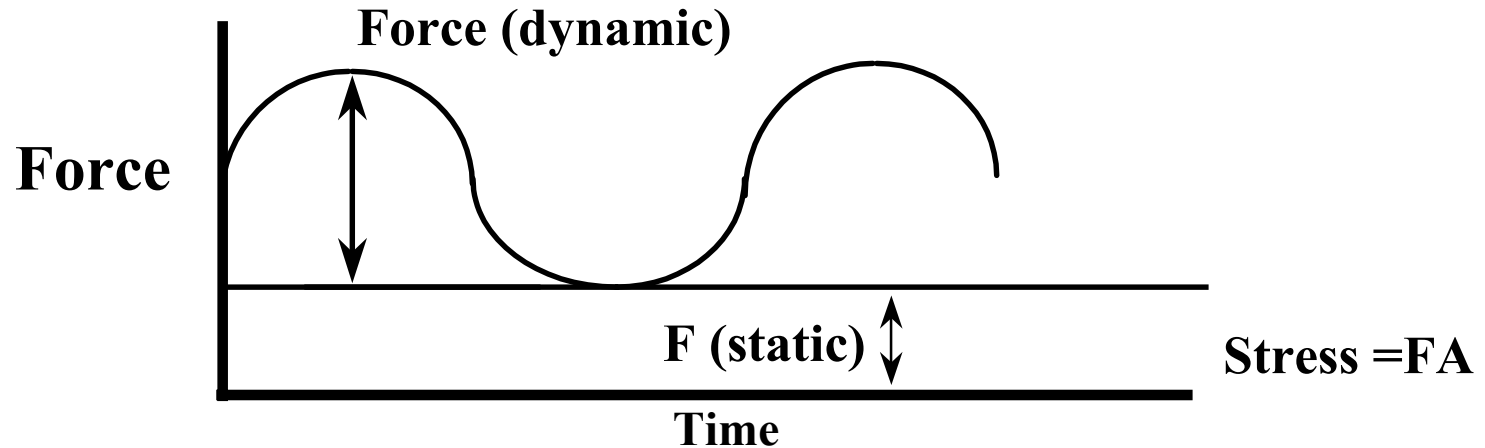


Creep is a fundamental engineering test.

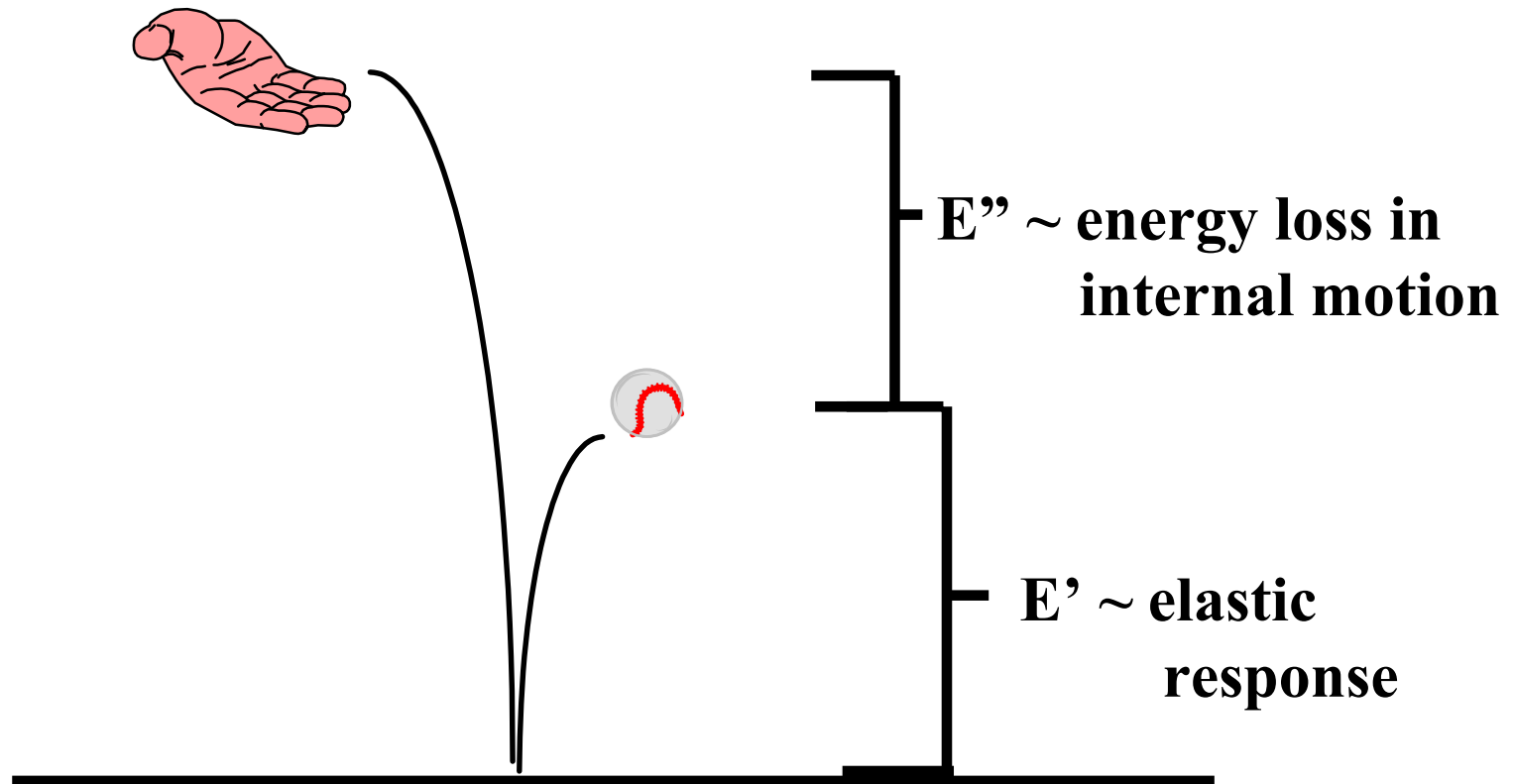
- Creep is used as a basic test for design.
- By looking at both the creep and recovery parts of the curve, we can begin to examine how polymers relax.



Dynamic Stress



Why? Let's bounce a ball.



All this is calculated from δ and k :

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

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

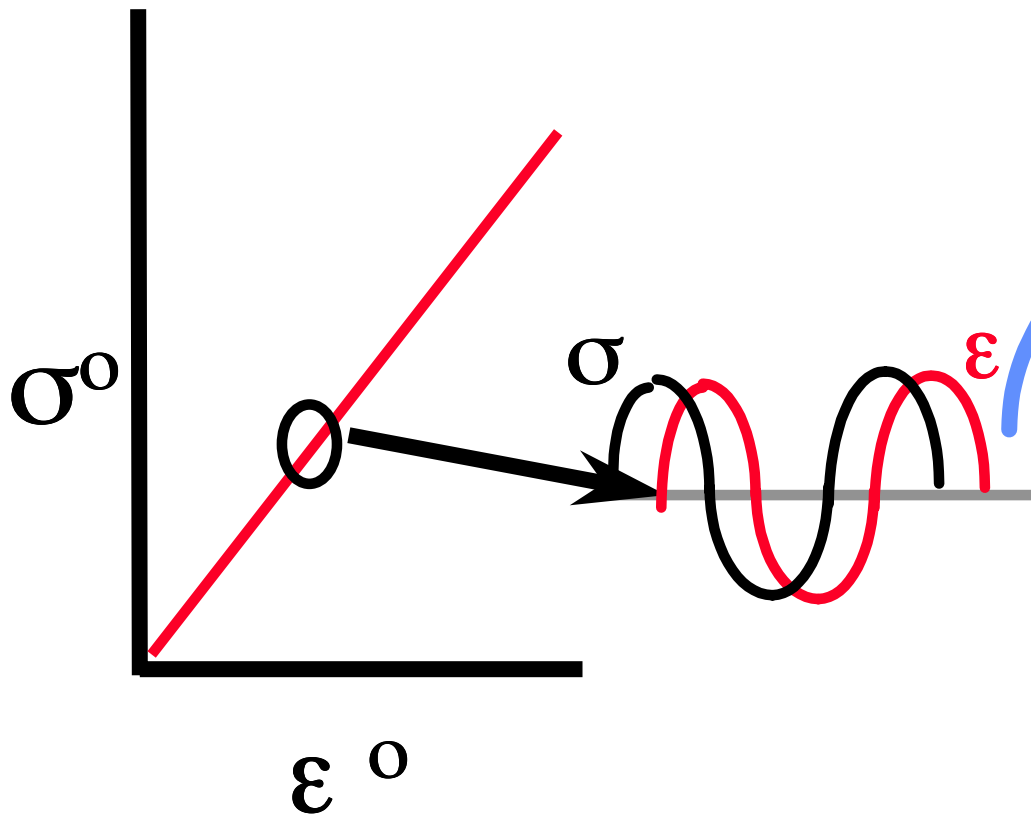
$$E^* = E' + iE'' = \text{SQRT}(E'^2 + E''^2)$$

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

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

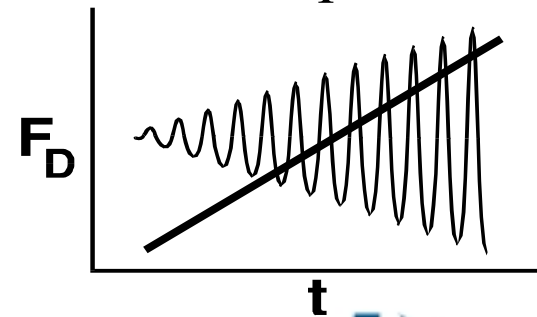
To apply this to materials...

Dynamic Stress Scan



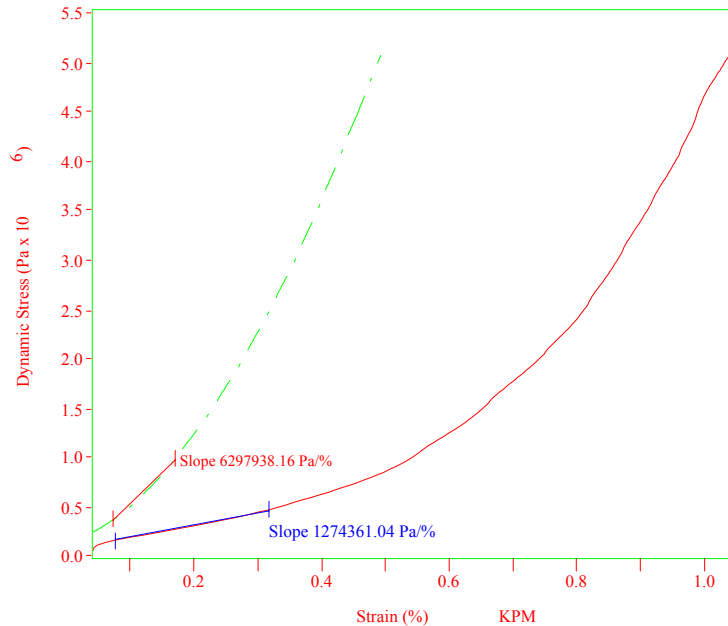
Since each part of the ramp has a sine wave stress associated with it, we get:

$\tan \delta$
 E^*, E', E''
 η
for each data point!!



For example, DSS Curves

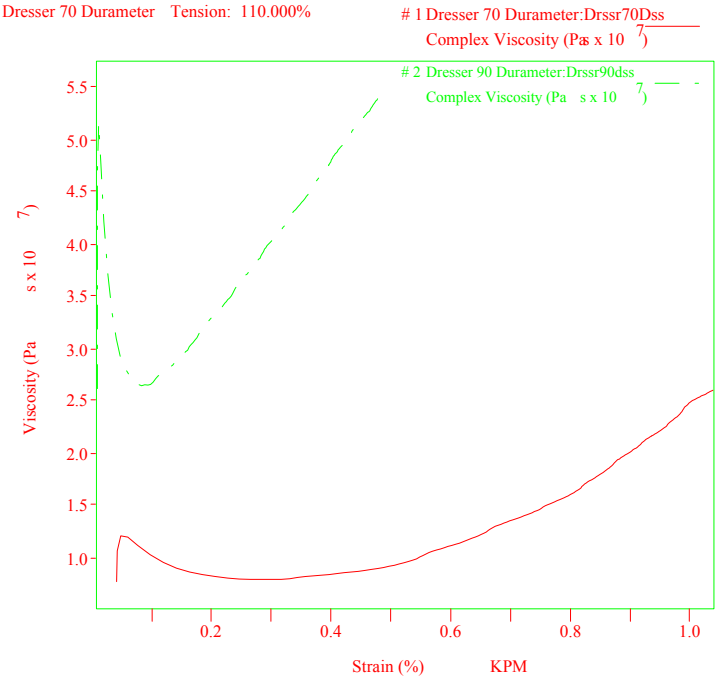
Curve 1: DMAC Stress Scan Parallel Plate
 File info: Drssr70Dss Thu Apr 14 16:44:41 1994
 Frequency: 1.00 Hz Stress Rate: 250.0mN/min
 Dresser 70 Durameter Tension: 110.000%



TEMP1: 10.5 C TIME1: -1.2 min

KPM
 PERKIN-ELMER
 7 Series Thermal Analysis System
 Thu Apr 14 16:59:58 1994

Curve 1: DMAC Stress Scan Parallel Plate
 File info: Drssr70Dss Thu Apr 14 16:44:41 1994
 Frequency: 1.00 Hz Stress Rate: 250.0mN/min
 Dresser 70 Durameter Tension: 110.000%

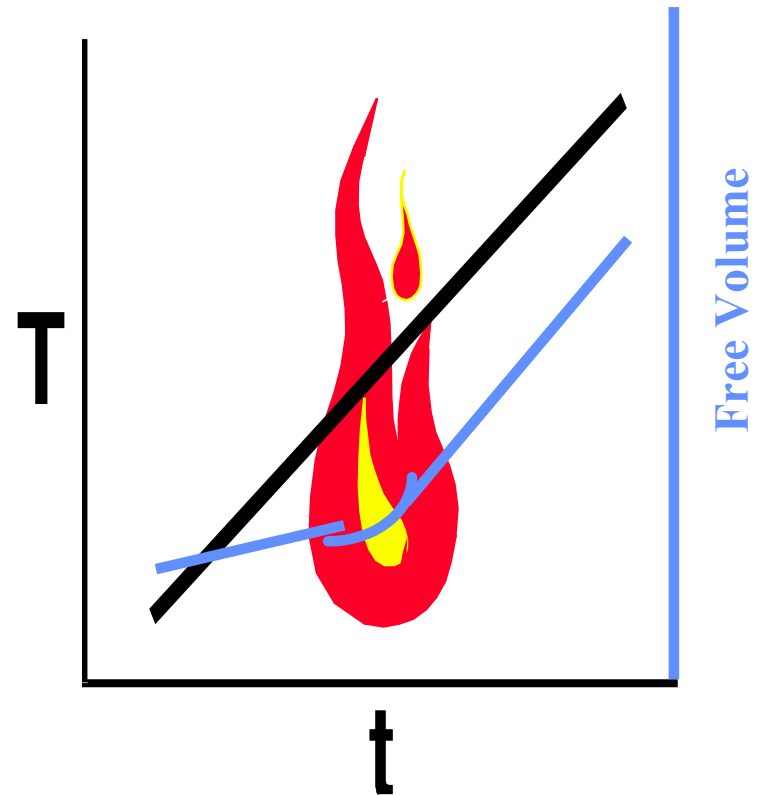


TEMP1: 10.5 C TIME1: -1.2 min

KPM
 PERKIN-ELMER
 7 Series Thermal Analysis System
 Thu Apr 28 20:28:00 1994

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.

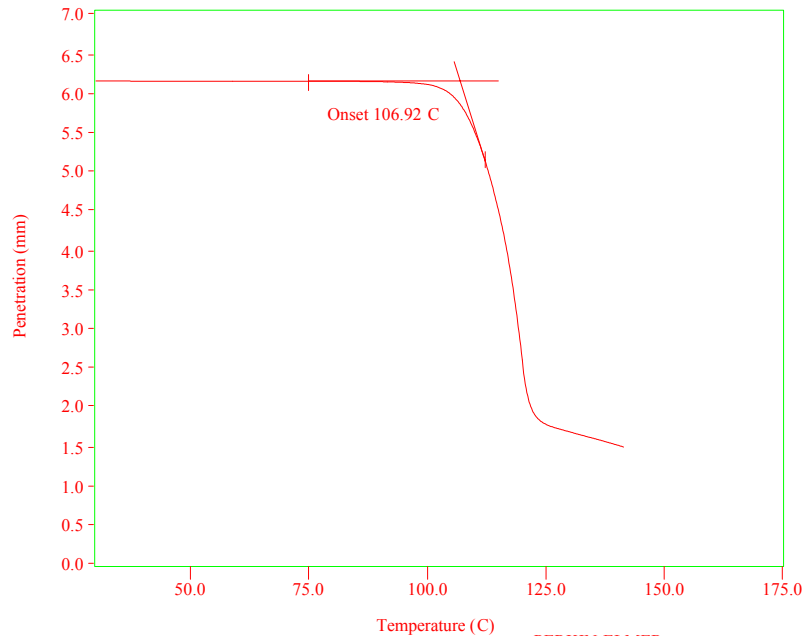
Curve 1: TMAin Penetration

File info: Tgflex Tue Oct 10 16:21:08 1995

Sample Height: 4.180 mmDC Force: 100.0 mN

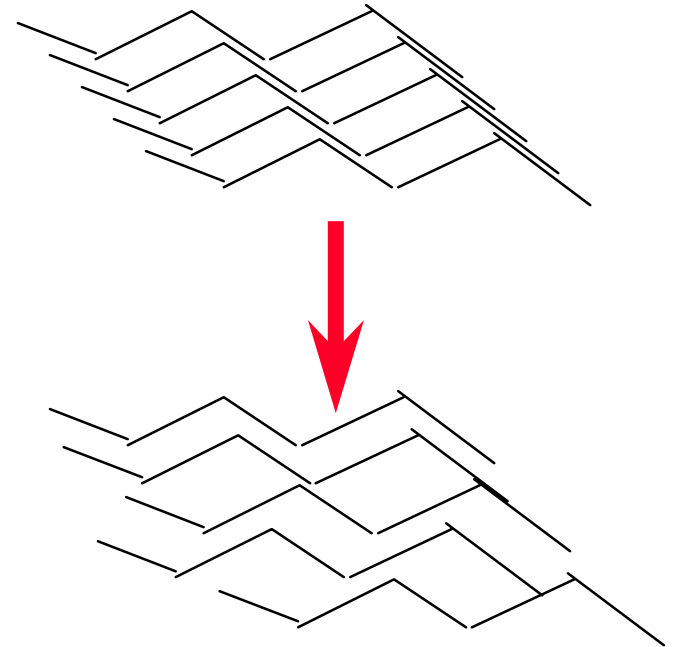
Tg by flex

1 Tg by flex:Tgflex
Penetration (mm)



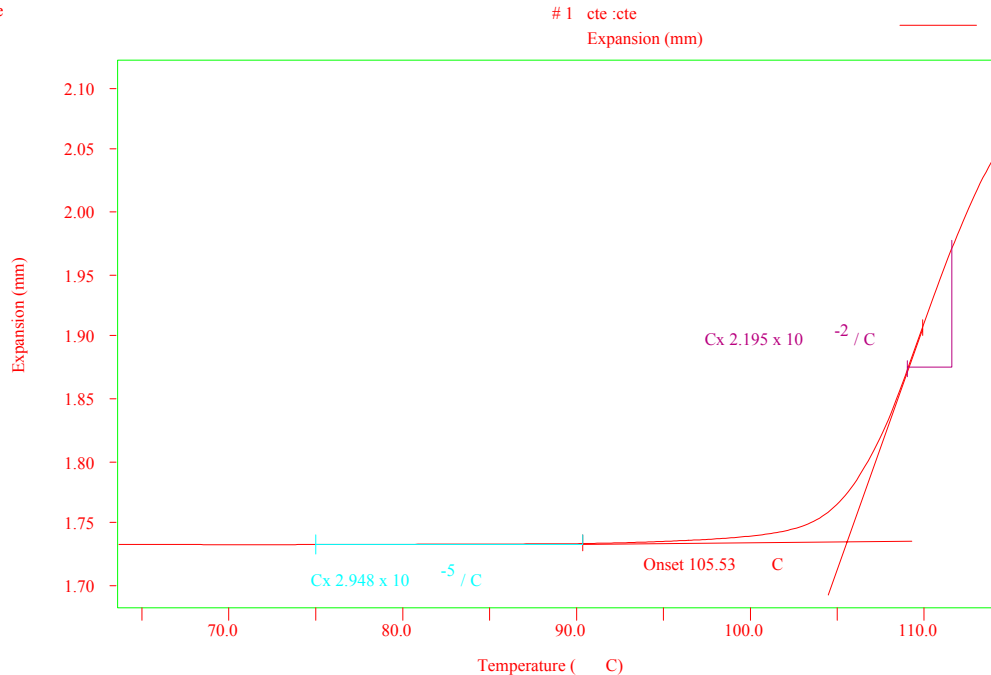
TEMP1: 30.0 C
TEMP2: 150.0 C
TIME1: 0.0 min
RATE1: 10.0 C/min

PERKIN-ELMER
7 Series Thermal Analysis System
Sun Nov 26 20:10:47 1995



TMA - It's all free volume.

Curve 1: TMA in Expansion
File info: cte Tue Oct 10 16:46:51 1995
Sample Height: 1.742 mm DC Force: 10.0 mN
cte

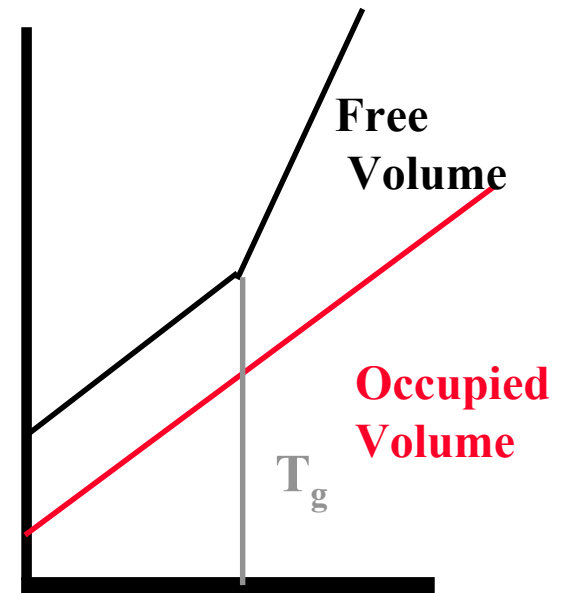


TEMP1: 30.0 C
TEMP2: 150.0 C

TIME1: 0.0 min

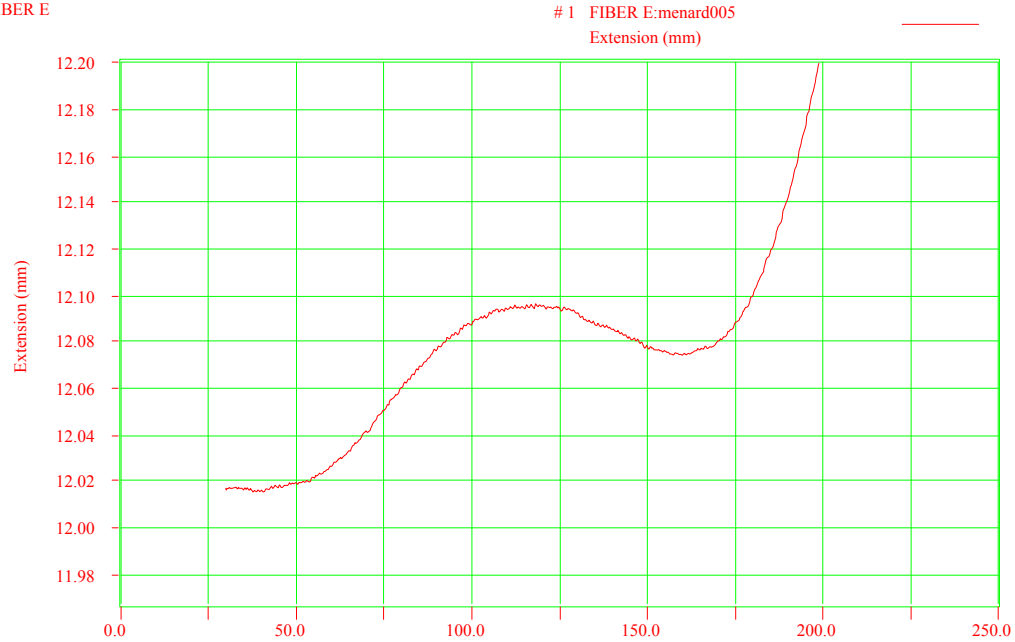
RATE1: 10.0 C/min

PERKIN-ELMER
7 Series Thermal Analysis System
Sun Nov 26 20:08:09 1995



And it's not just Tg.

Curve 1: TMA in Extension
File info: menard005 Tue Feb 21 12:28:20 1995
Sample Height: 12.017 mm DC Force: 0.0 mN
FIBER E



He/20psi/H/Chiller
TEMP1: 30.0 C
TEMP2: 250.0 C
TIME1: 0.0 min
RATE1: 5.0 C/min

Temperature (C)

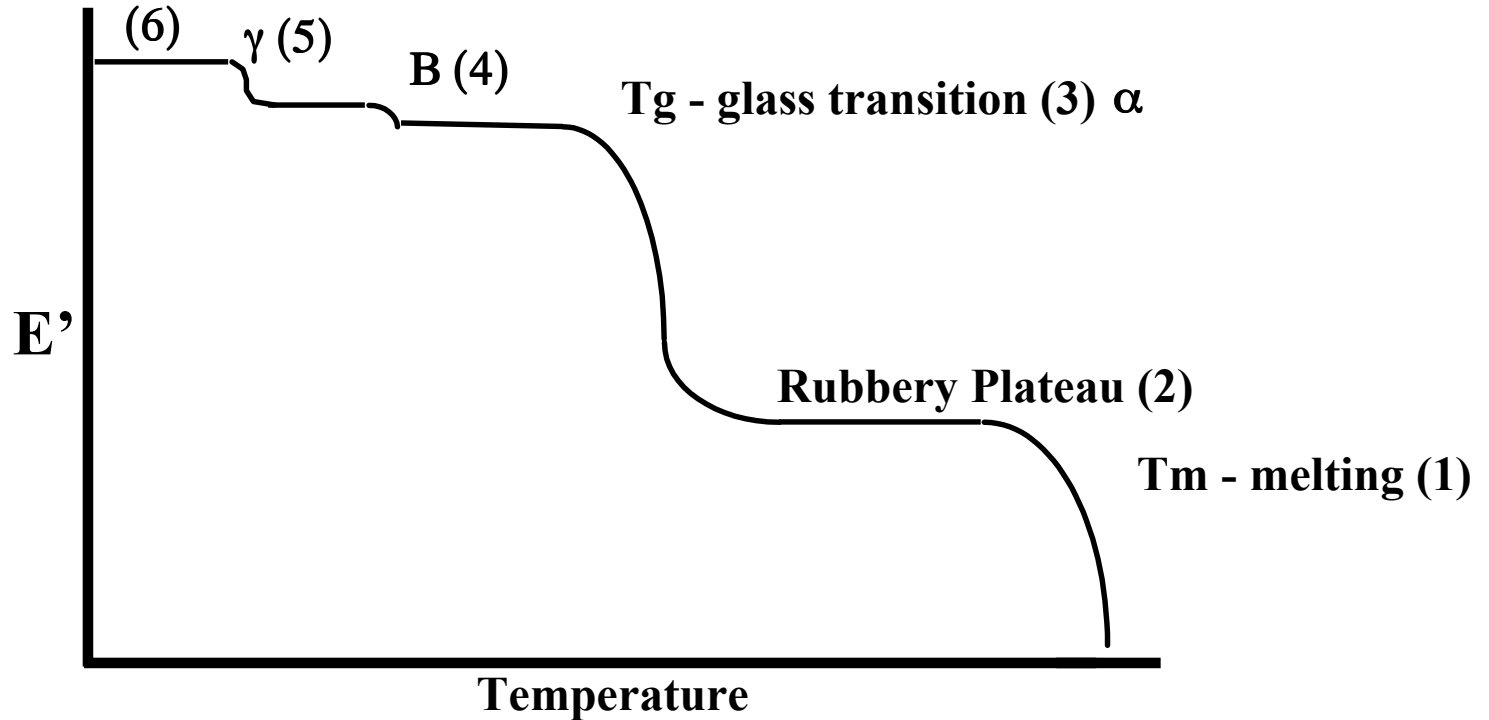
Tech.Support Lab/K.Menard
PERKIN-ELMER
7 Series Thermal Analysis System
Tue Feb 21 12:29:39 1995

(the traditional way to do heat set)

Time Temperature Scans at a Fixed Frequency

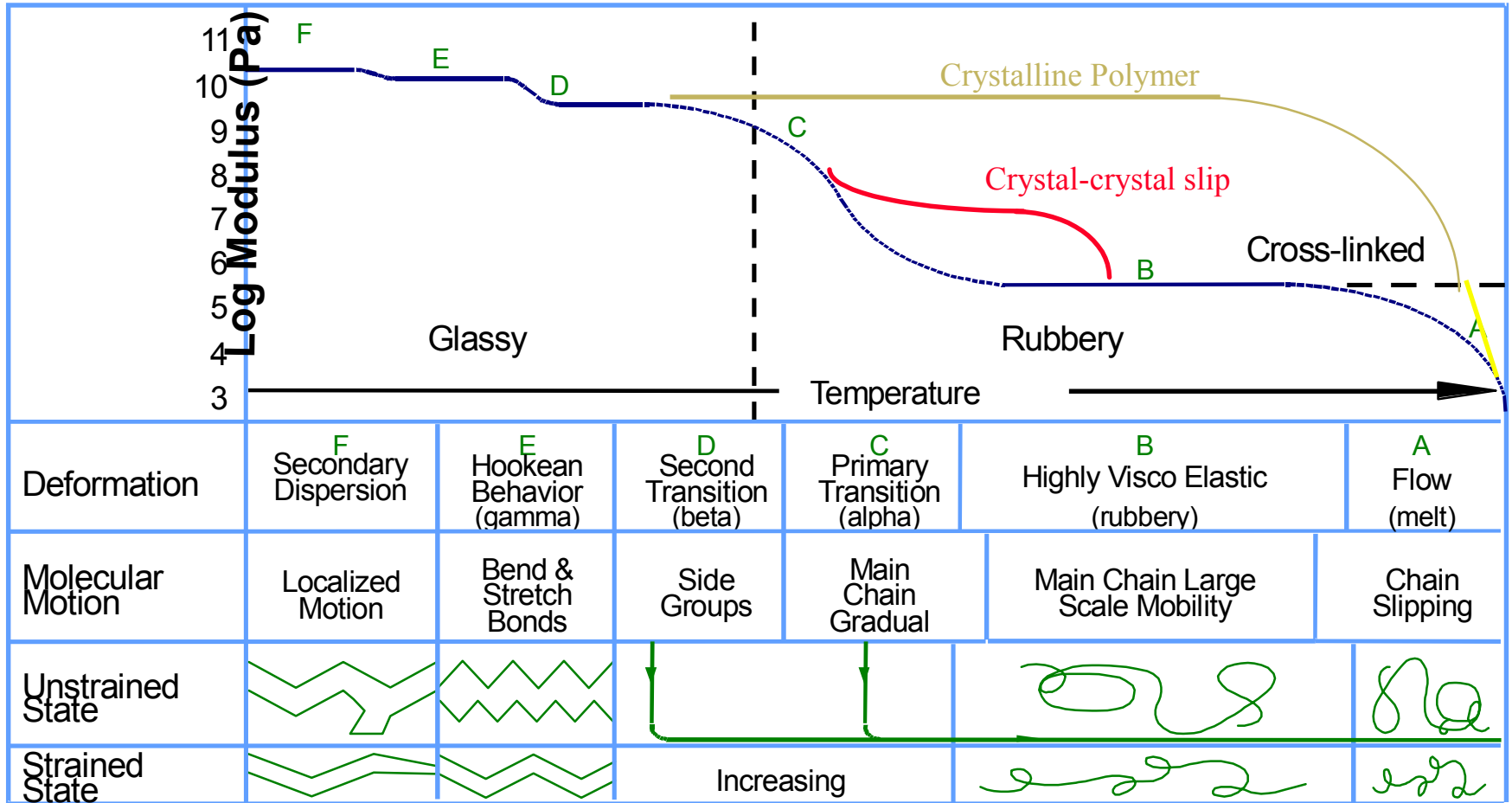
- hold frequency constant and vary temperature or time at temperature
- allows detection of transitions in material
- allows one to study cures
- most sensitive method for finding T_g
- can also get changes in dimension (TMA) while collecting DMA data
- Best probe of polymer relaxations as function of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

Idealized Multi-Event DMA Scan



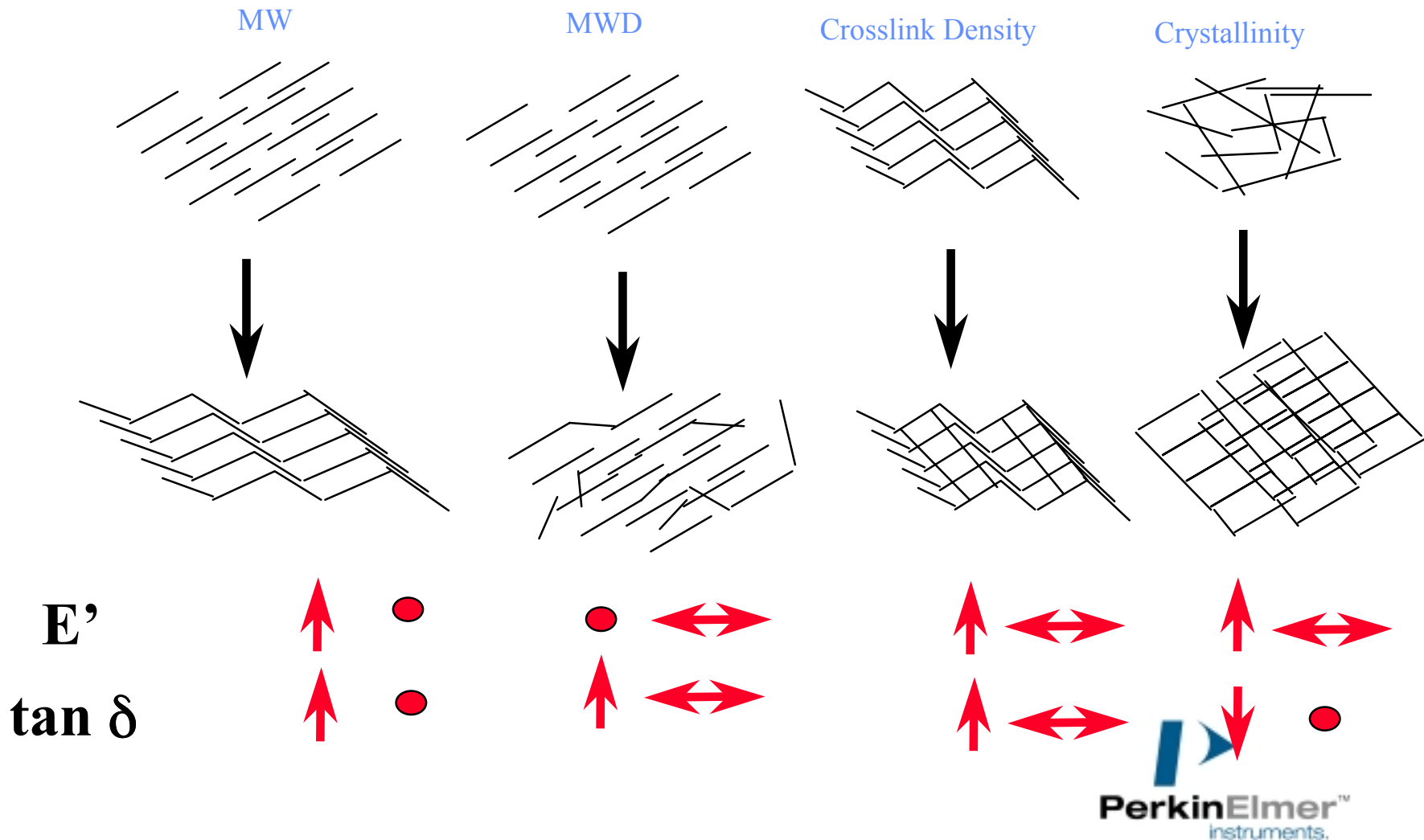
(6)	(5)	(4)	(3)	(2)	(1)
local	bend	side	gradual	large	chain
motions	and	groups	main	scale	slippage
	stretch		chain	chain	

In more detail...



R. Seymour, 1971

Common changes show as:



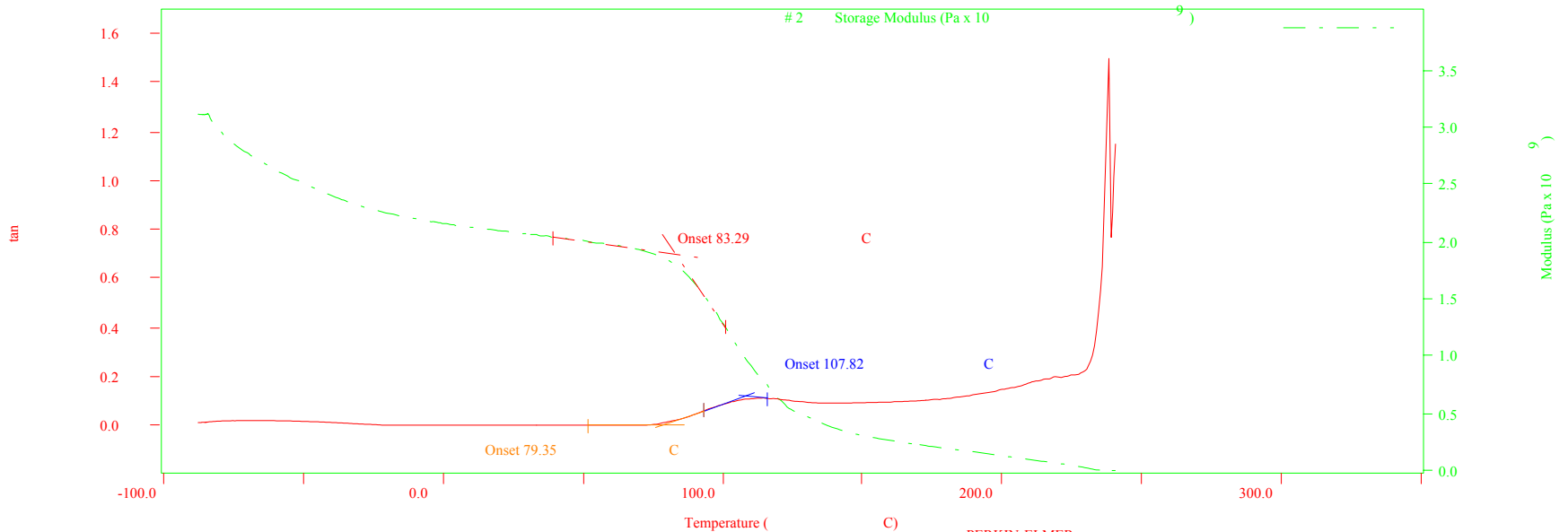
Tg are easily seen, as in PET Film

Curve 1: DMA
File info:
Frequency: 1.00 Hz
pet film

Temp/Time Scan in Extension
demofilm Wed Oct 11 17:06:48 1995
Amplitude: 21.949u
Tension: 110.000%

1 pet film:demofilm
tan

2 Storage Modulus (Pa x 10⁹)



TEMP1: 100.0 C
TEMP2: 250.0 C

TIME1: 0.0 min

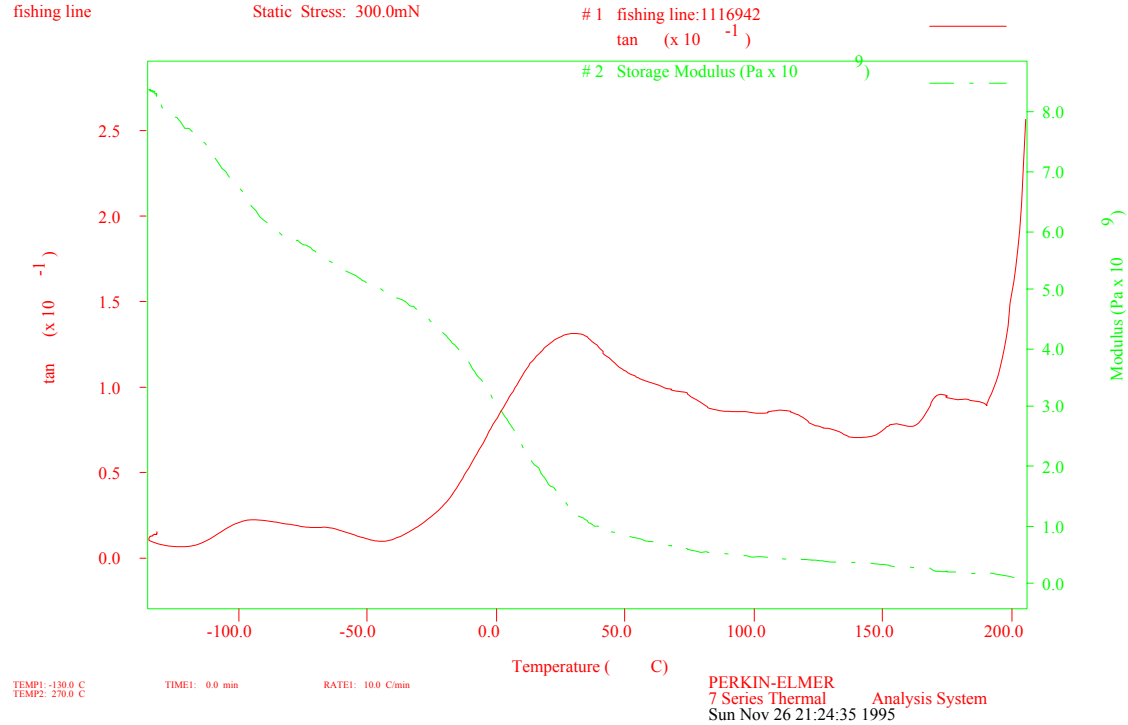
RATE1: 10.0 C/min

PERKIN-ELMER
7 Series Thermal
Sun Nov 26 21:02:11 1995

Analysis System

or in PP fishing line.

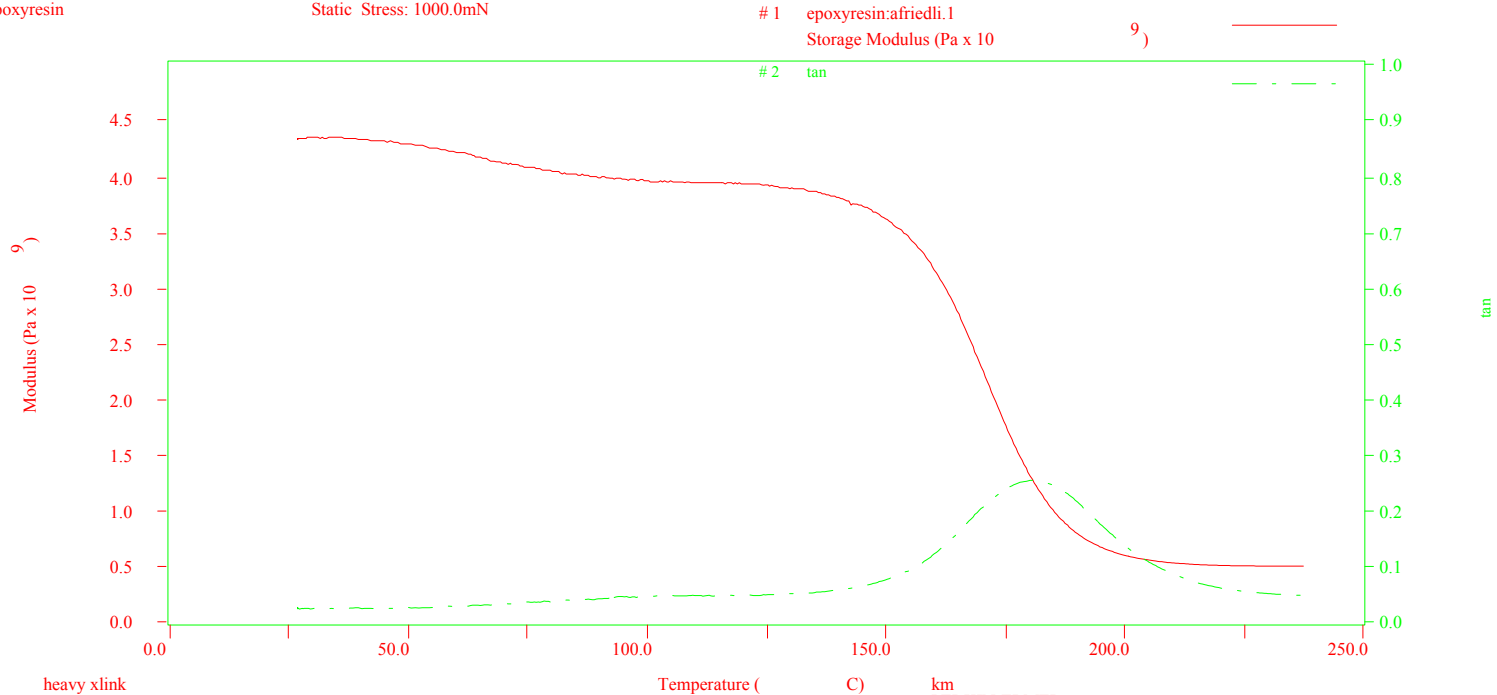
Curve 1: DMA Temp/Time Scan in Extension
File info: 1116942 Wed Nov 16 13:20:39 1994
Frequency: 1.00 Hz Dynamic Stress: 200.0mN
fishing line Static Stress: 300.0mN



Sample prep can be minimal if only temperatures are needed.

Transitions are clearly seen in highly crosslinked samples

Curve 1: DMA Temp/Time Scan in 3 Point Bending
File info: afriedli.1 Thu Feb 17 12:14:11 1994
Frequency: 1.00 Hz Dynamic Stress: 800.0mN
epoxyresin Static Stress: 1000.0mN



heavy xlink
TEMP1: 30.0 C
TEMP2: 250.0 C

TIME: 0.0 min

RATE: 10.0 C/min

Temperature (C)

km
PERKIN-ELMER
7 Series Thermal
Thu Jun 23 13:45:10 1994

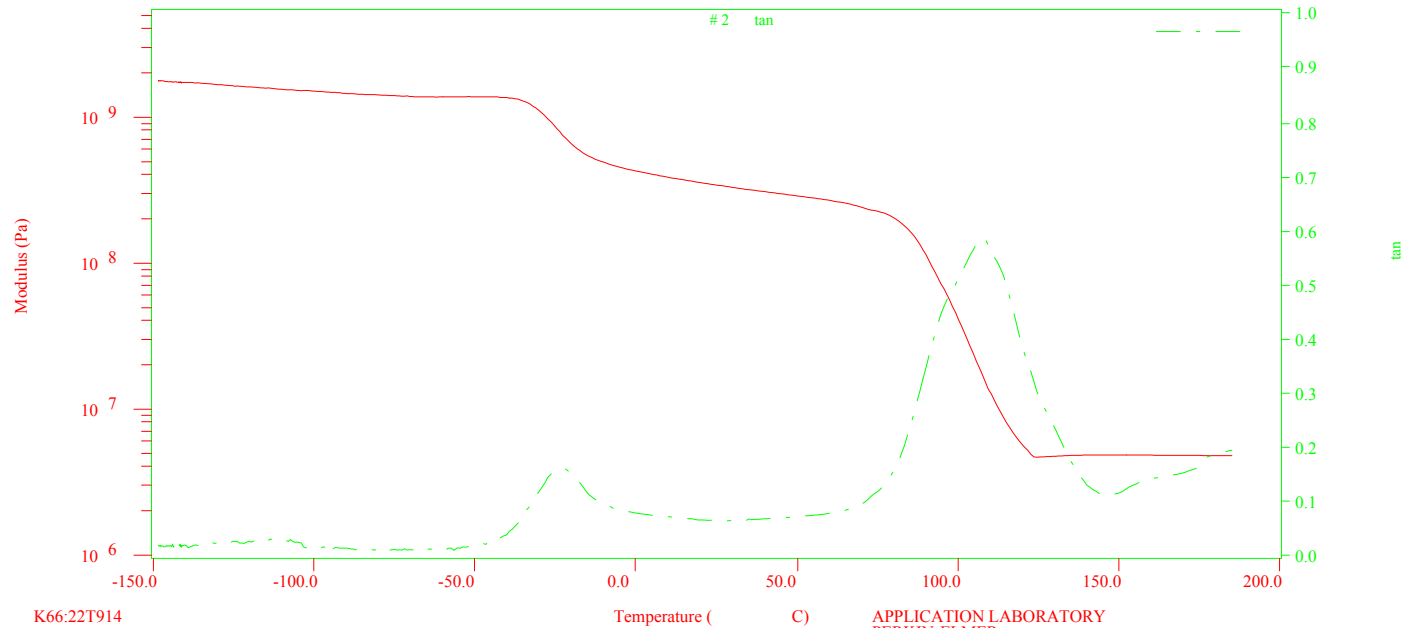
Analysis System

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

as well as in blends.

Curve 1: DMA Temp/Time Scan in 3 Point Bending
File info: sbr14 Thu Feb 15 10:45:19 1990
Frequency: 1.00 Hz Dynamic Stress: 2.00e+05Pa
STYRENE BUTADIENE RUBBE Tension: 110.000%

1 STYRENE BUTADIENE RUBBER:sbr14
Storage Modulus (Pa) L

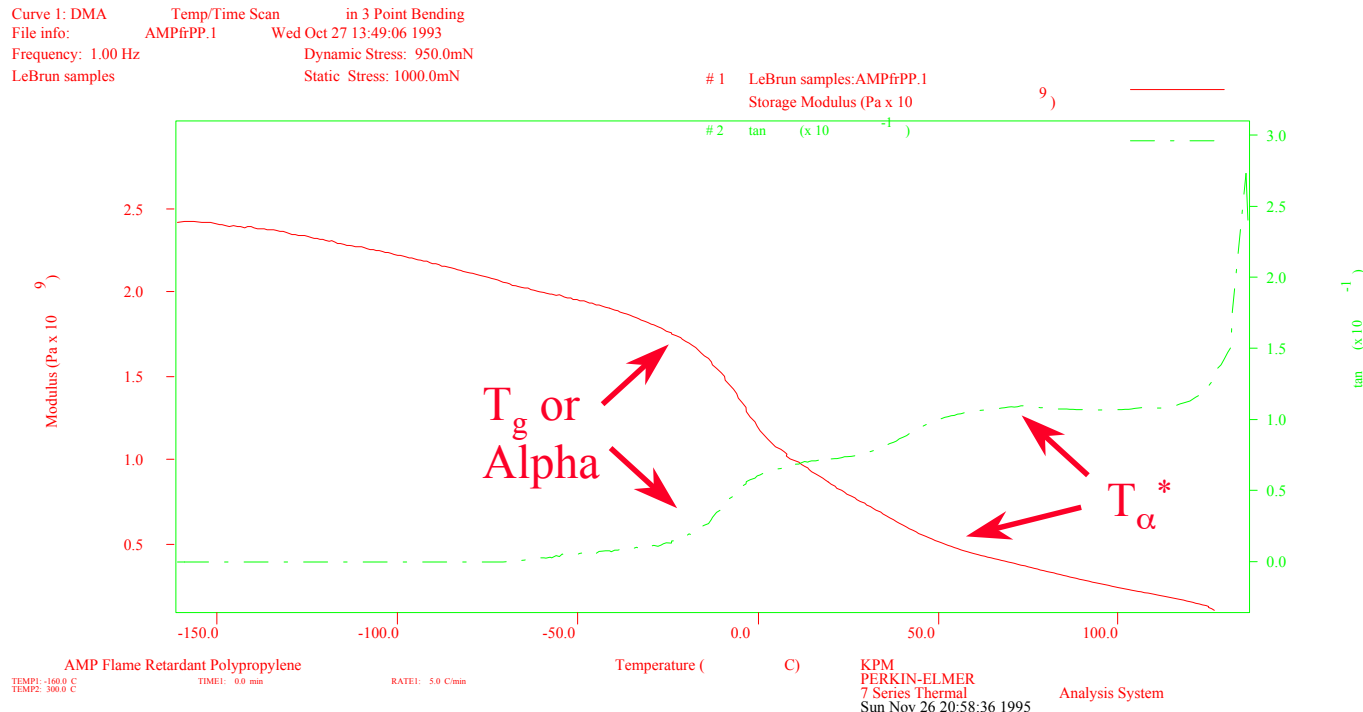


K66:22T914
TEMP1: -180.0 C
TEMP2: 250.0 C
TIME: 0.0 min
RATE: 50 C/min

APPLICATION LABORATORY
PERKIN-ELMER
7 Series Thermal
Sun Nov 26 20:54:43 1995
Analysis System

It's not always so simple:

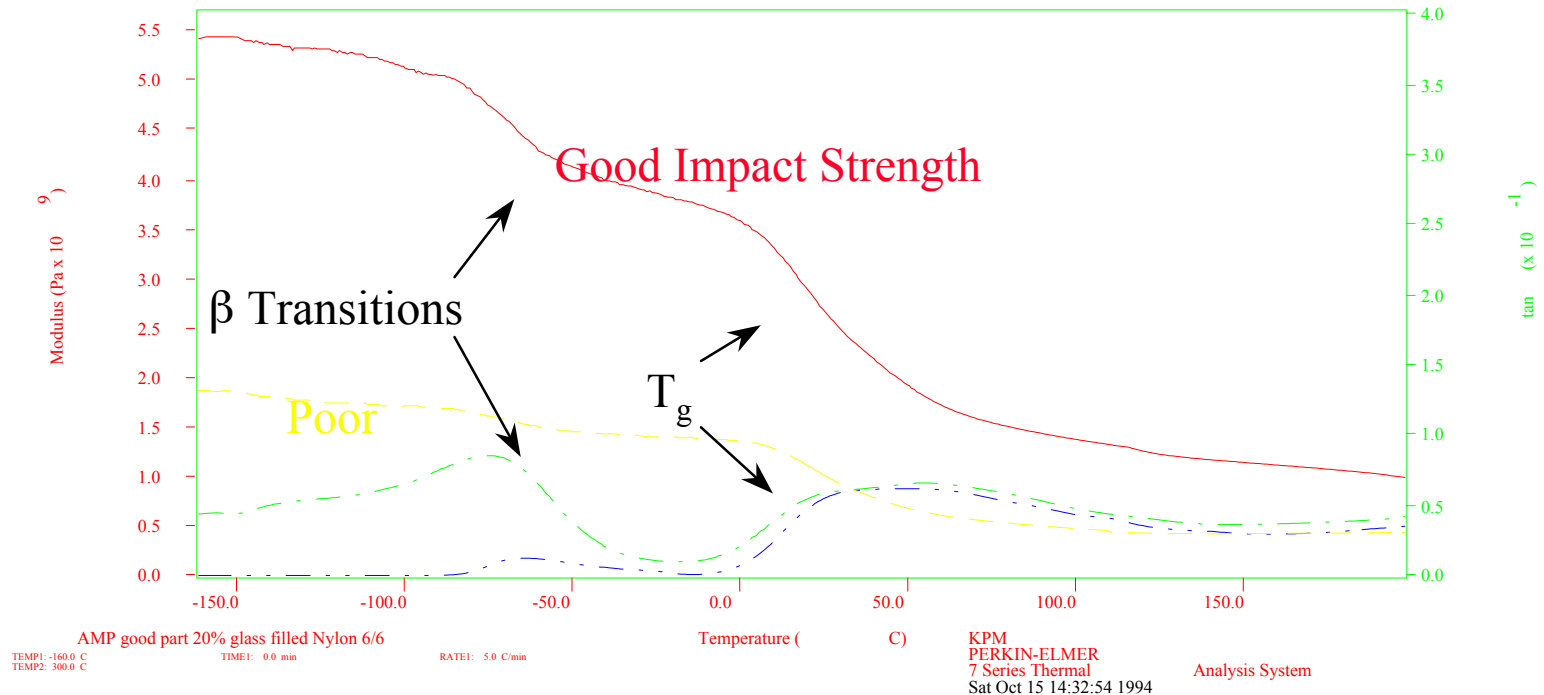
For example, crystal-crystals slips can cause α^* transitions



Higher Order Transitions affect toughness

Curve 1: DMA Temp/Time Scan in 3 Point Bending
File info: AMP66gp.1 Tue Oct 26 16:05:29 1993
Frequency: 1.00 Hz Dynamic Stress: 190.0mN
LeBrun samples Static Stress: 200.0mN

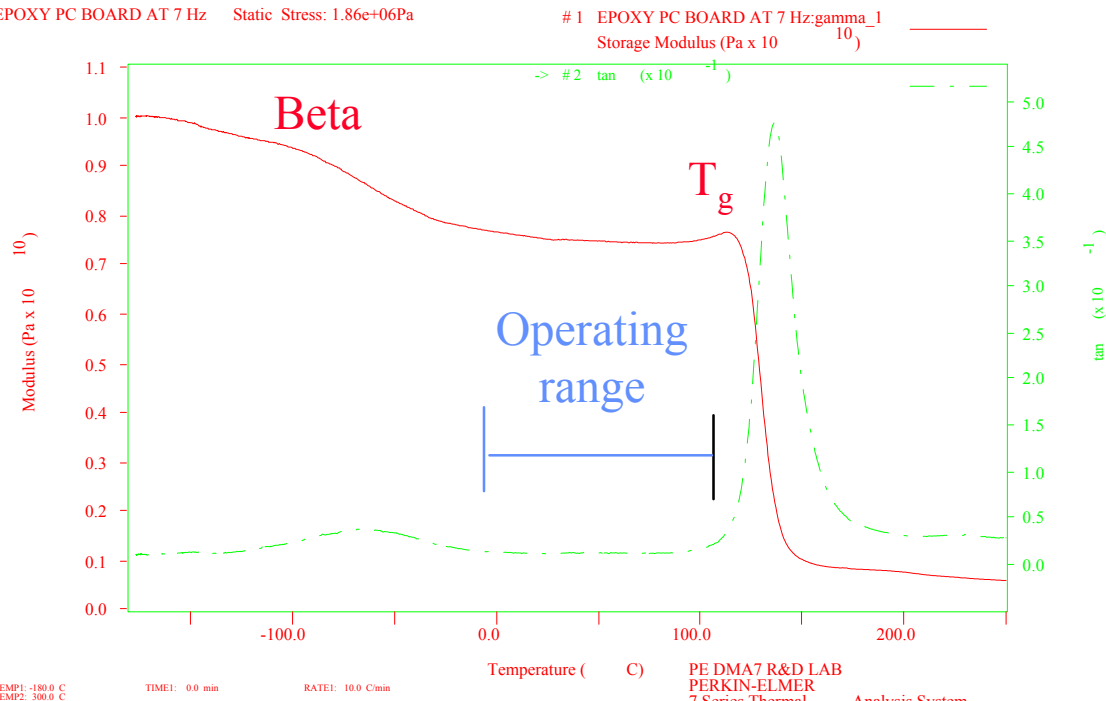
LeBrun samples



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

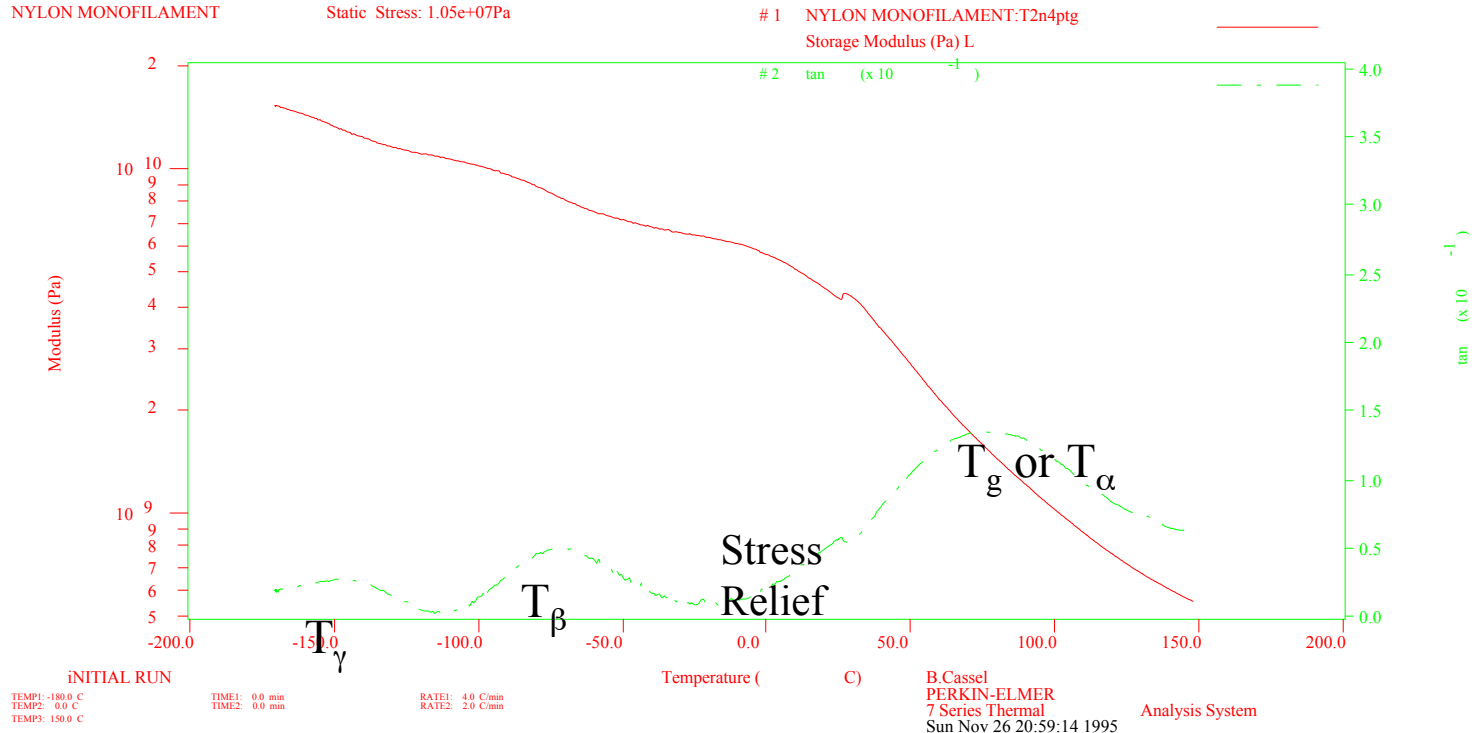
...and also define operating range.

Curve 1: DMA Temp/Time Scan in 3 Point Bending
File info: gamma_1 Thu Jun 30 02:17:24 1988
Frequency: 7.00 Hz Dynamic Stress: 1.86e+06Pa
EPOXY PC BOARD AT 7 Hz Static Stress: 1.86e+06Pa



It can get complex...

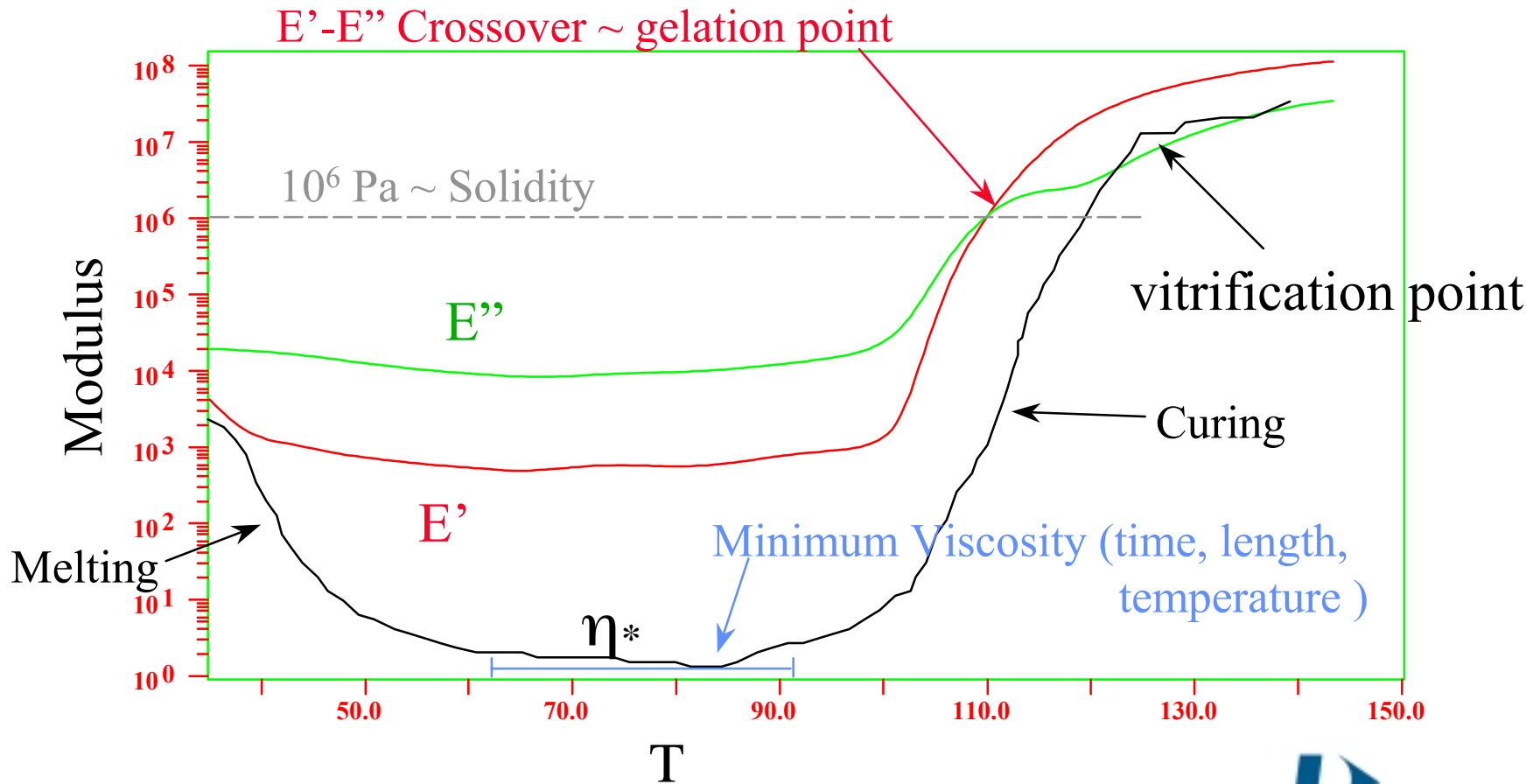
Curve 1: DMA Temp/Time Scan in Extension
 File info: T2n4ptg Fri Jan 18 18:14:51 1991
 Frequency: 1.00 Hz Dynamic Stress: 1.00e+07Pa
 NYLON MONOFILAMENT Static Stress: 1.05e+07Pa



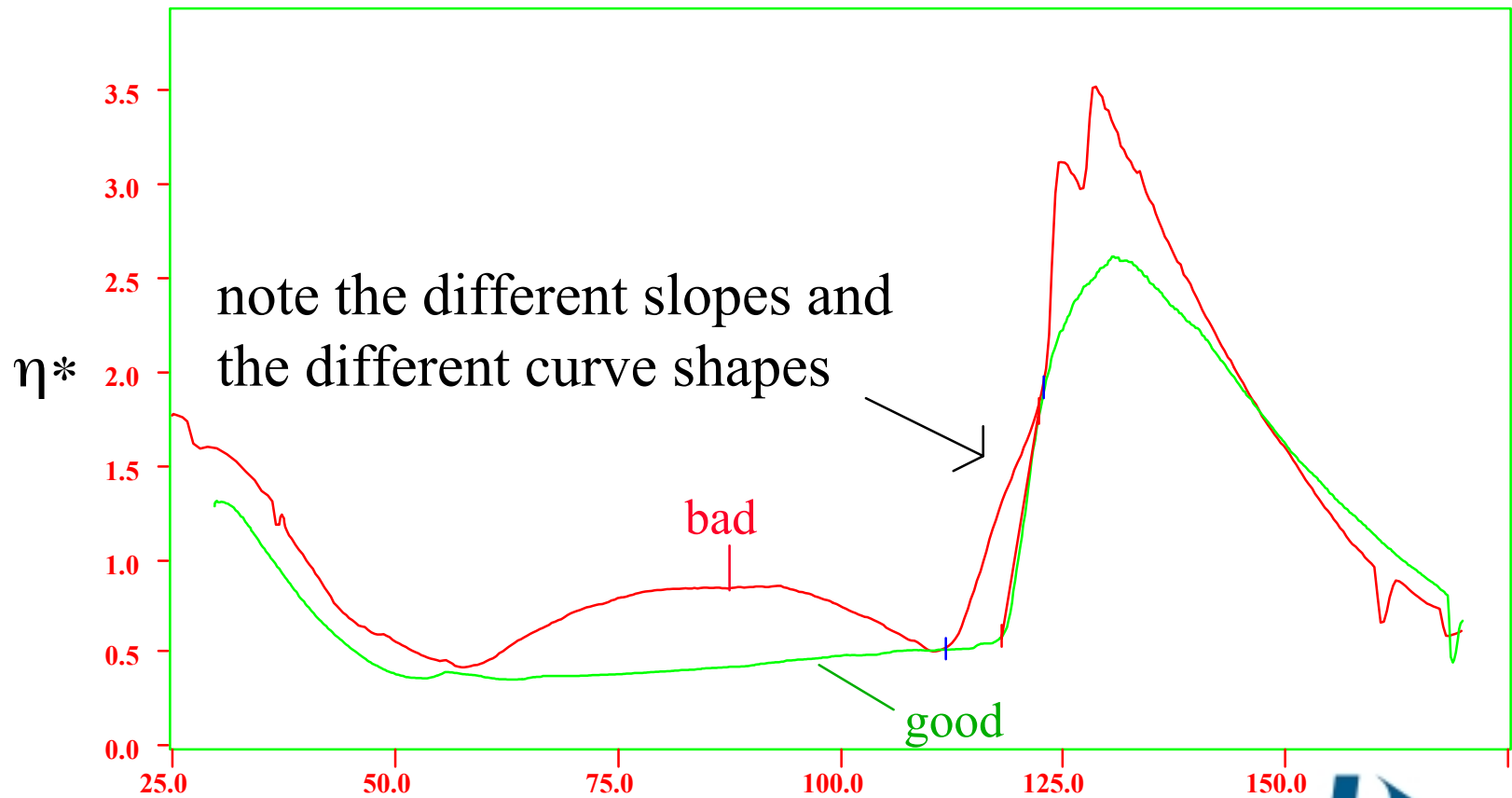
Curing of Thermosets

- 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

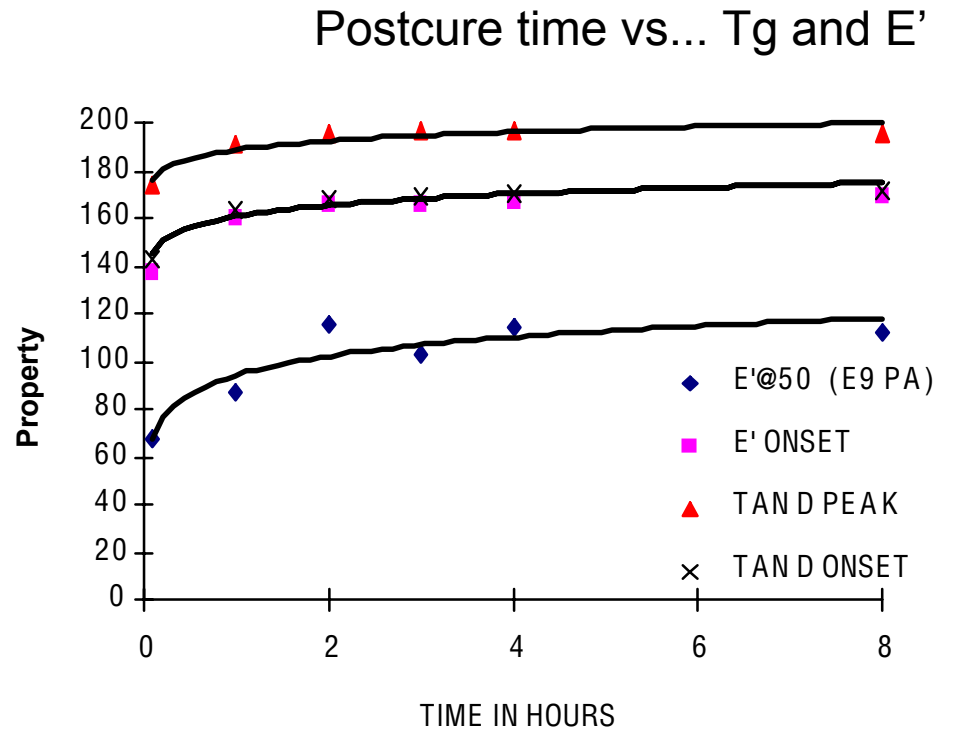
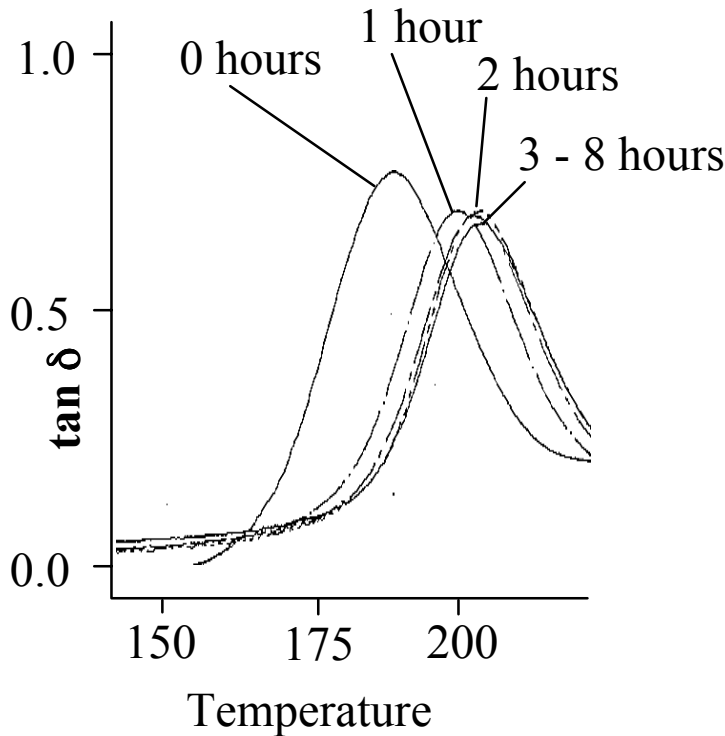
Analysis of a Cure by DMA



QC can often be done by simply fingerprinting the resin.



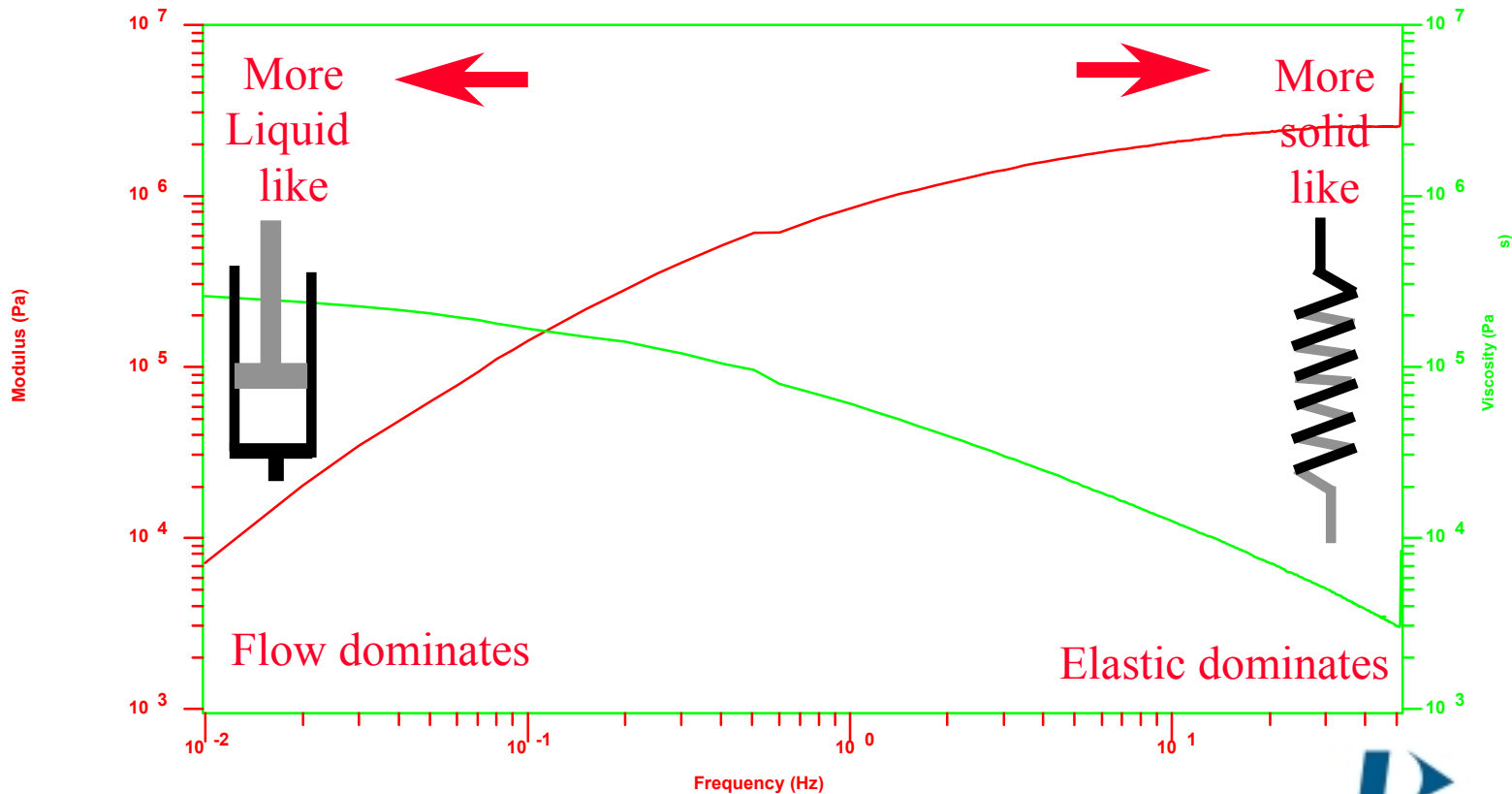
Postcure studies allow process optimization:



Frequency Scans

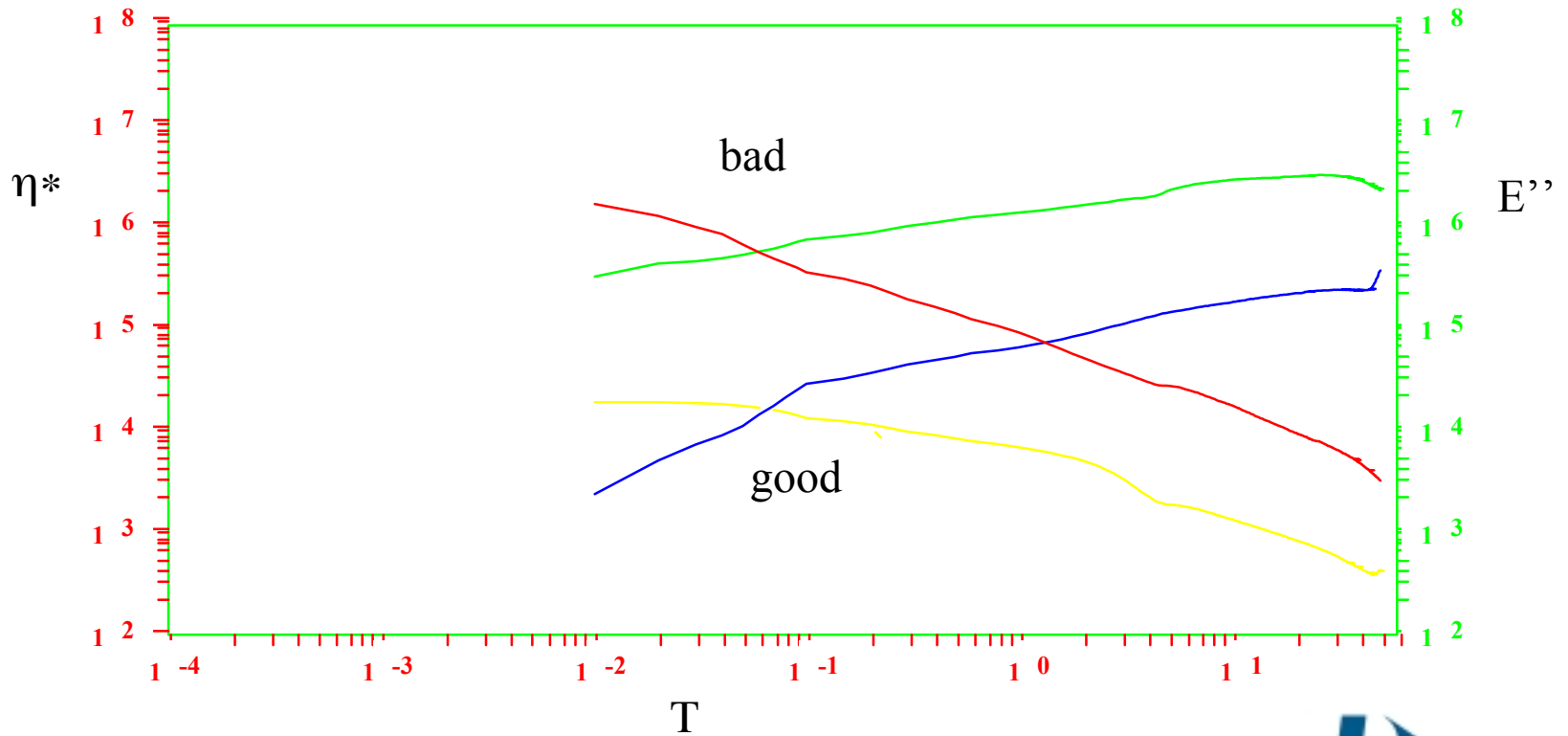
- **hold temperature constant and vary frequency**
- **allows one to look at trends in material**
- **can estimate changes in MW and MWD**
- **looks at both tack-like and peel-like behavior**
- **can use data for Time Temperature Superposition to extend frequency range or predict age life.**

Frequency determines the type of response



For example, two hot melt adhesives...

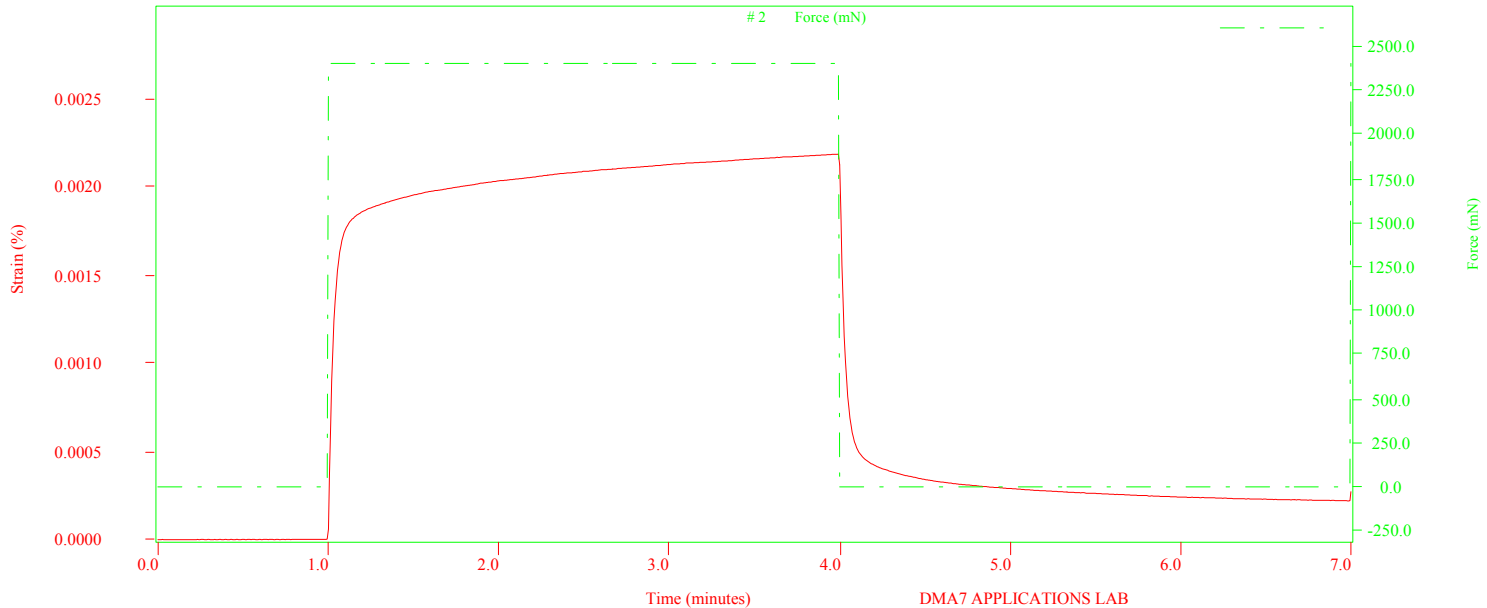
show affect of rate (peel vs.... tack)



Creep can look at distortion under load,

Curve 1: DMA Creep Recovery in 3 Point Bending
File info: cr_ptfe-5 Wed Jun 29 15:31:18 1988
Sample Height: 3.300 mm Creep Stress: 1.50e+06Pa
PTFE - CREEP/RELAXATION

Recovery Stress: 6.25e+02Pa
1 PTFE - CREEP/RELAXATION AT -5C:cr_ptfe-5
Strain (%)



TEMP1: -15.0 C

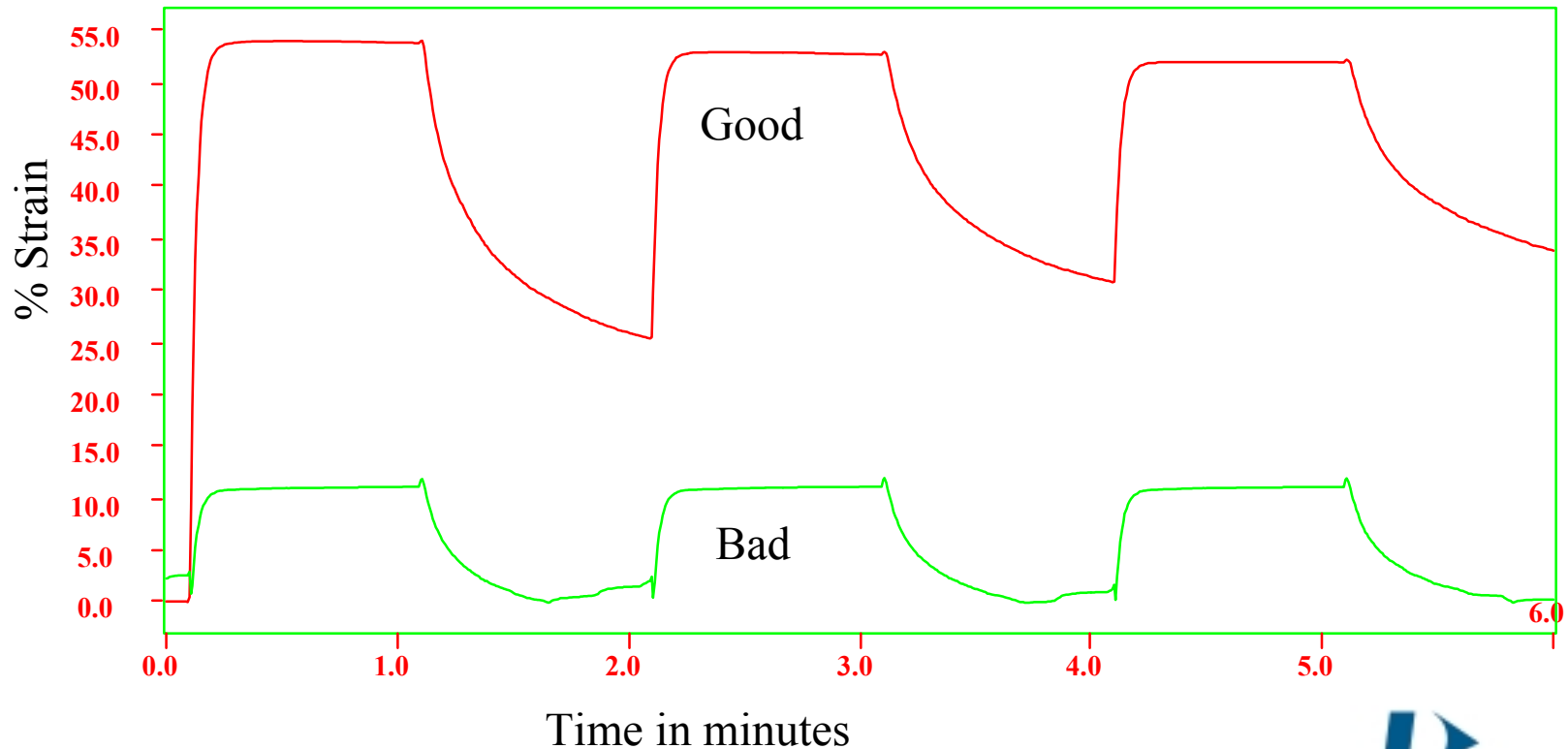
TIME1: 7.0 min

Time (minutes)

DMA7 APPLICATIONS LAB
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7 Series Thermal Analysis System
Thu Apr 28 20:32:20 1994

cyclic application of loads,

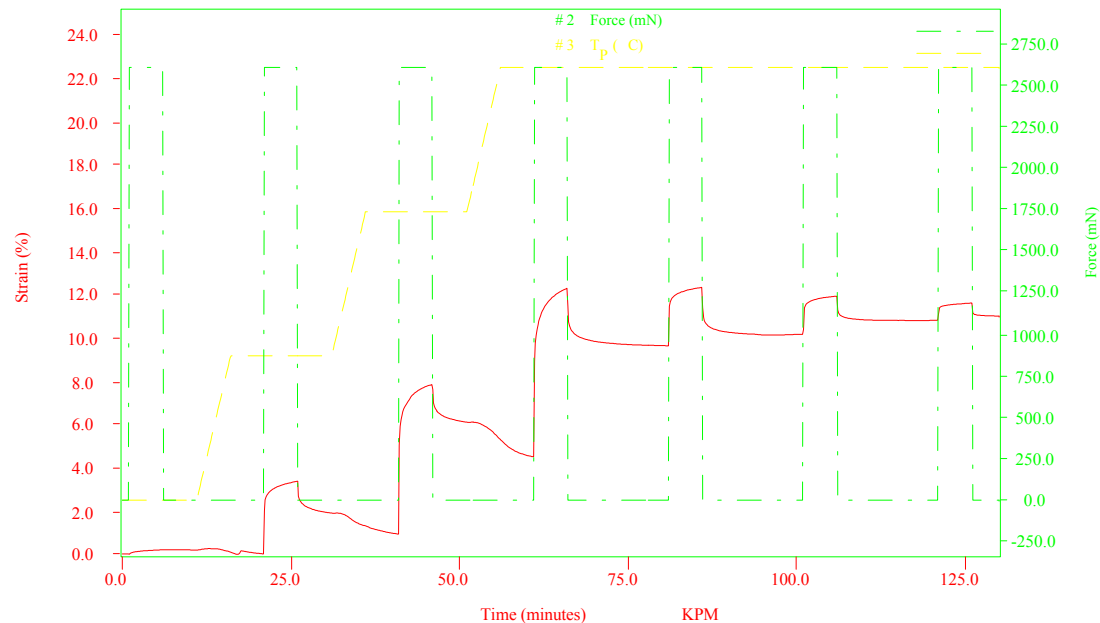
Differences can be seen in good and bad samples and get more apparent with several cycles. Here the bad material is not flowing enough to fill the pores and form a mechanical bond.



and with varying temperatures.

Curve 1: DMA Creep Recovery in Parallel Plate
File info: DR90D2.1 Fri Jul 23 12:23:50 1993
Sample Height: 2.836 mm Creep Stress: 2600.0mN
Dresser 90 D

Recovery Stress: 1.0mN
1 Dresser 90 D:DR90D2.1
Strain (%)



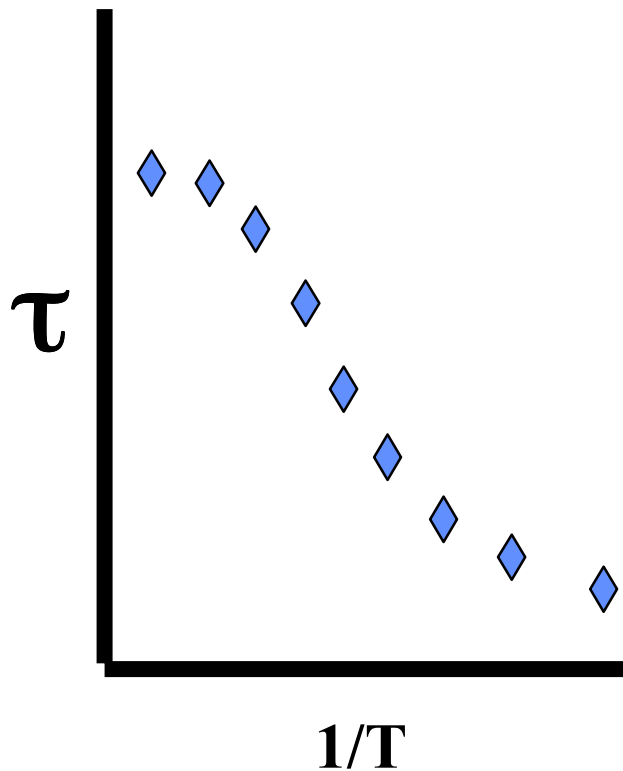
TEMP1: -50.0 C
TEMP2: 0.0 C
TEMP3: 80.0 C
TEMP4: 100.0 C

TIME1: 11.0 min
TIME2: 15.0 min
TIME3: 15.0 min
TIME4: 75.0 min

RATE1: 10.0 C/min
RATE2: 10.0 C/min
RATE3: 10.0 C/min

KPM
PERKIN-ELMER
7 Series Thermal Analysis System
Sun Nov 26 20:41:31 1995

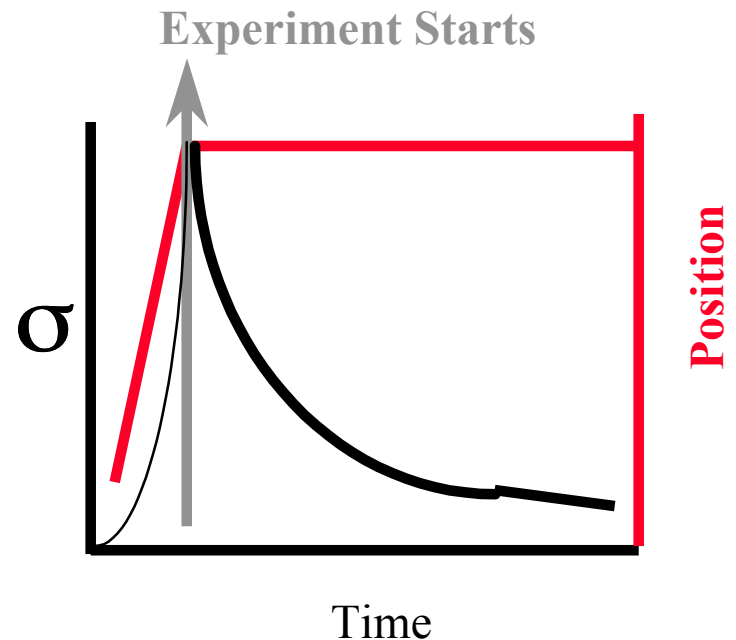
And you can tabulate this stuff graphically...



- 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.)

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.

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.

Specialized Testing is Possible...

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

Time-Temperature Superposition (TTS)

DEA/DMA

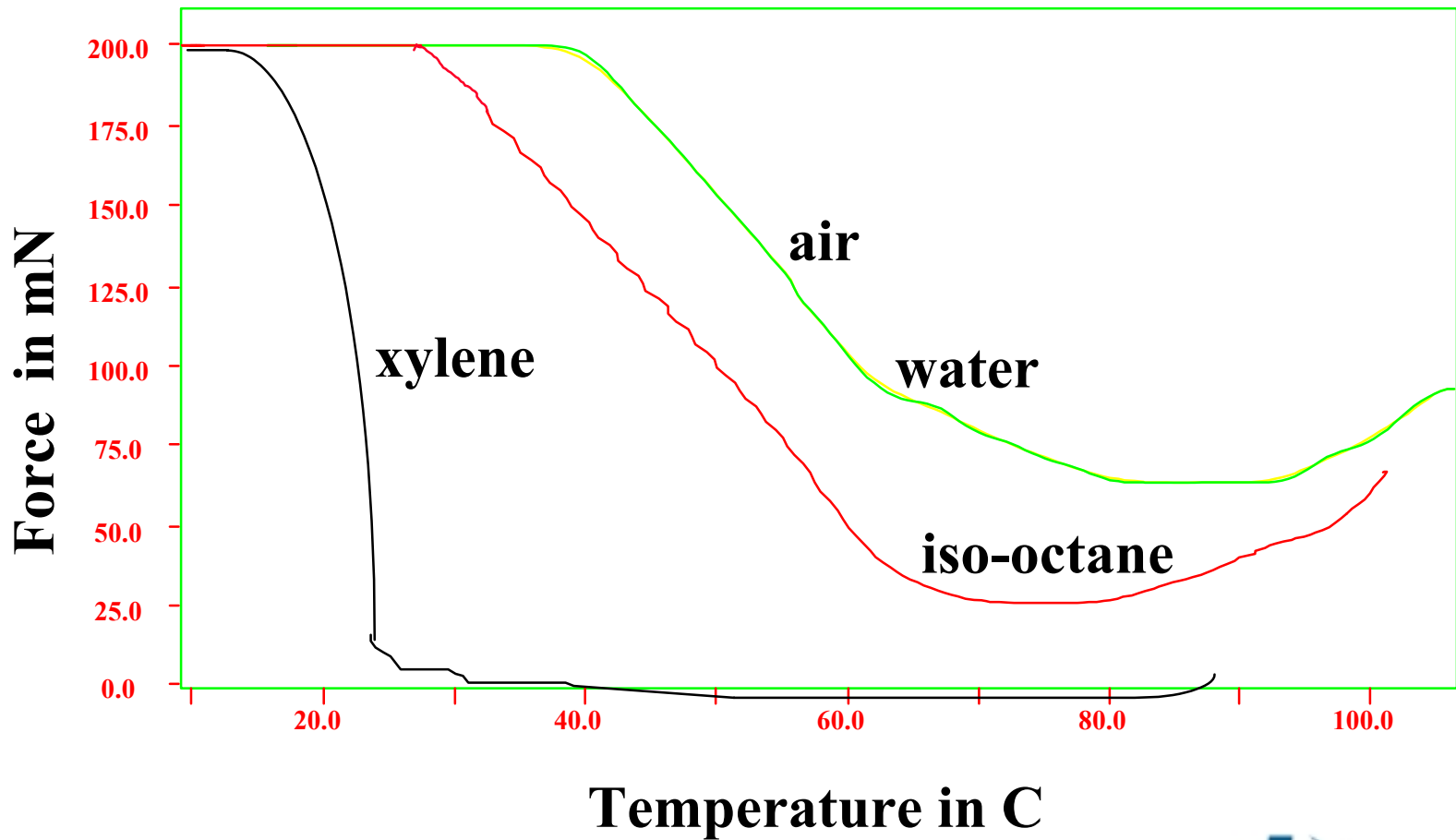
Tests in Solution

Microscopic DMA

Photo DMA

DMA-?

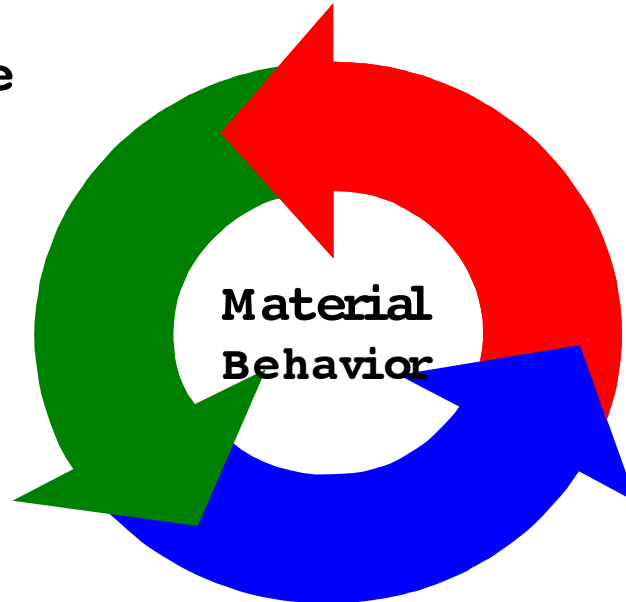
PP fibers in solvent



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

Conclusions

- **DMA allows you to perform 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 overlaid with DSC, TGA, TMA, and DTA for easier analysis.**

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