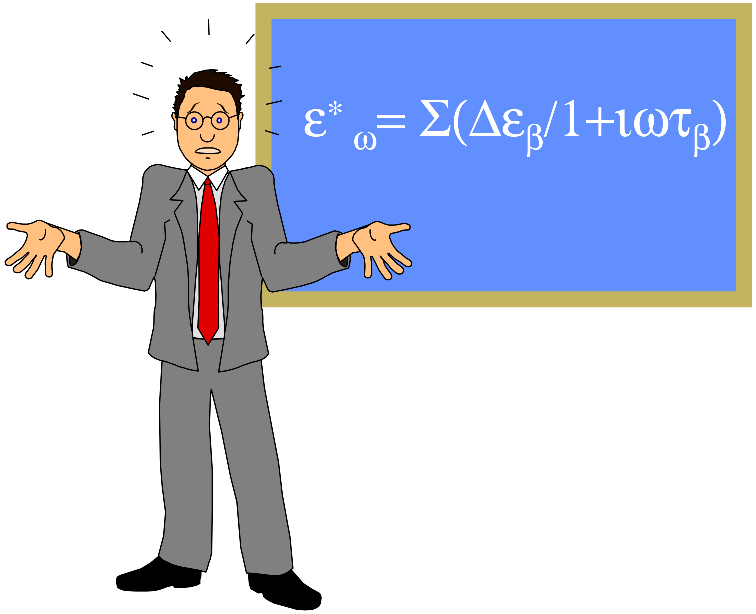
Dynamic Mechanical Analysis (DMA)
Basics and Beyond



Dr. Lin Li
Thermal Analysis
PerkinElmer Inc.
April 2000

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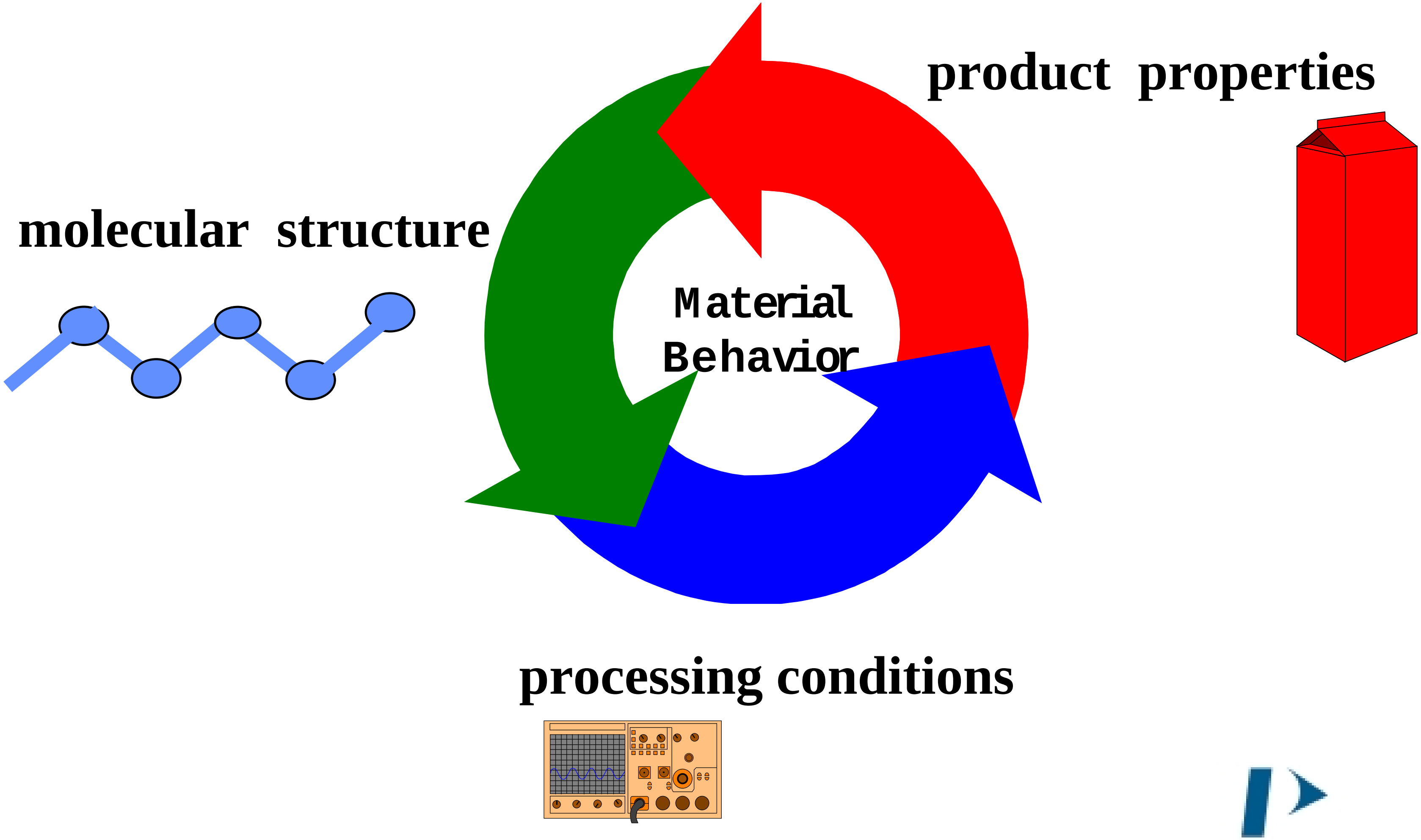
The DMA lets you relate:



product properties

molecular structure

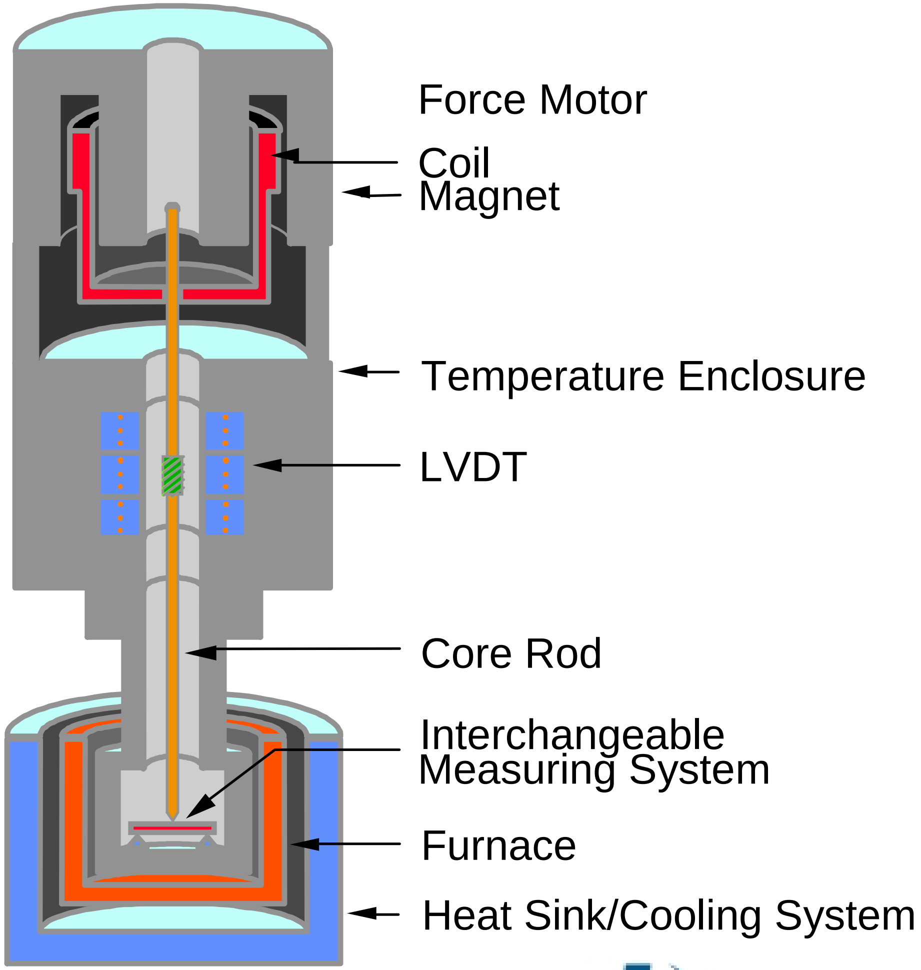
Material Behavior

processing conditions

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.



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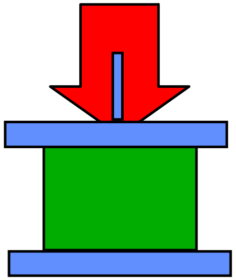
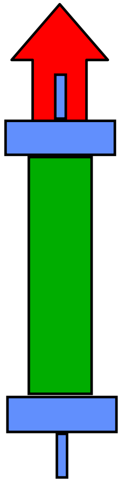
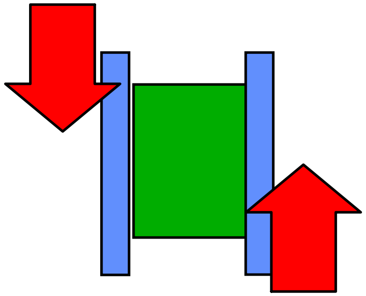
Outstanding Flexibility 1: Multiple Geometries



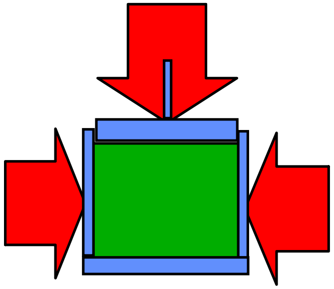
Compressive



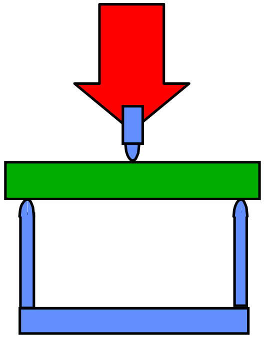
Extension



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

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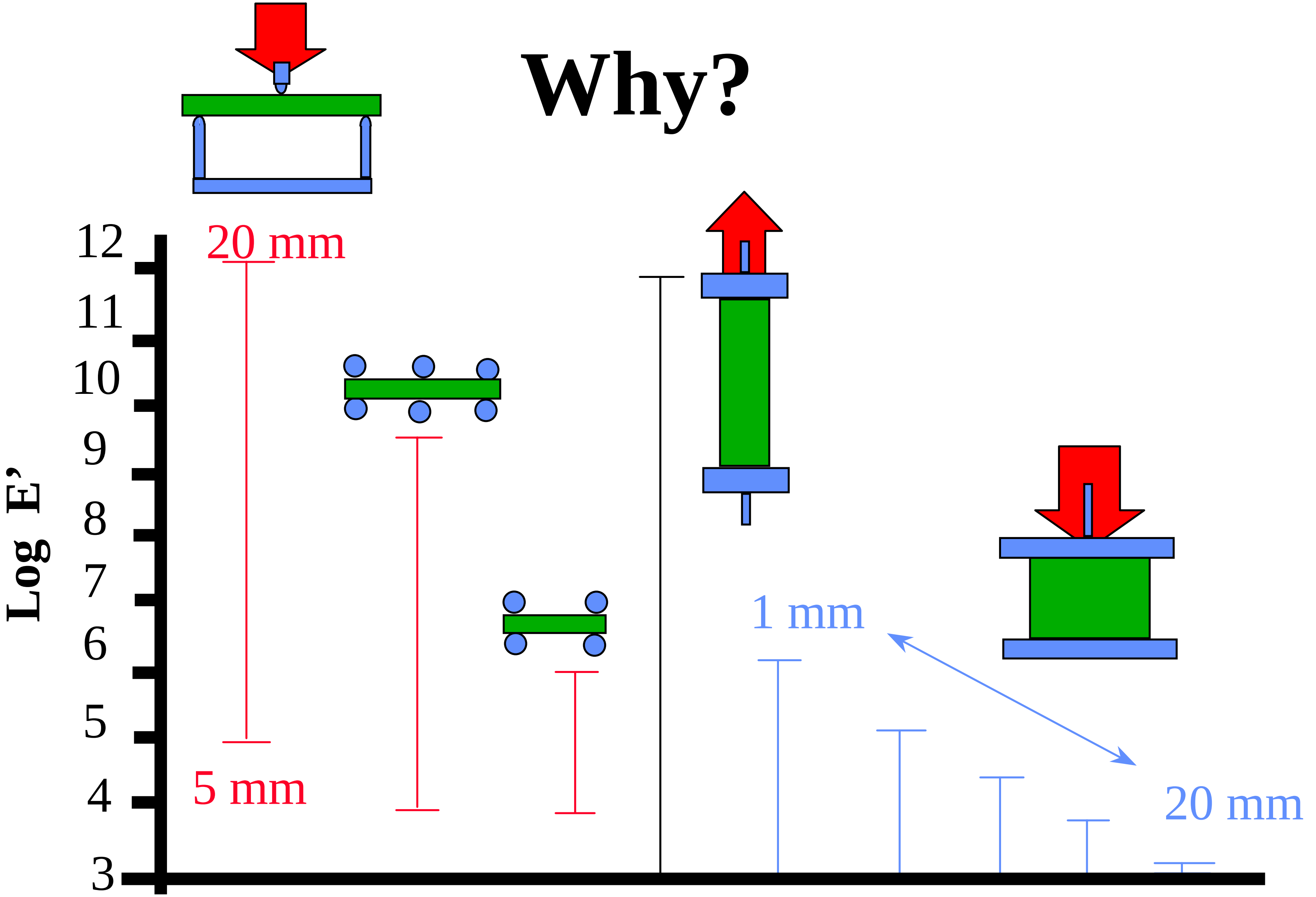
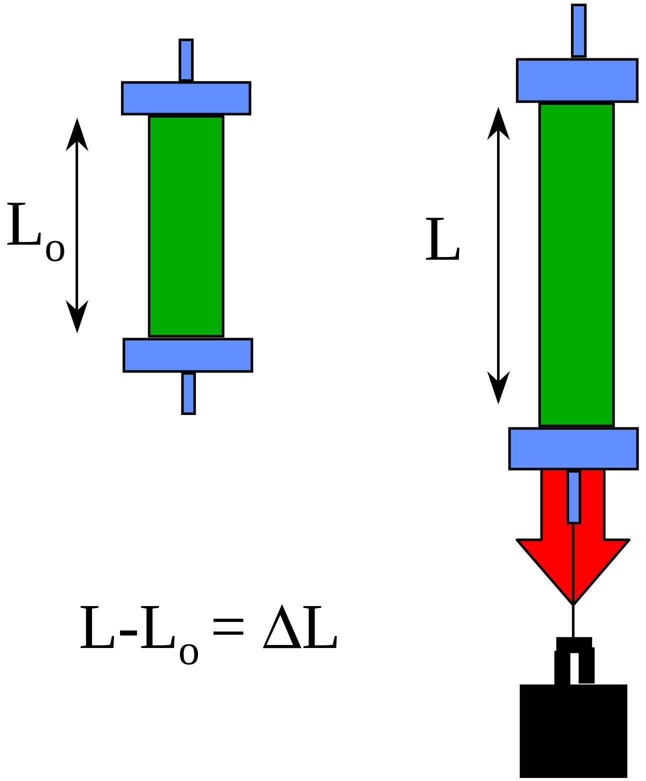
Why?



Stress Causes Strain...



$$L\text{-}L_o = \Delta L$$

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

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

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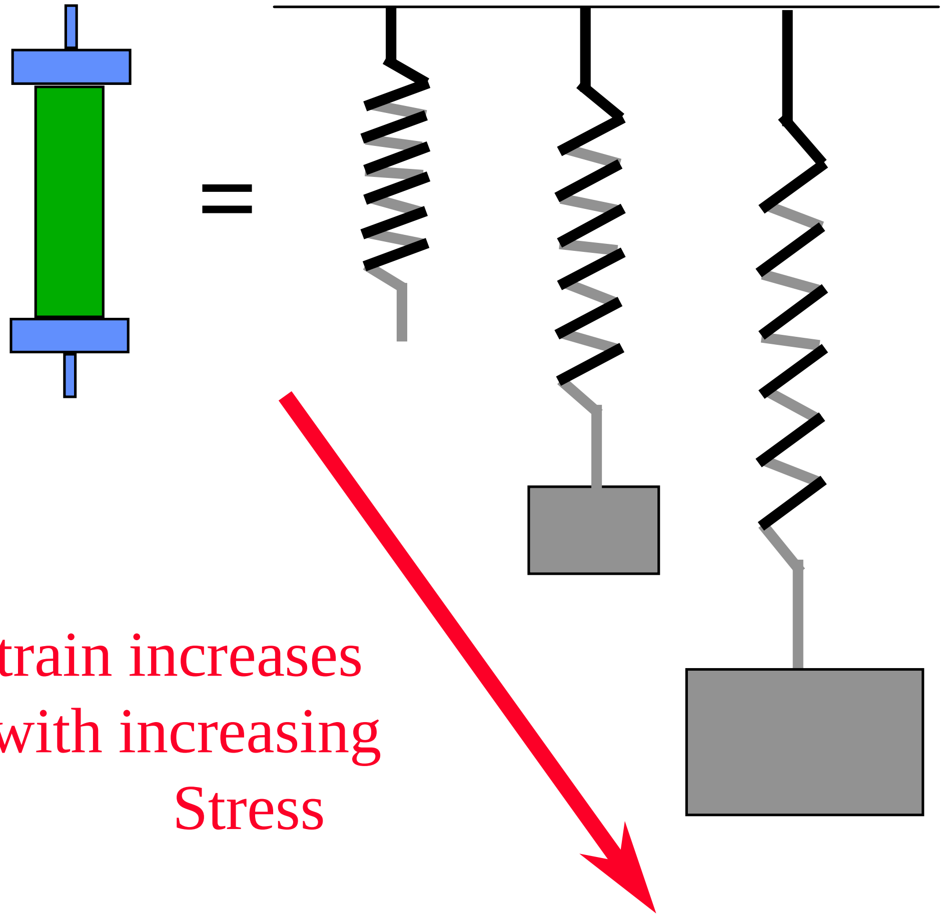
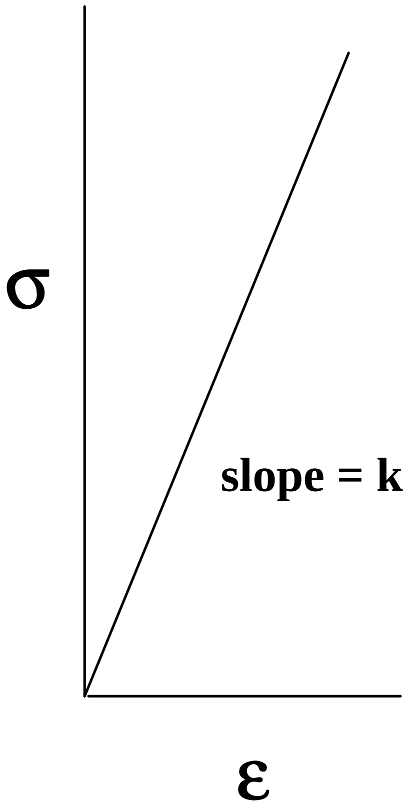
The Elastic Limit: Hooke's Law

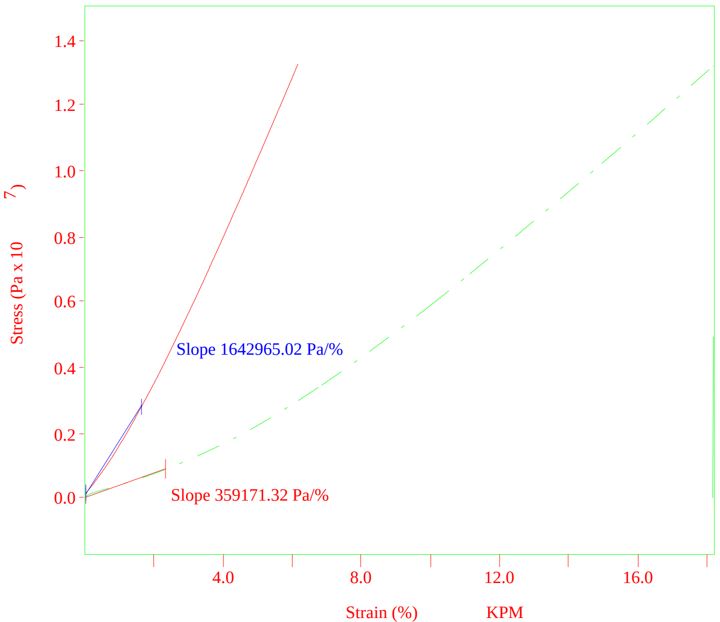


Strain increases with increasing Stress



Real vs... Hookean Stress-Strain Curves

Curve 1: DMA Creep Recovery in Parallel Plate
File info: Drssr90R.2 Thu Apr 14 15:16:52 1994
Sample Height: 3.359 mm Creep Stress: 2600.0mN Recovery Stress: 1.0mN
Dresser 90 Durameter



TEMP1: 20.0 C TIME1: 5.3 min

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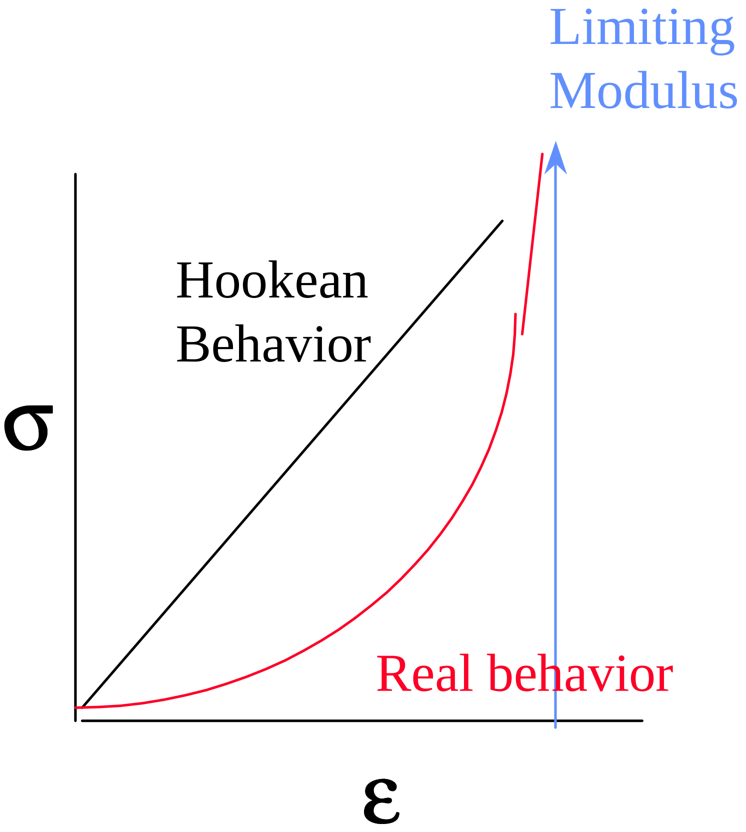
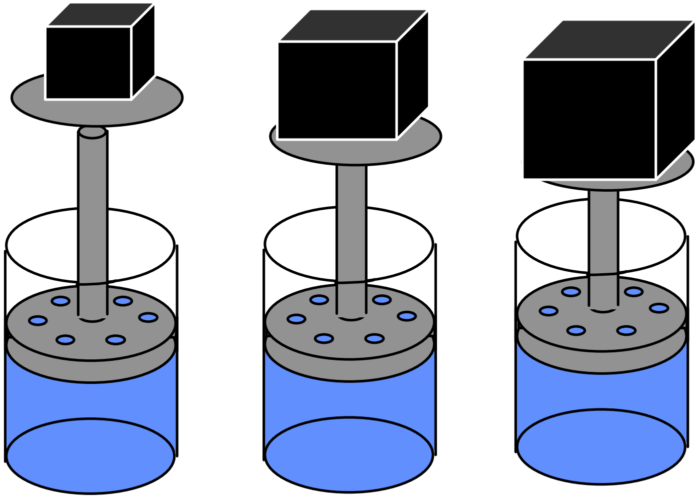
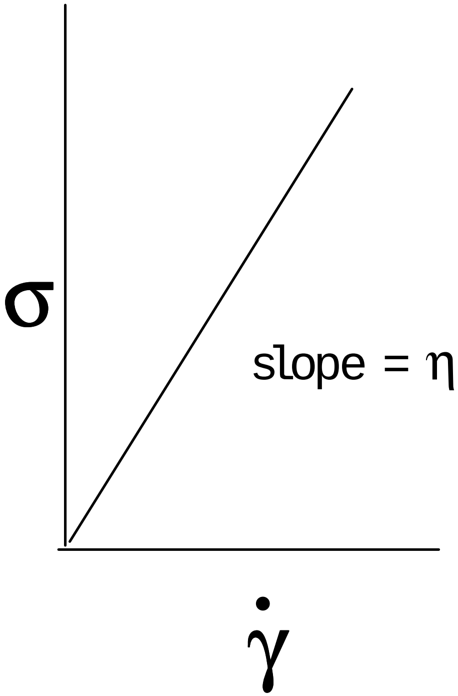
Thu Apr 14 16:34:38 1994



The Viscous Limit: Newtonian Behavior





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

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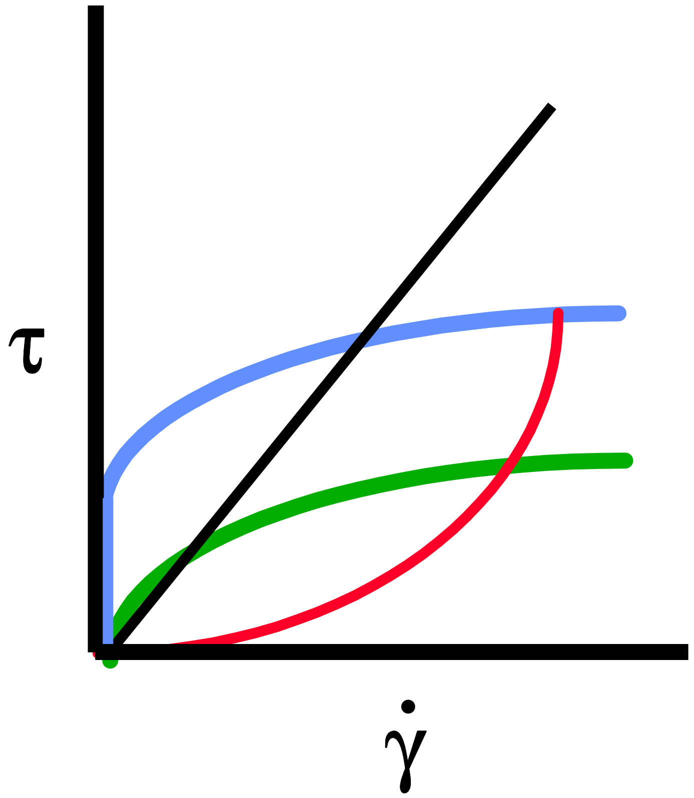
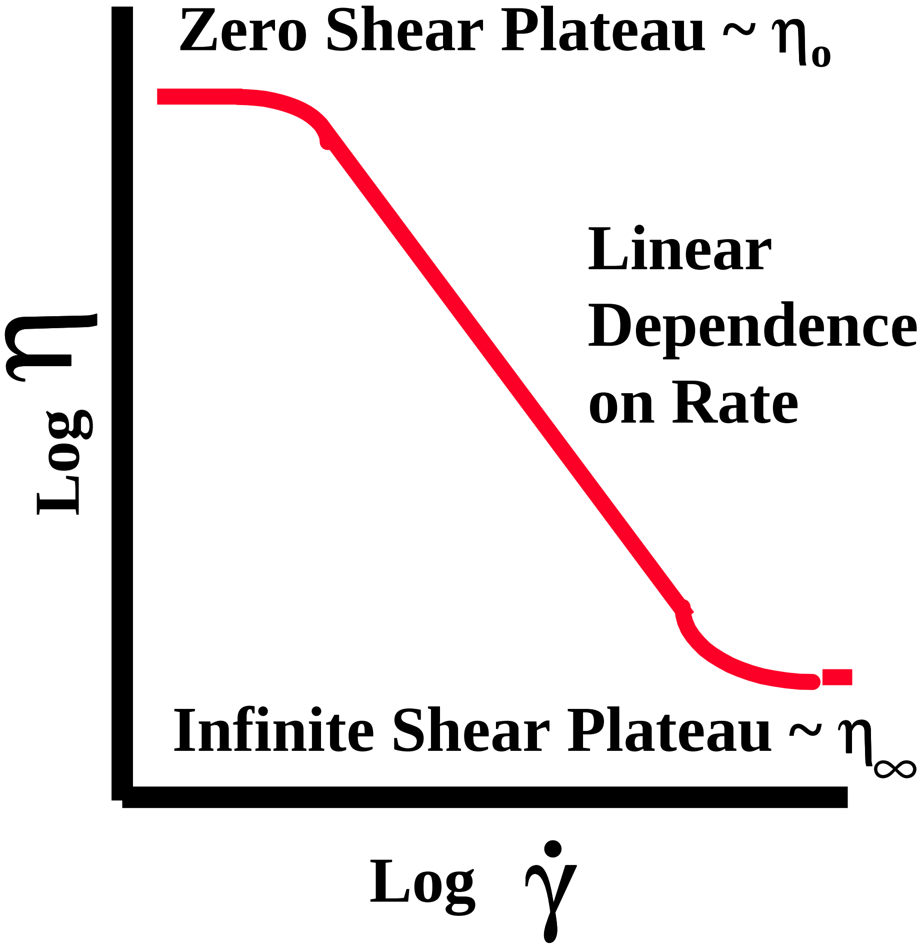
Viscosity Effects



- 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.

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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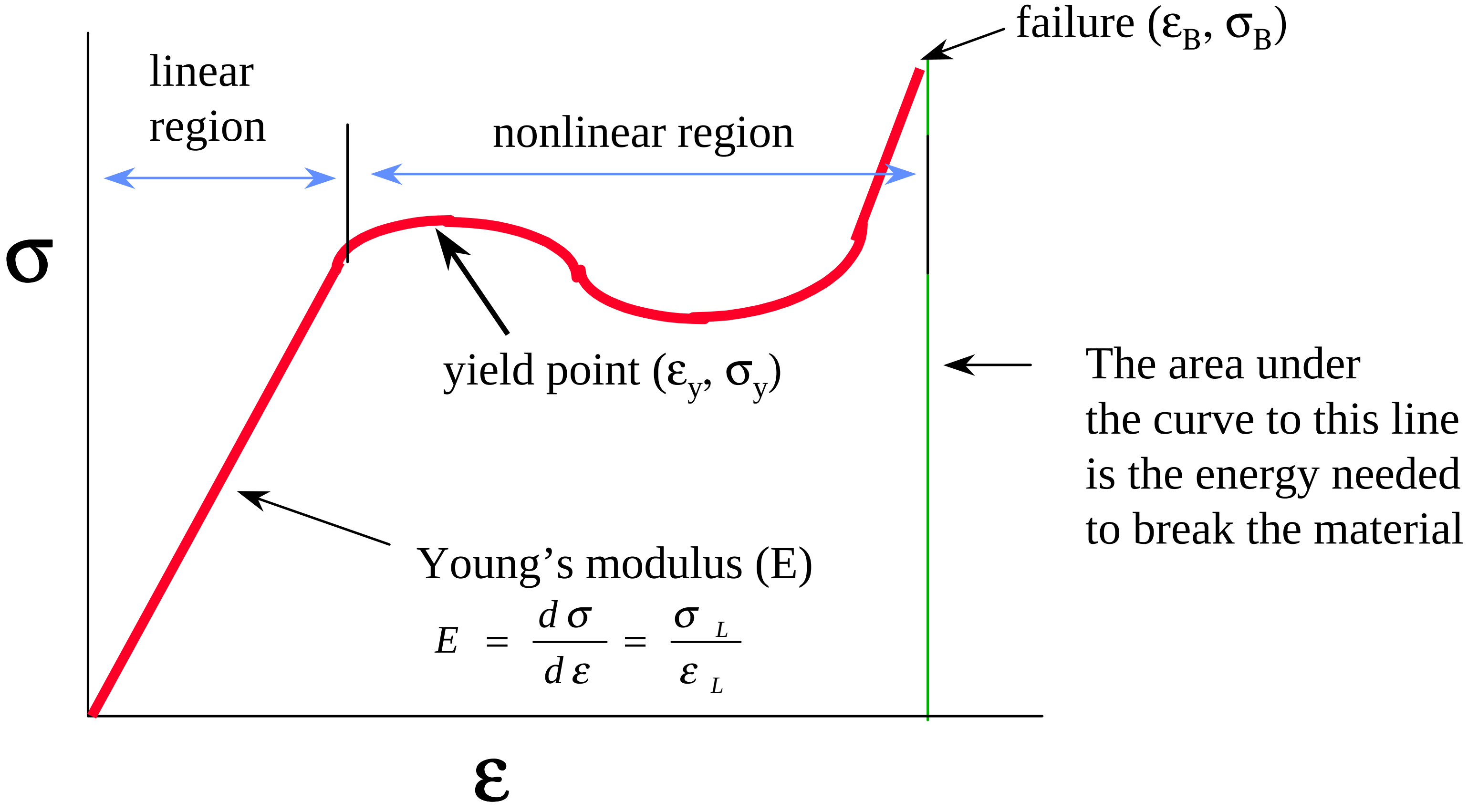
Analyzing a Stress-Strain Curve



failure (ε_B, σ_B)

linear region

nonlinear region

σ

yield point (ε_y, σ_y)

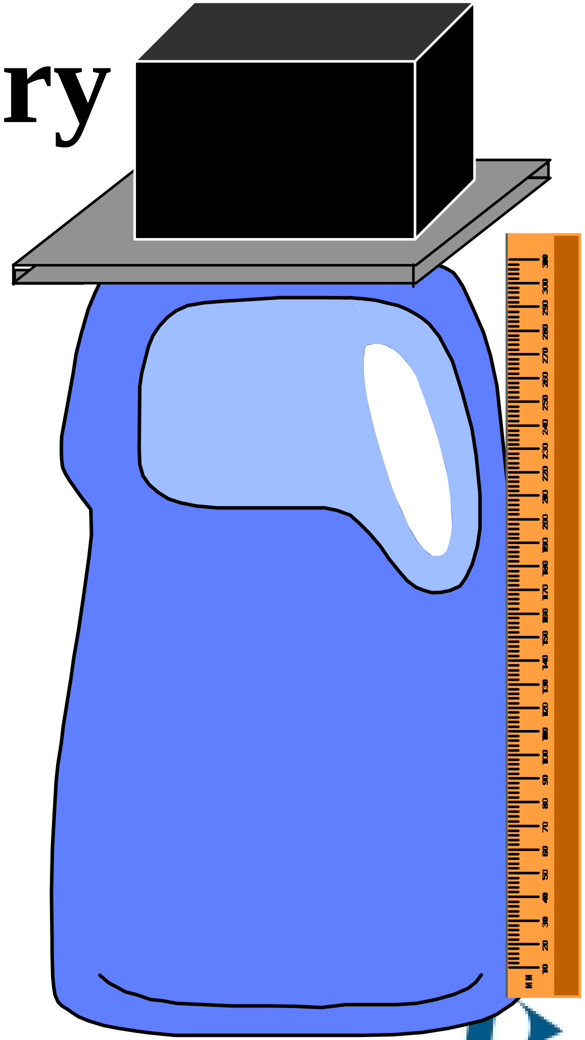
The area under the curve to this line is the energy needed to break the material

Young's modulus (E)

$$E = \frac{d\sigma}{d\varepsilon} = \frac{\sigma_L}{\varepsilon_L}$$

ε

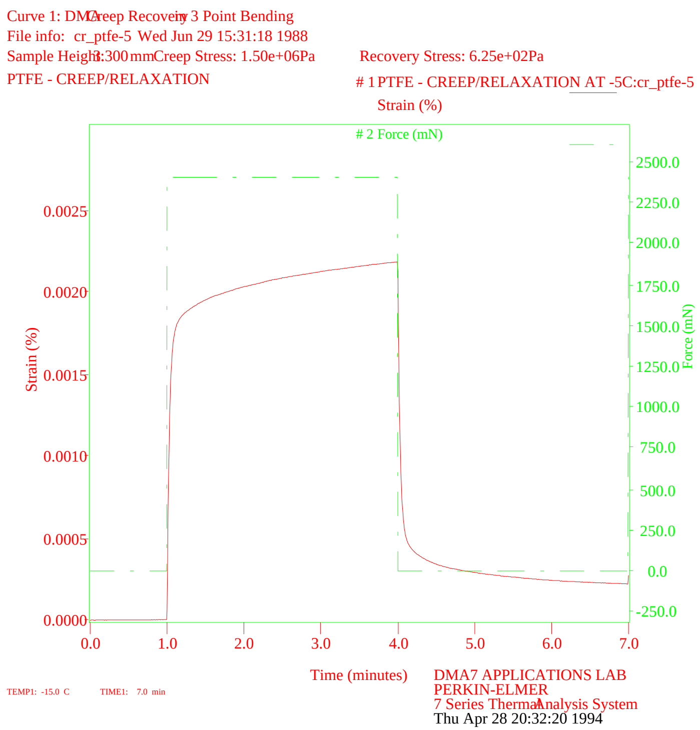
Under Continuos Loads: Creep Recovery



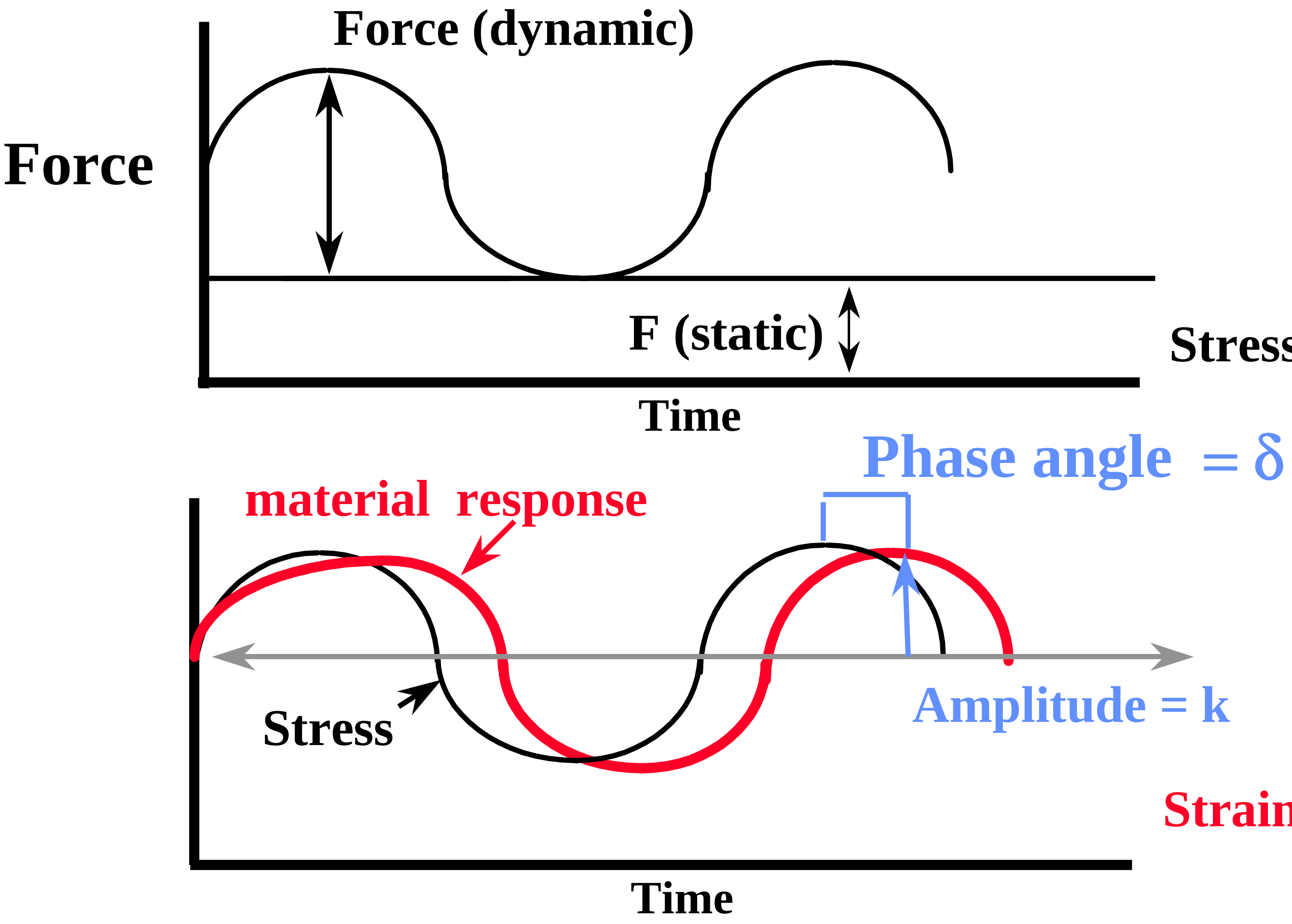
- Applying a constant load for long times and removing it from a sample.
- Allows one to see the distortion under constant load **and** also how well it recovers.

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.



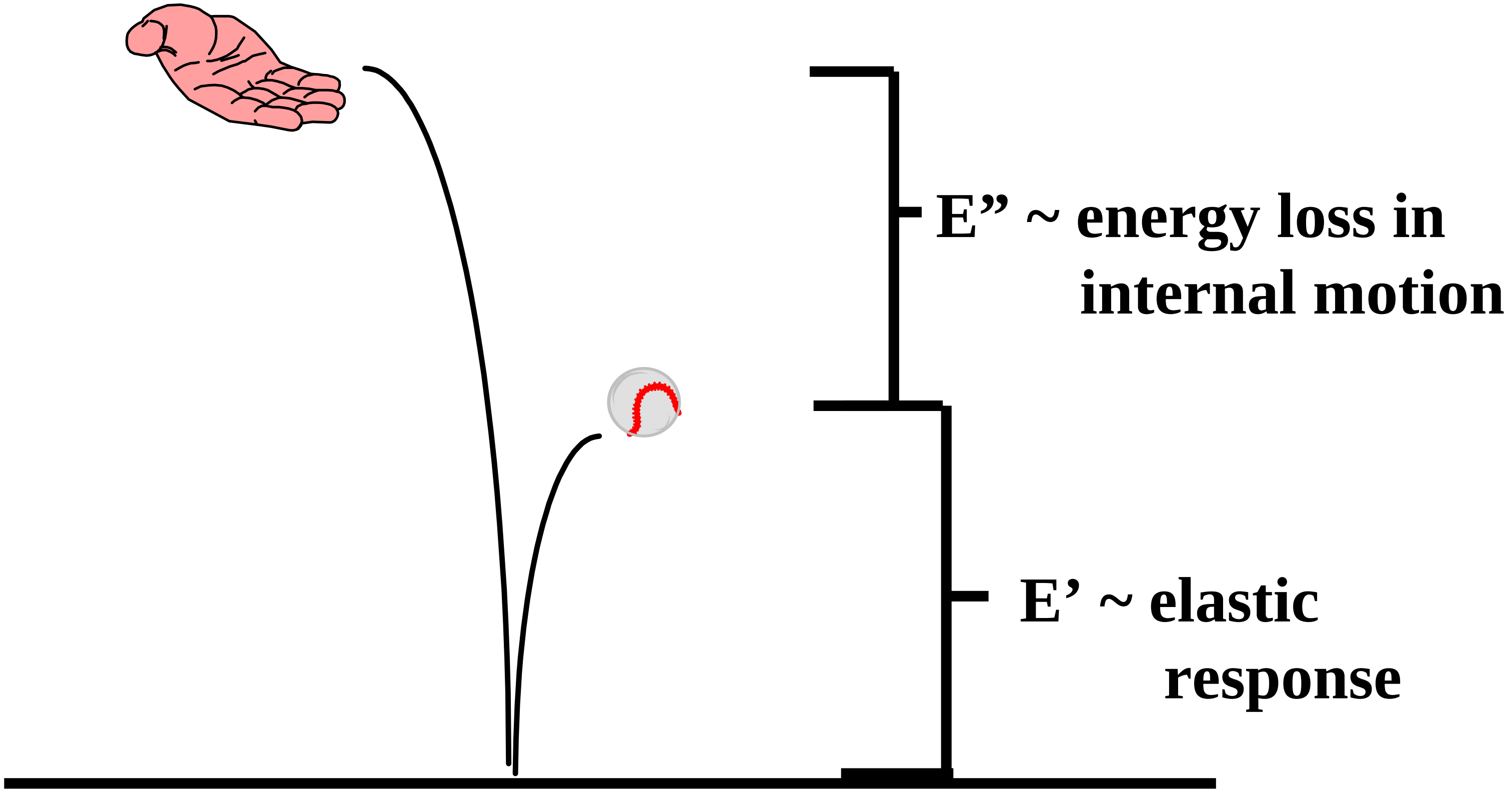
Dynamic Stress



Stress =FA

Strain $=y^o/y$

Why? Let’s bounce a ball.



E” ~ energy loss in internal motion

E’ ~ elastic response

All this is calculated from δ and k:

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

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

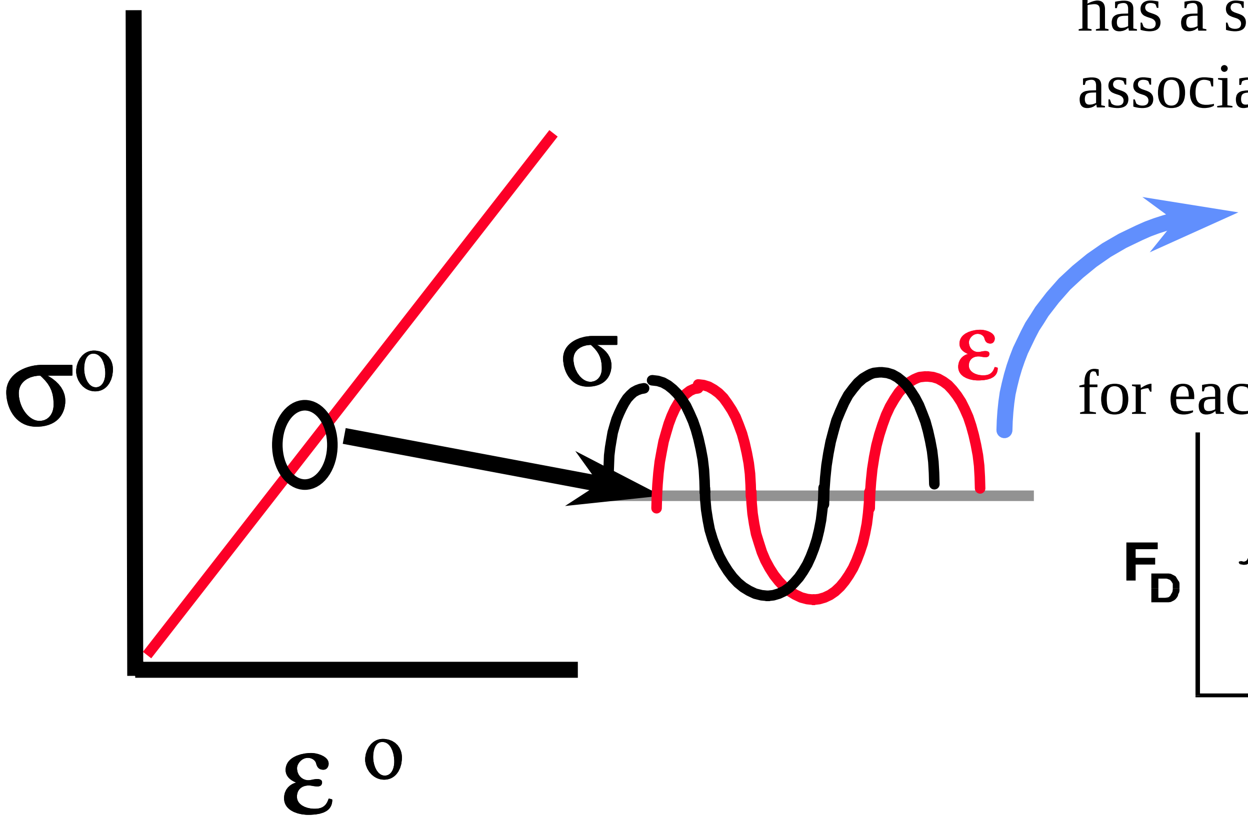
$$E^* = E' + iE'' = \mathrm{SQRT}(E'^2 + E''^2)$$

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

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

To apply this to materials...

Dynamic Stress Scan



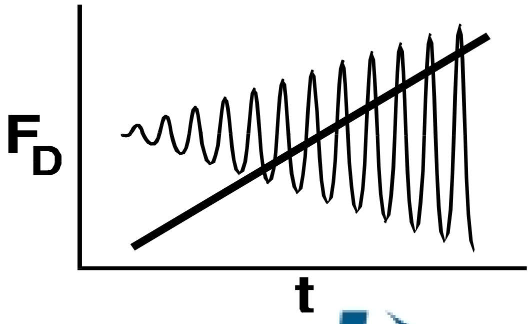
Since each part of the ramp has a sine wave stress associated with it, we get:

tan δ

E*, E’, E”

η

for each data point!!



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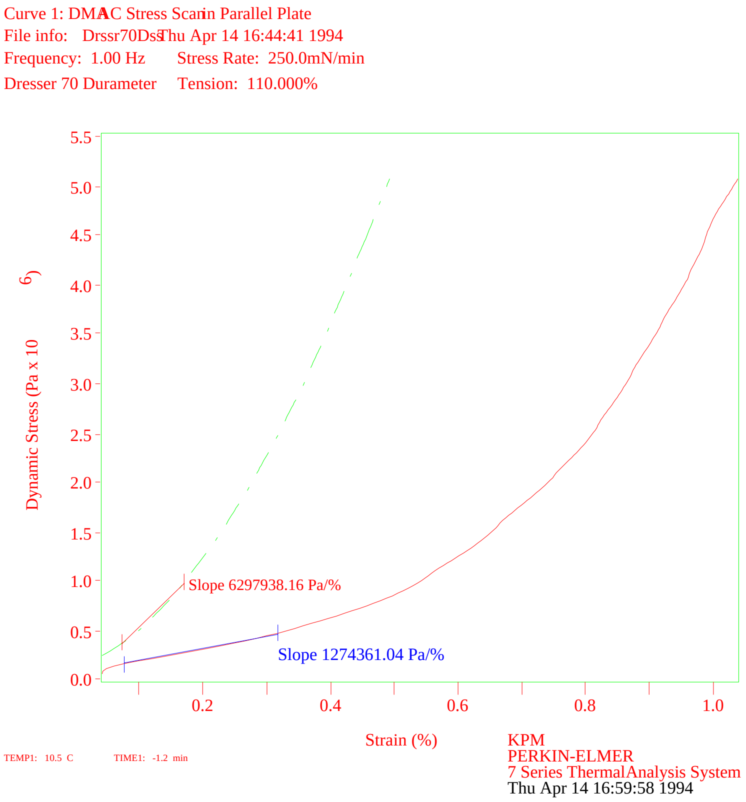
For example, DSS Curves



Curve 1: DMA AC Stress Scan in 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

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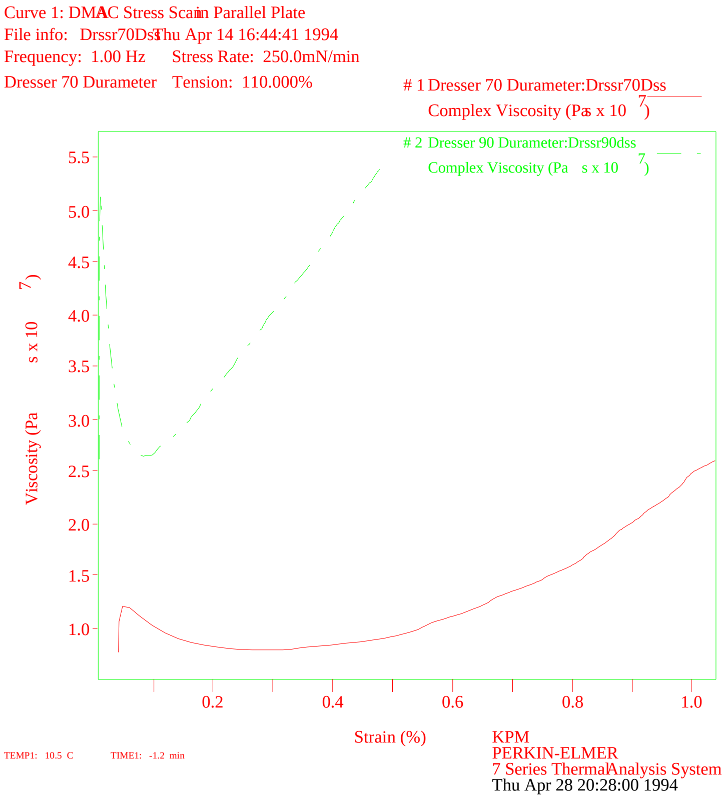
Thu Apr 14 16:59:58 1994



Curve 1: DMA AC Stress Scan in 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

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Thu Apr 28 20:28:00 1994

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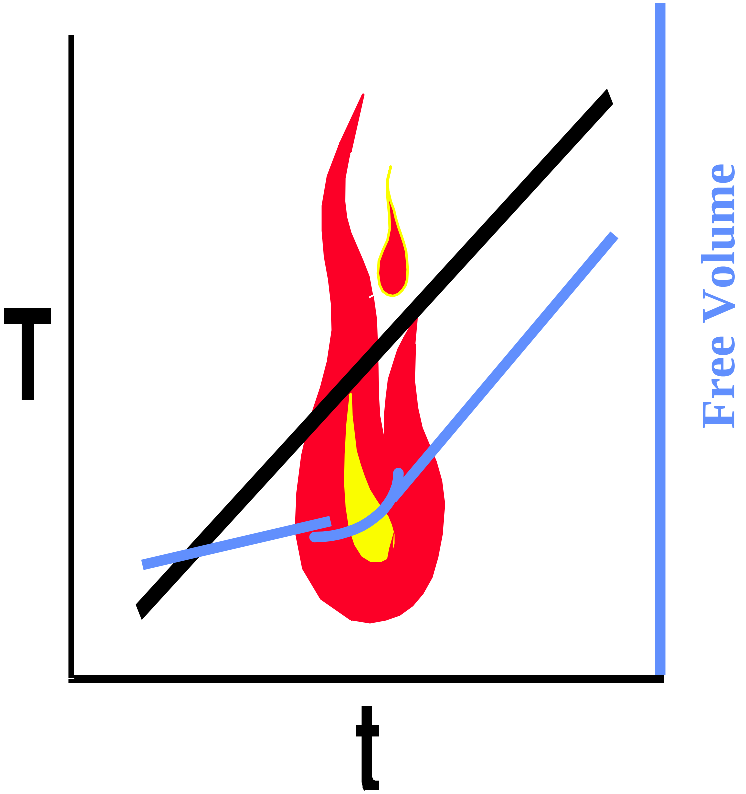
Now, let's induce temperature as a variable.

- 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.



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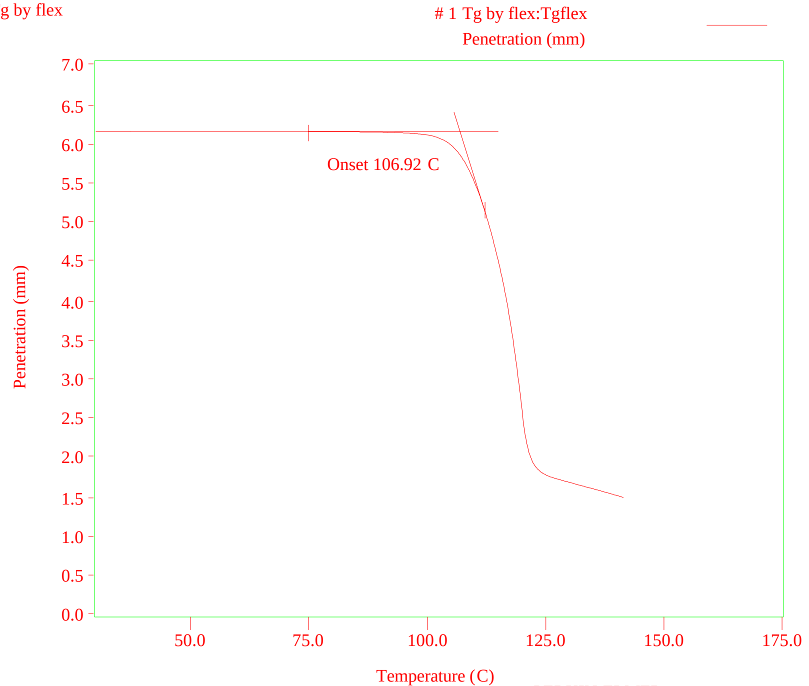
Thermomechanical Analysis as a starting Point.

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



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

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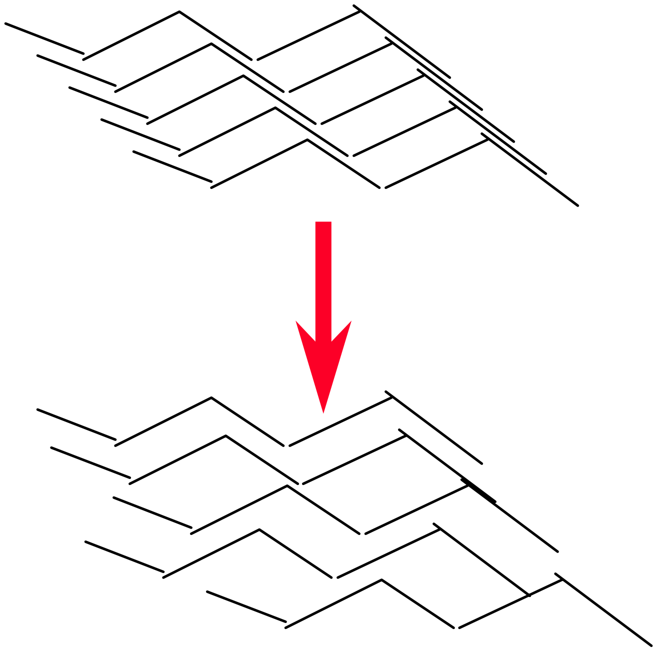
Sun Nov 26 20:10:47 1995



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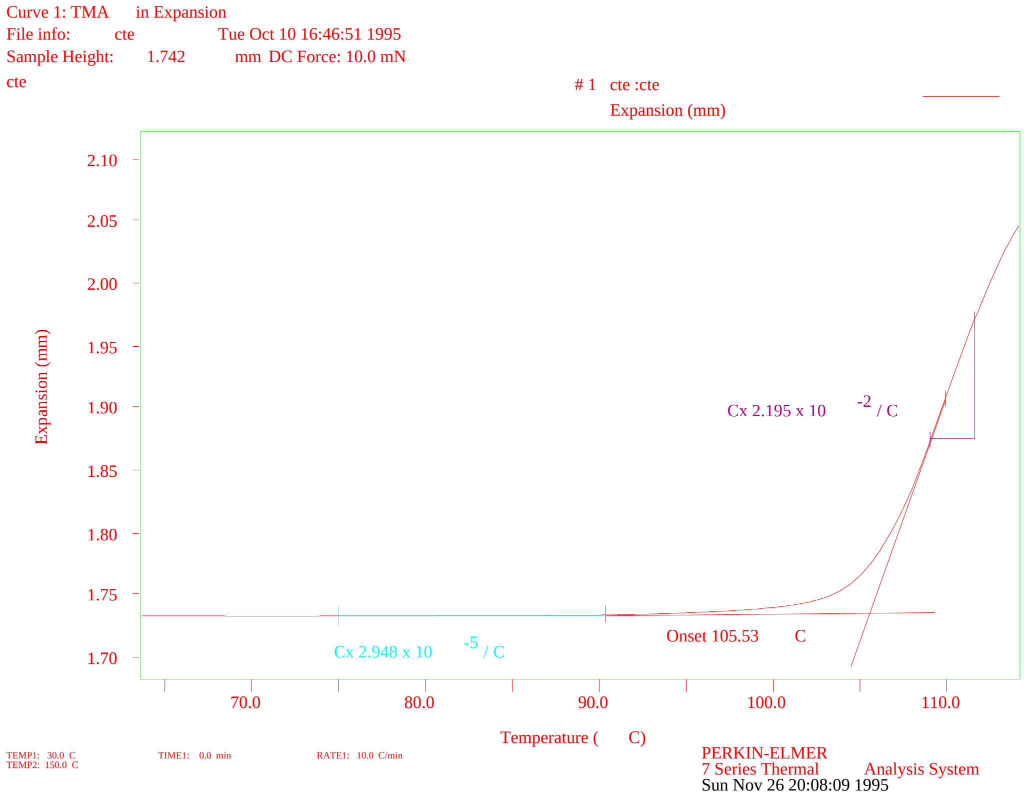
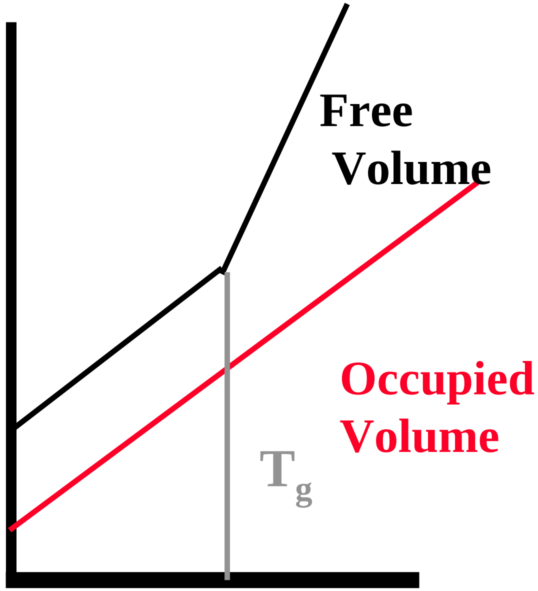
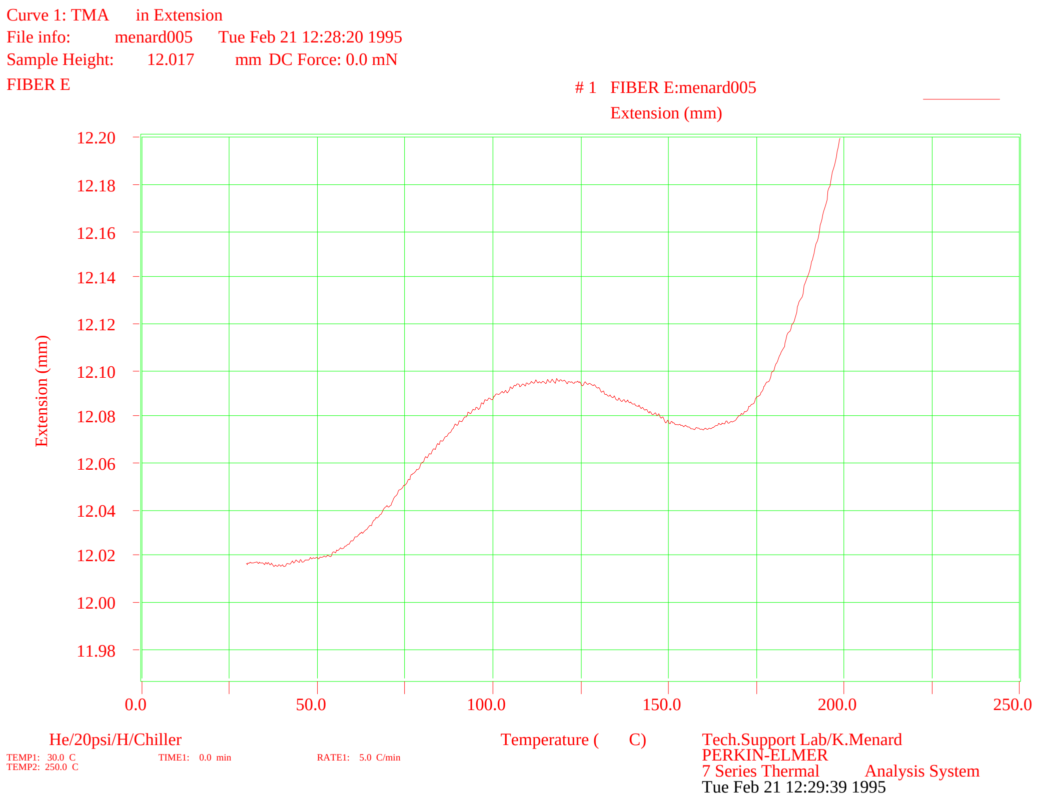
TMA - It’s all free volume.





And it’s not just Tg.



(the traditional way to do heat set)

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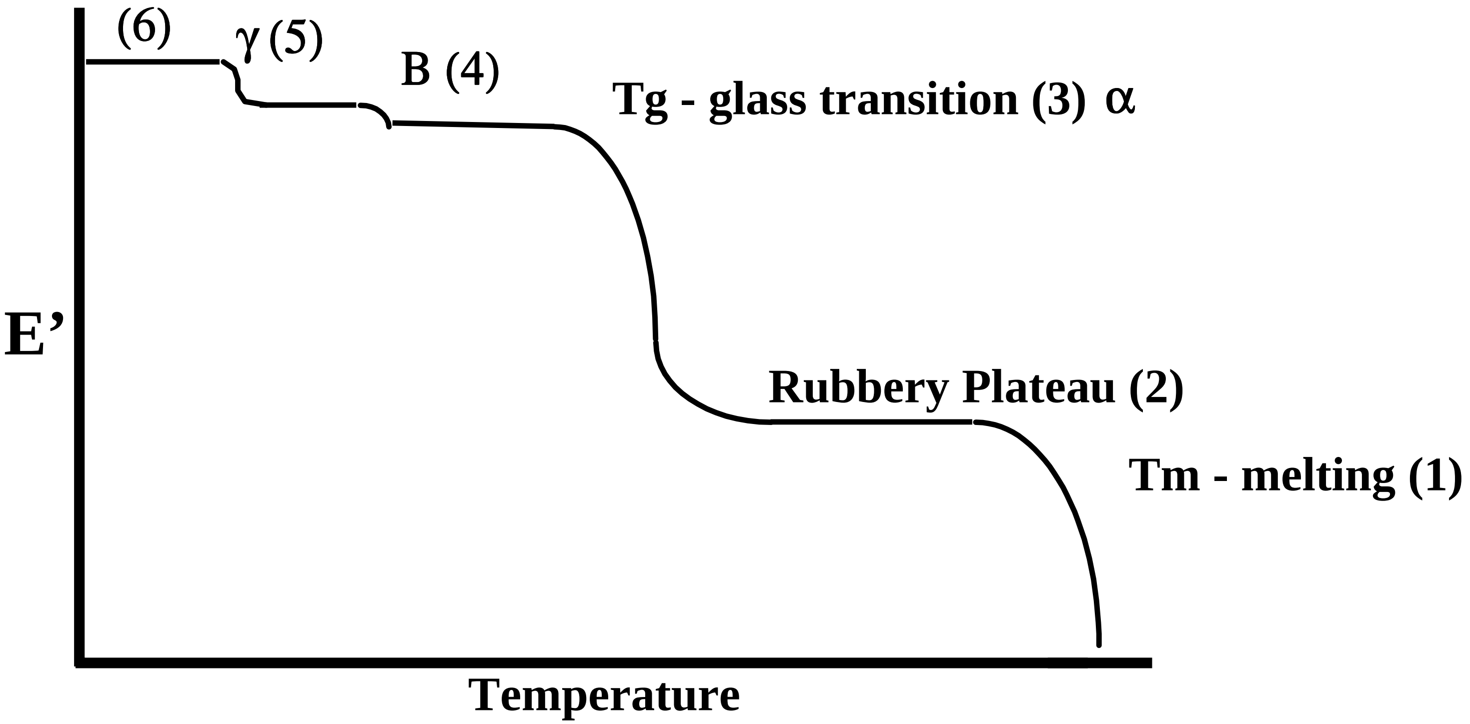
Time Temperature Scans at a Fixed Frequency

- 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

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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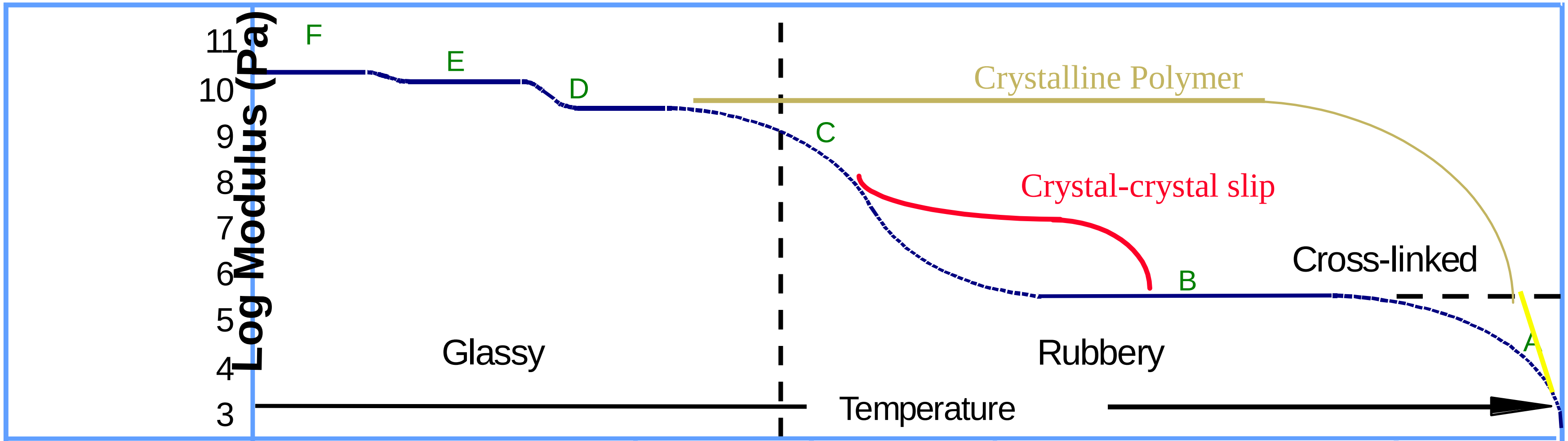
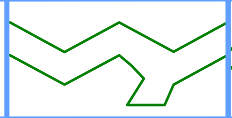
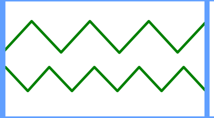
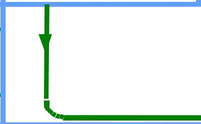
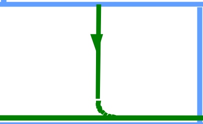
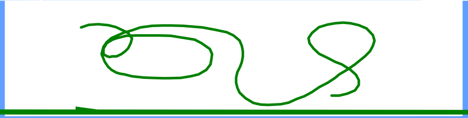
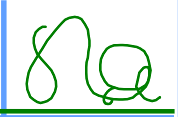
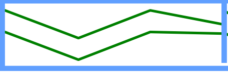
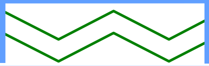
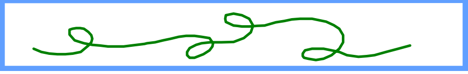
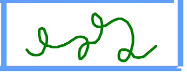
In more detail...



	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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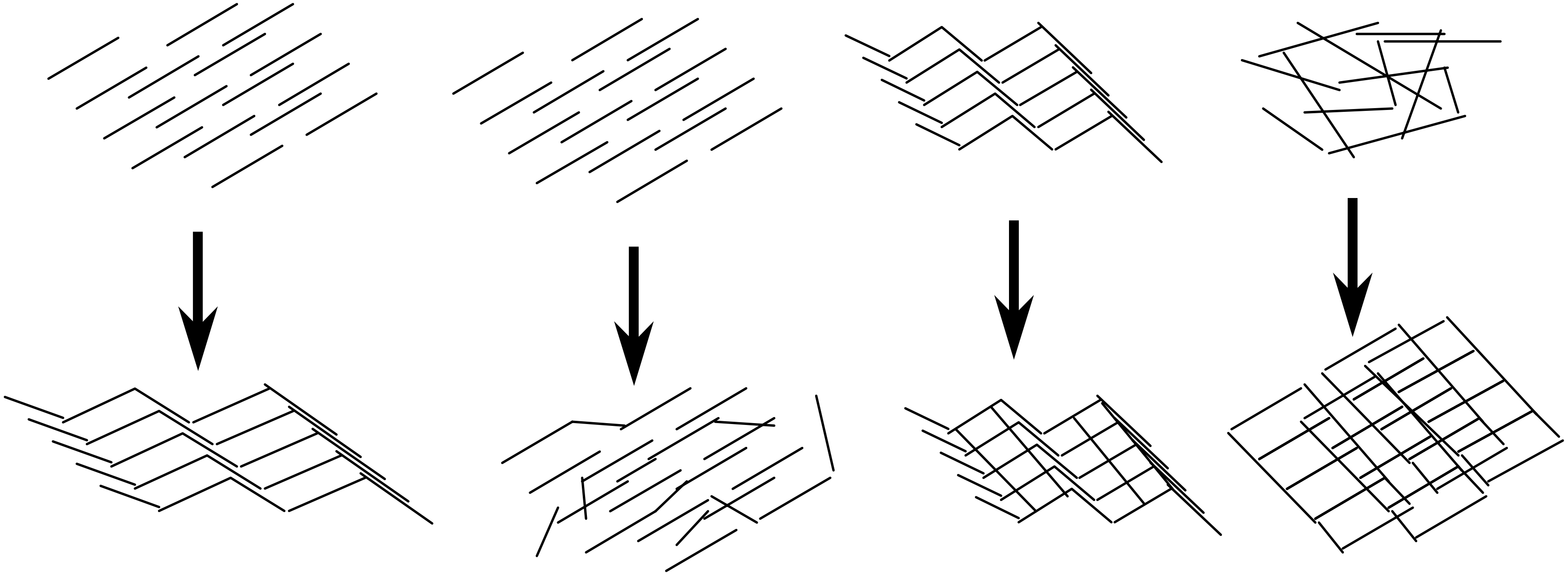
Common changes show as:



	MW	MWD	Crosslink Density	Crystallinity
E’	↑ ●	● ↔	↑ ↔	↑ ↔
tan δ	↑ ●	↑ ↔	↑ ↔	↓ ●

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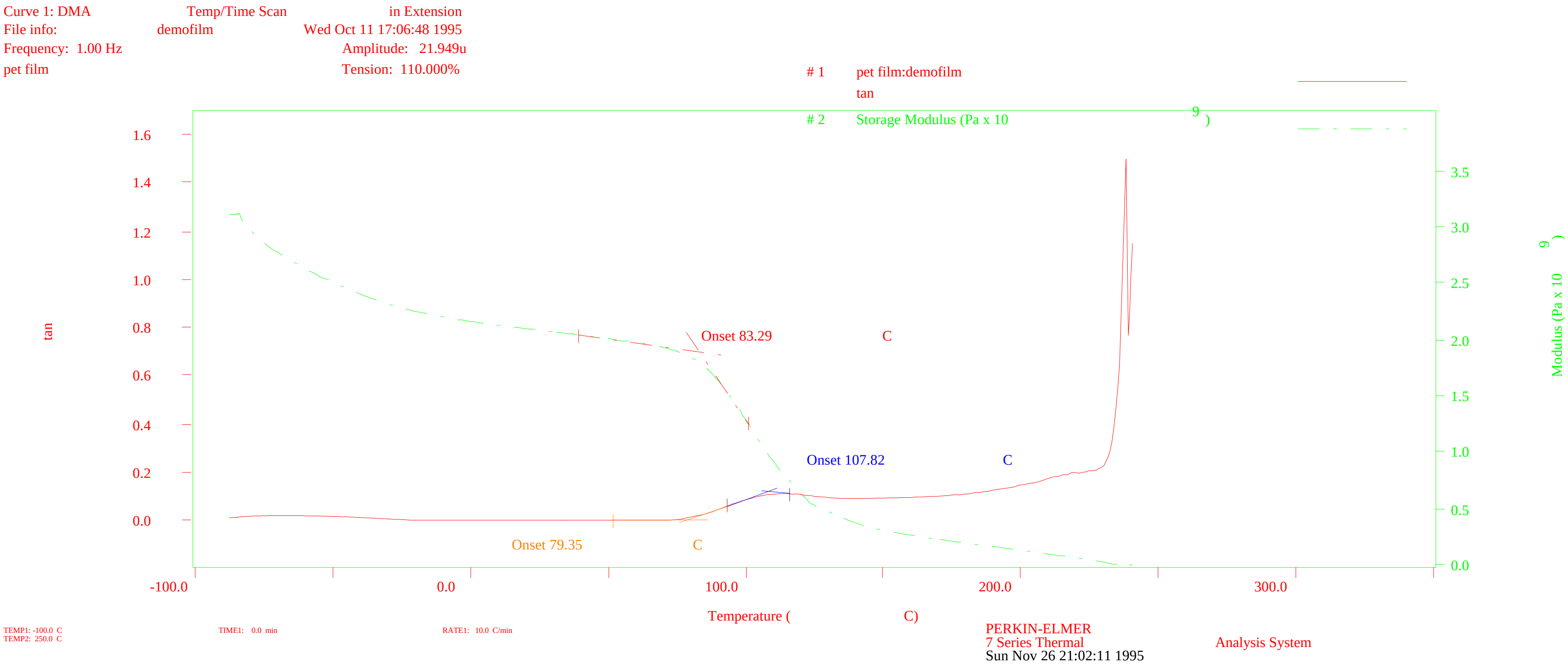
Tg are easily seen, as in PET Film


Curve 1: DMA Temp/Time Scan in Extension
File info: demofilm Wed Oct 11 17:06:48 1995
Frequency: 1.00 Hz Amplitude: 21.949u
pet film Tension: 110.000%

1 pet film:demofilm
tan
2 Storage Modulus (Pa x 10 ^{9})

TEMP1: -100.0 C
TEMP2: 250.0 C
TIME1: 0.0 min
RATE1: 10.0 C/min

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Sun Nov 26 21:02:11 1995

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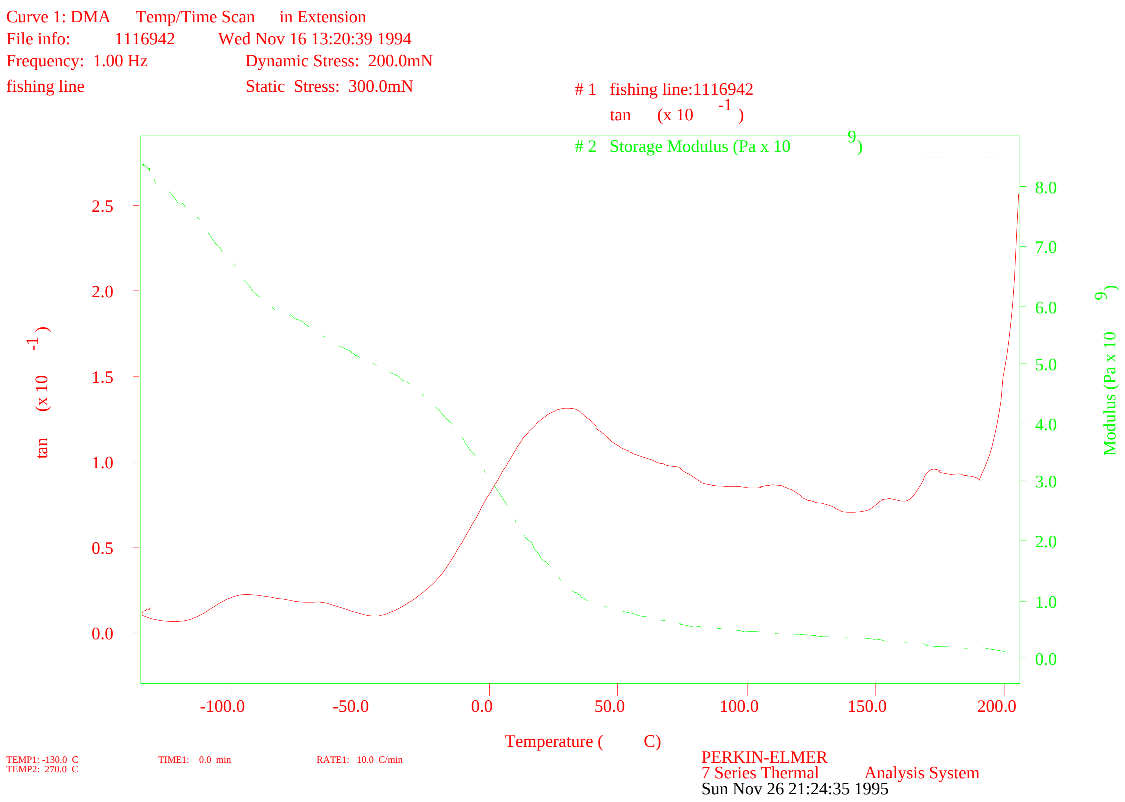
or in PP fishing line.



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

TEMP1: -130.0 C
TEMP2: 270.0 C
TIME1: 0.0 min
RATE1: 10.0 C/min

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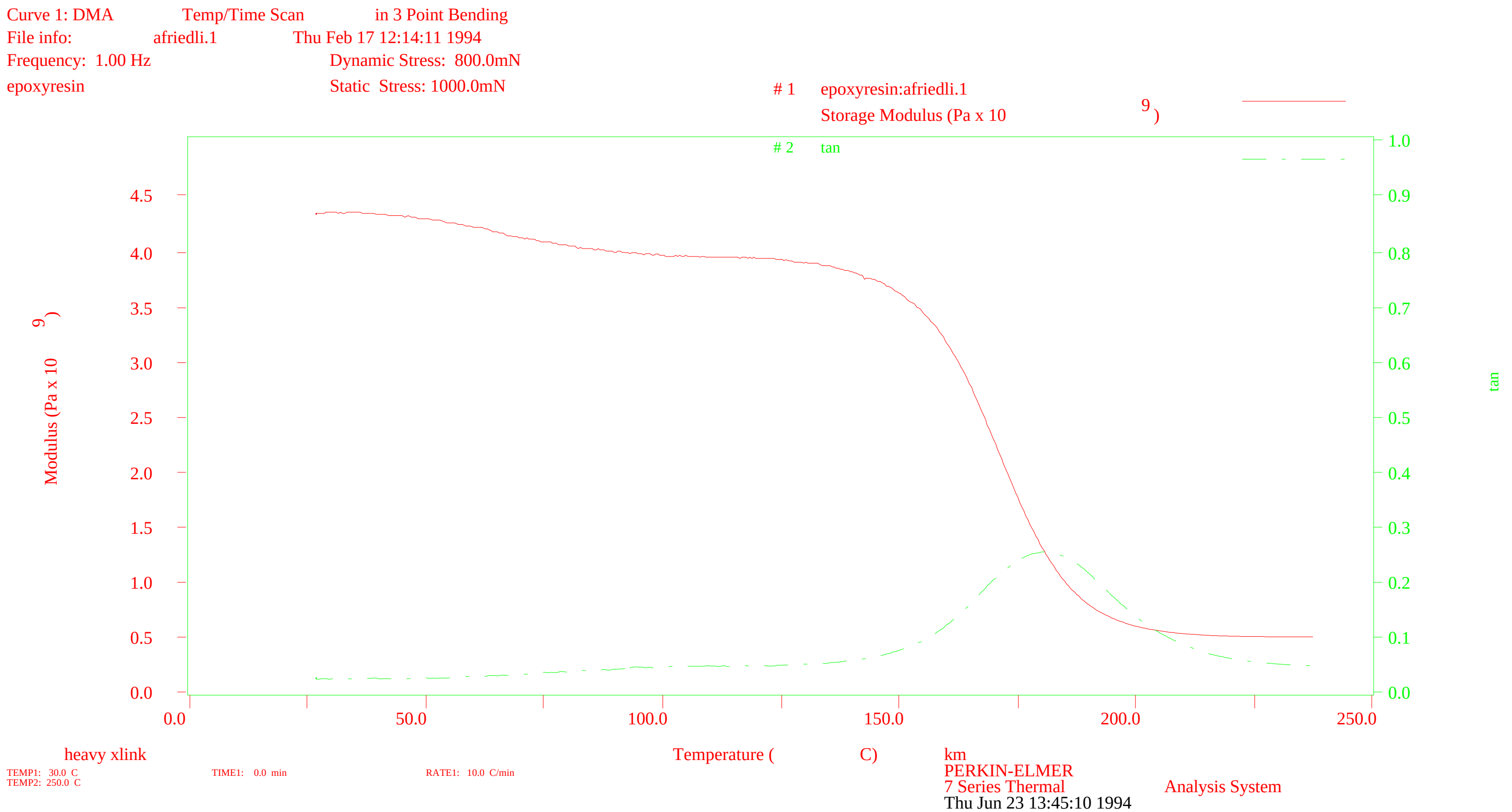
Sun Nov 26 21:24:35 1995

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

1 epoxyresin:afriedli.1
Storage Modulus (Pa x 10^9)
2 tan

heavy xlink
TEMP1: 30.0 C
TEMP2: 250.0 C
TIME1: 0.0 min
RATE1: 10.0 C/min
km
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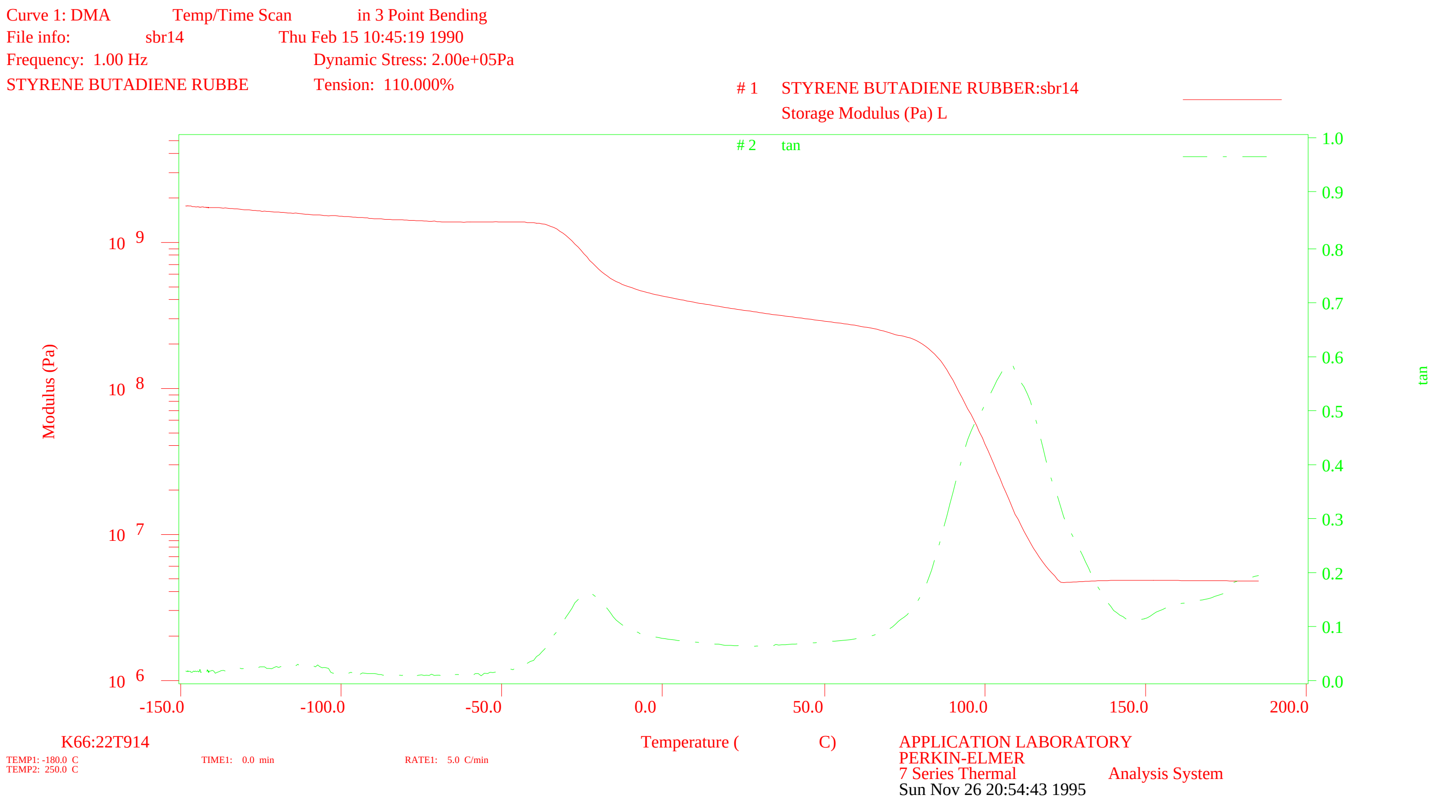
7 Series Thermal Analysis System
Thu Jun 23 13:45:10 1994

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%

K66:22T914
TEMP1: -180.0 C TIME1: 0.0 min RATE1: 5.0 C/min
TEMP2: 250.0 C

APPLICATION LABORATORY
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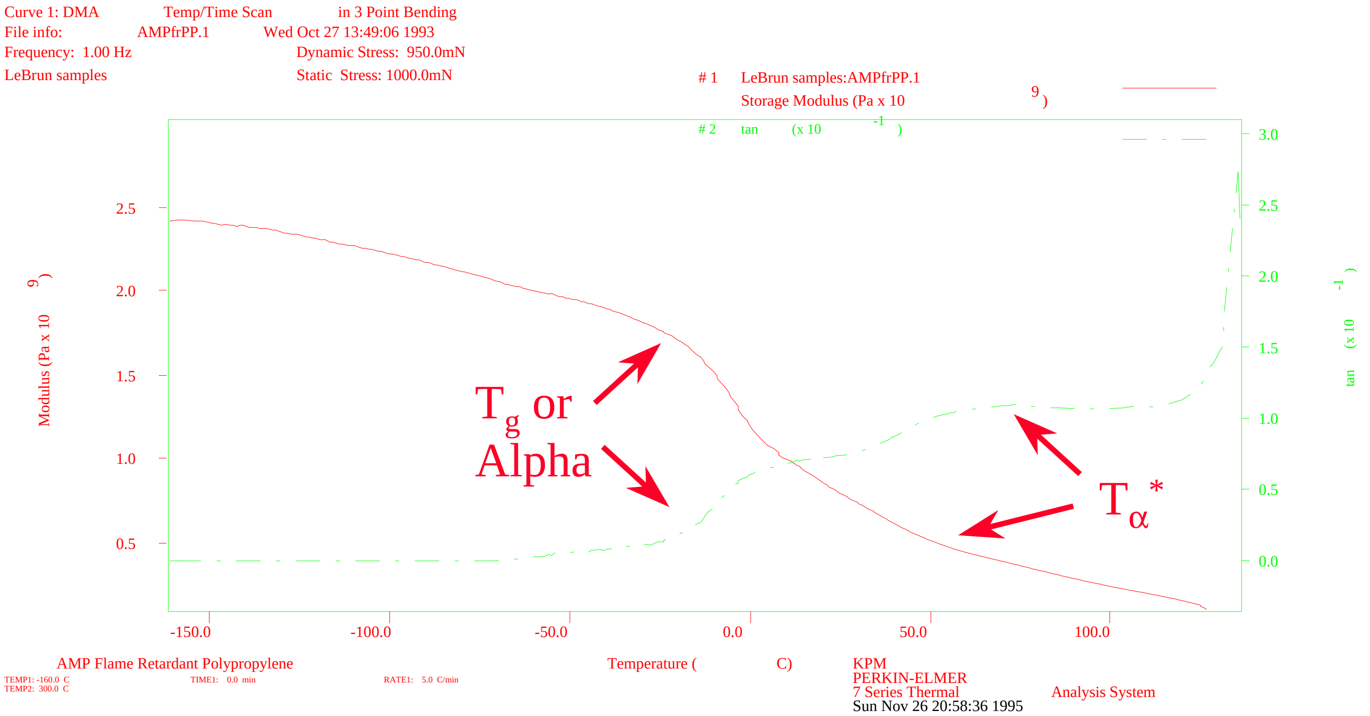
Sun Nov 26 20:54:43 1995

It’s not always so simple:

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



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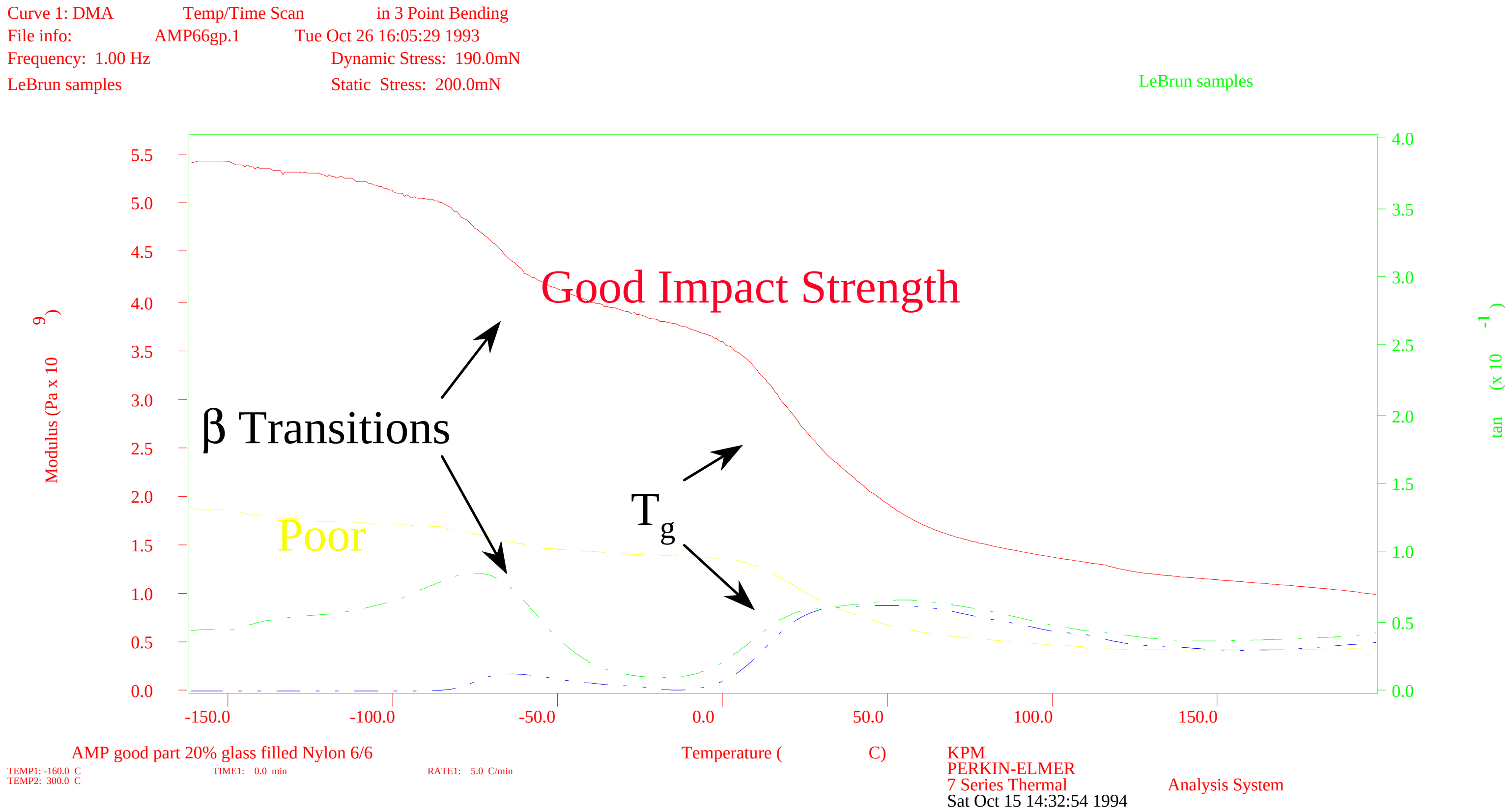
Higher Order Transitions affect toughness



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

AMP good part 20% glass filled Nylon 6/6

TEMP1: -160.0 C TIME1: 0.0 min RATE1: 5.0 C/min
TEMP2: 300.0 C

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

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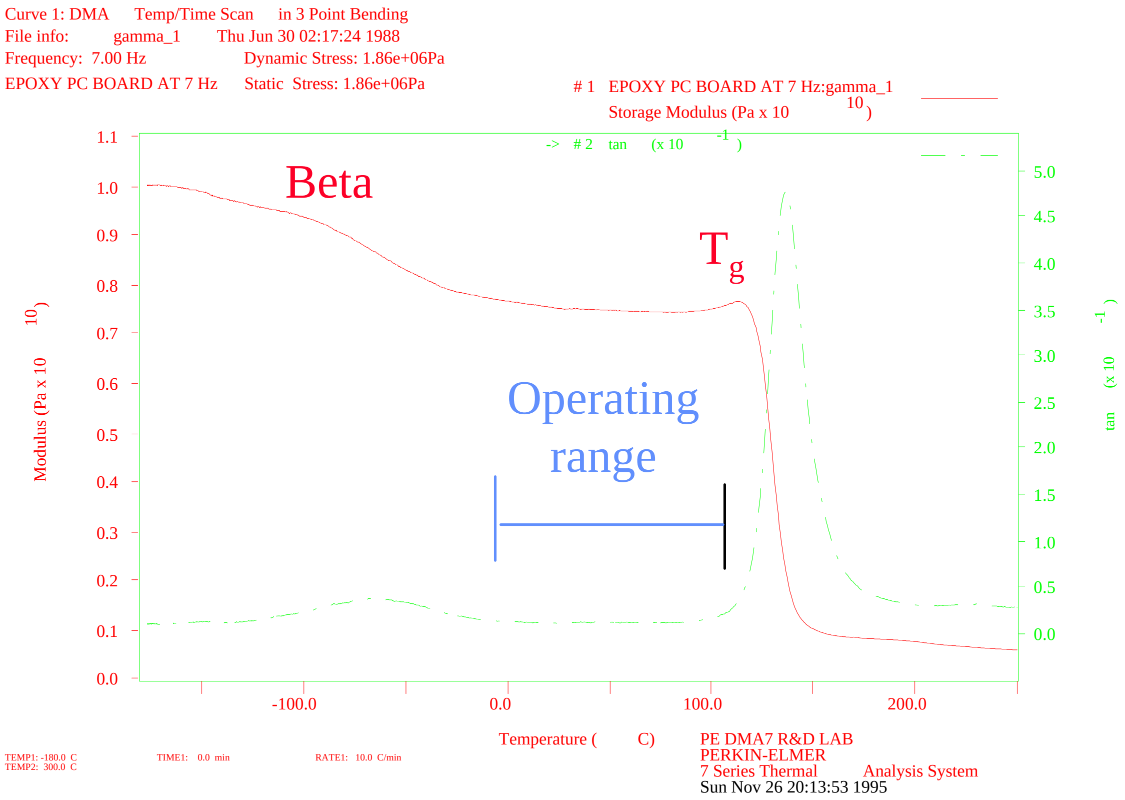
...and also define operating range.



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

TEMP1: -180.0 C TEMP2: 300.0 C
TIME1: 0.0 min
RATE1: 10.0 C/min

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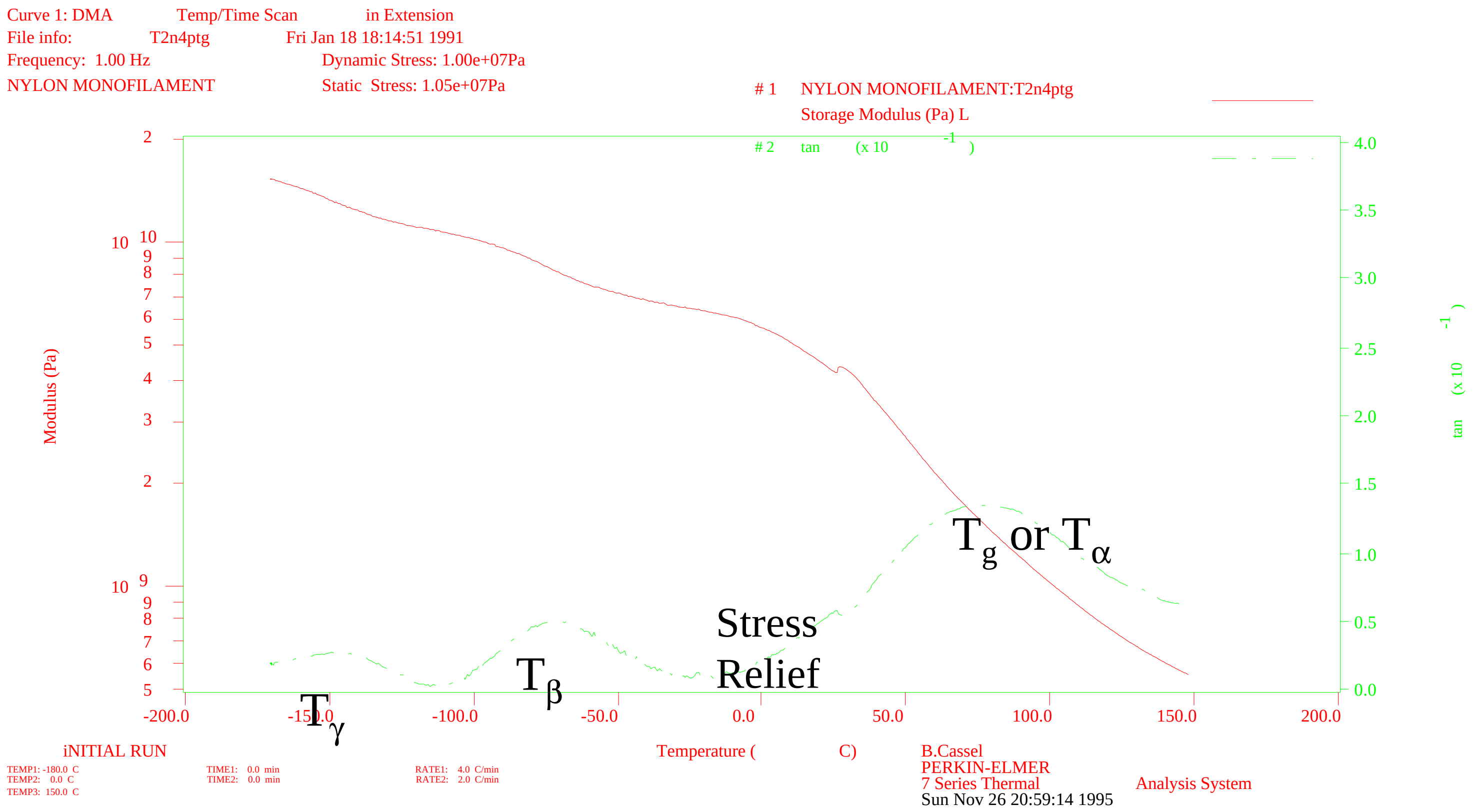
It can get complex...



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

1 NYLON MONOFILAMENT:T2n4ptg
Storage Modulus (Pa) L
2 tan (x 10 $^{-1}$)

iNITIAL RUN
TEMP1: -180.0 C
TEMP2: 0.0 C
TEMP3: 150.0 C
TIME1: 0.0 min
TIME2: 0.0 min
RATE1: 4.0 C/min
RATE2: 2.0 C/min

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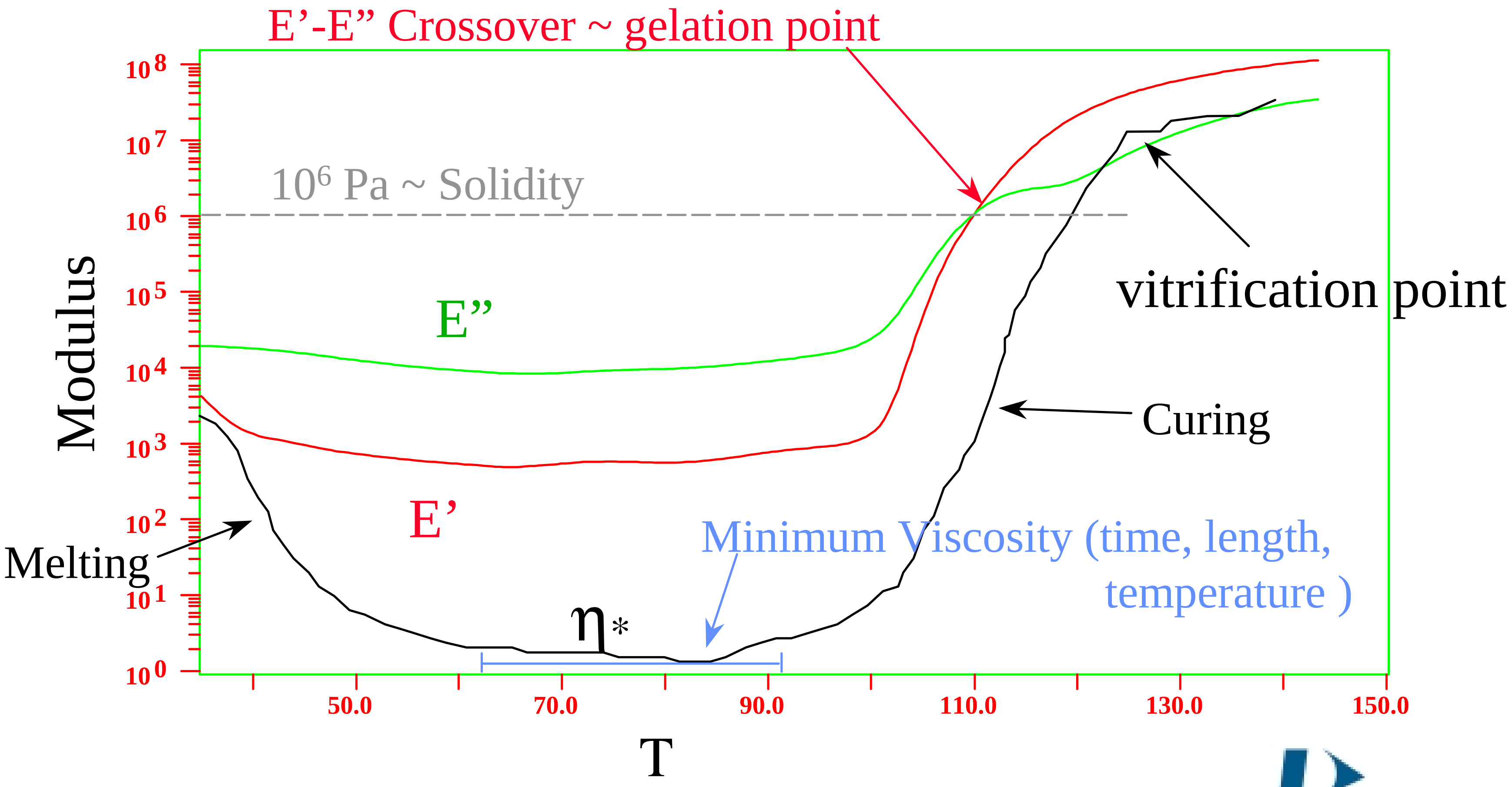
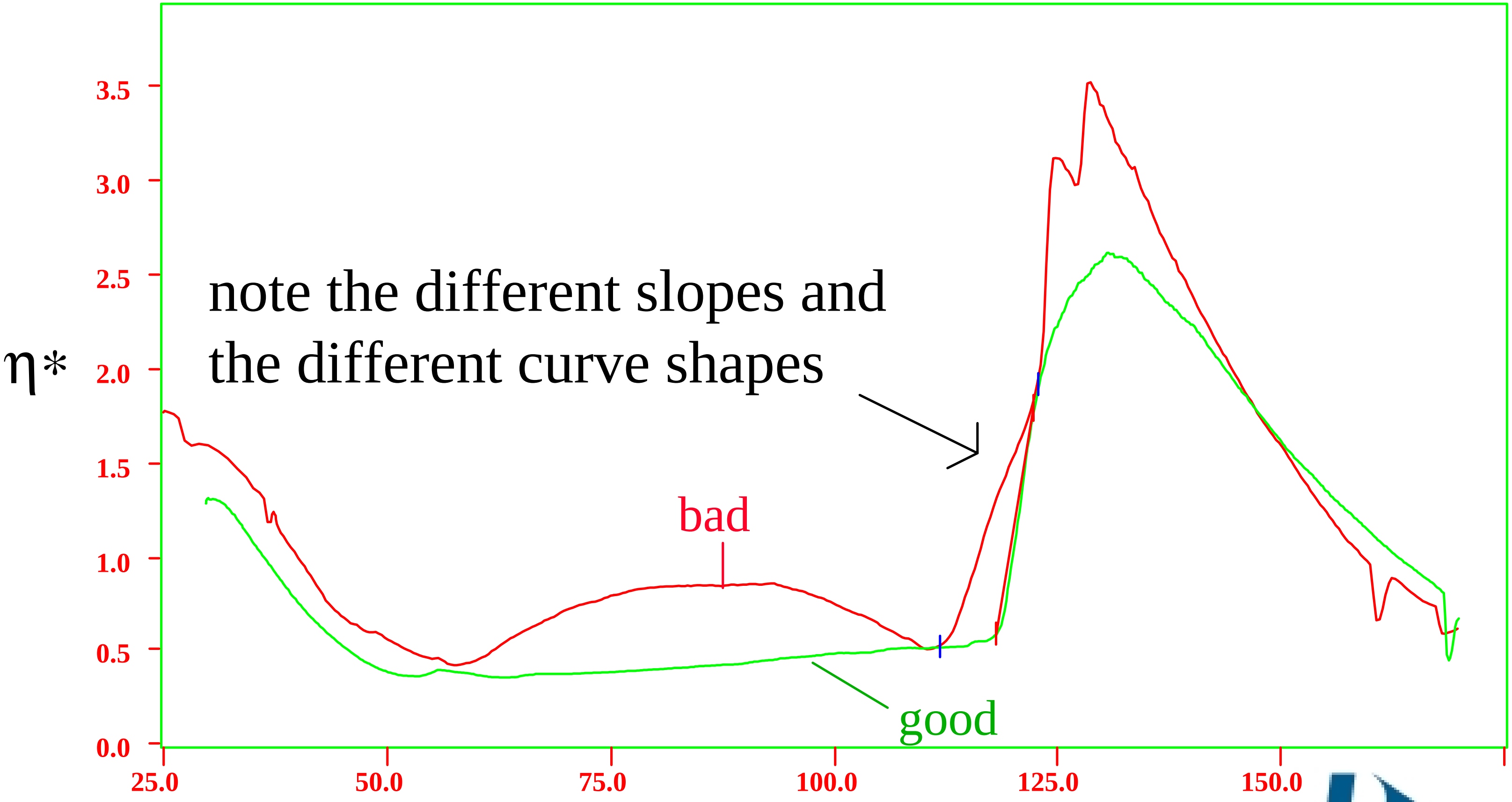
Curing of Thermosets

- **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**

Analysis of a Cure by DMA



QC can often be done by simply fingerprinting the resin.



note the different slopes and the different curve shapes

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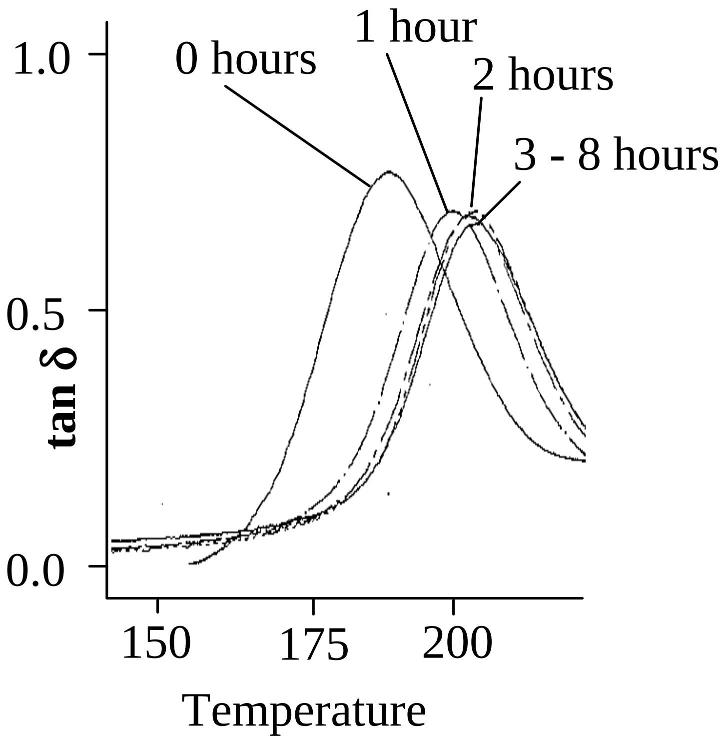
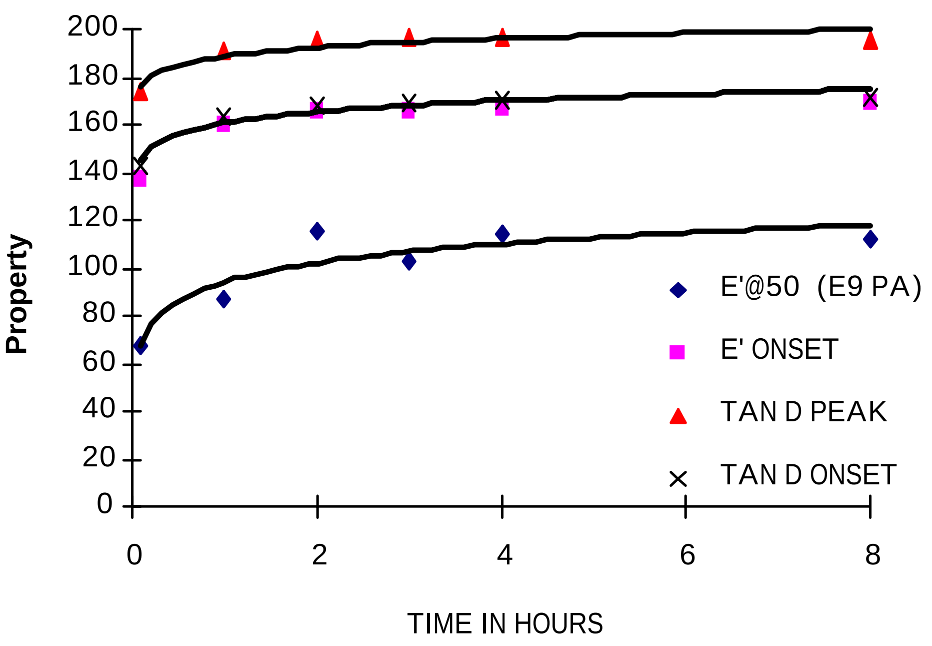
Postcure studies allow process optimization:



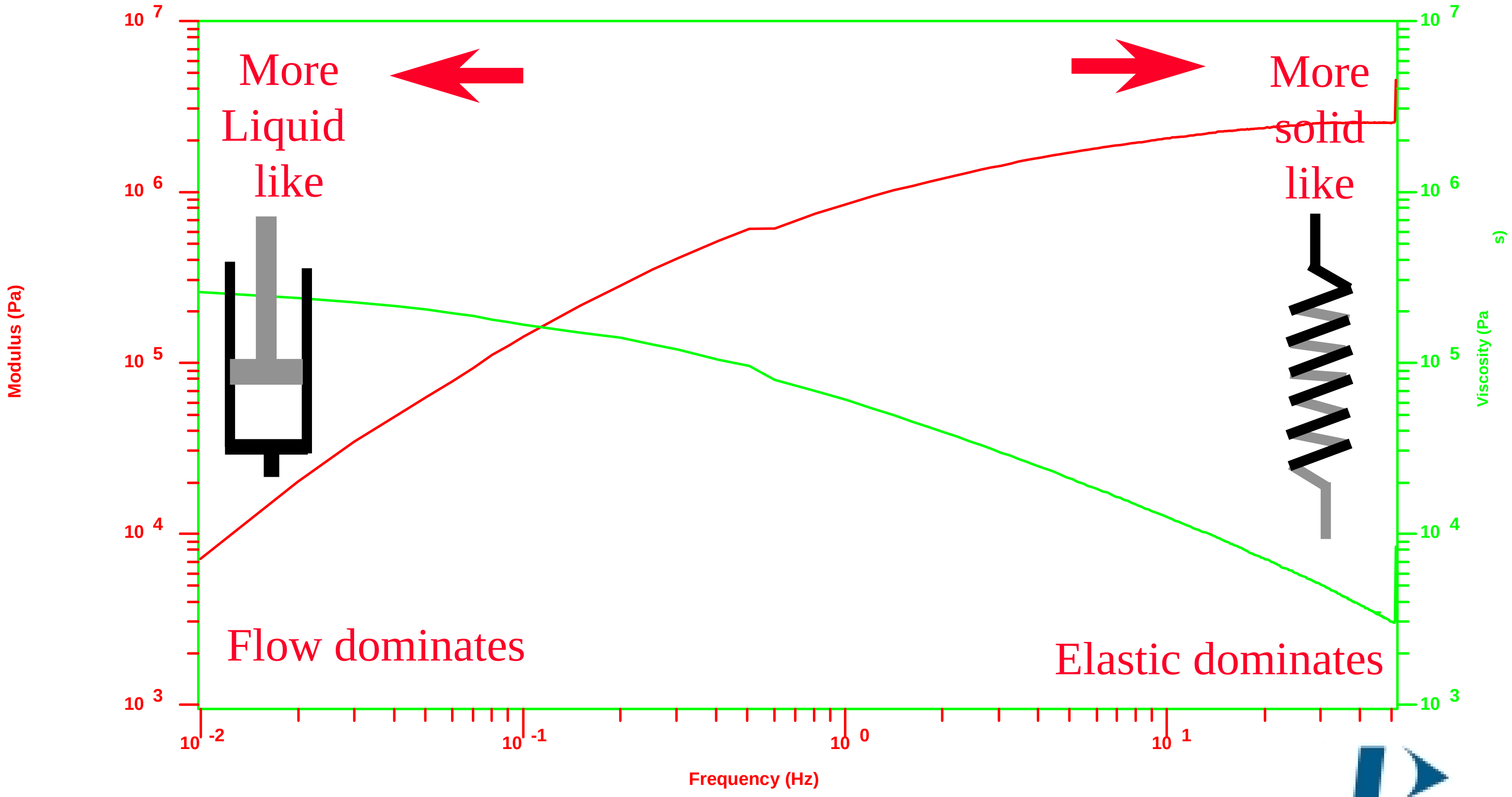
Postcure time vs... Tg and E’



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



More Liquid like

More solid like

Flow dominates

Elastic dominates

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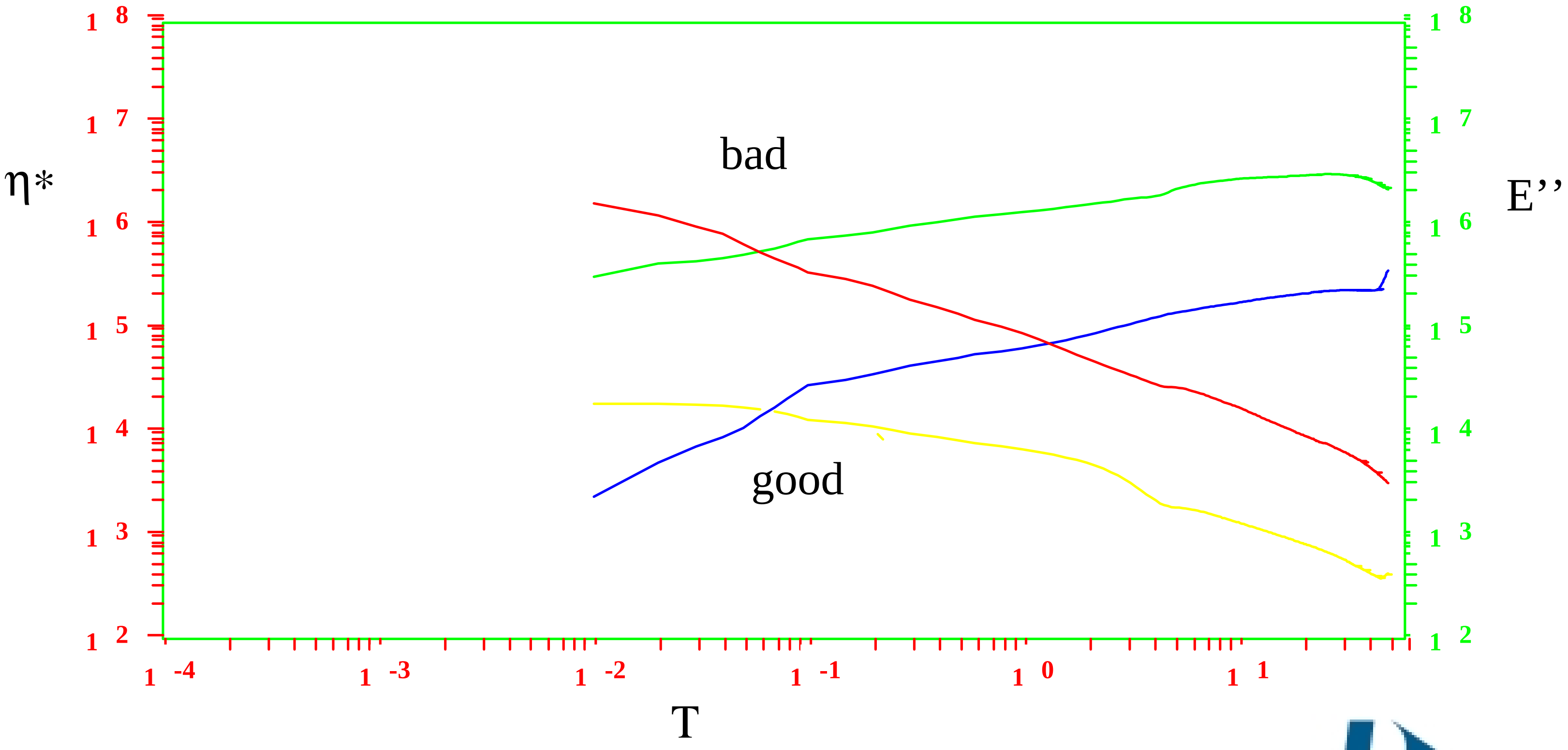
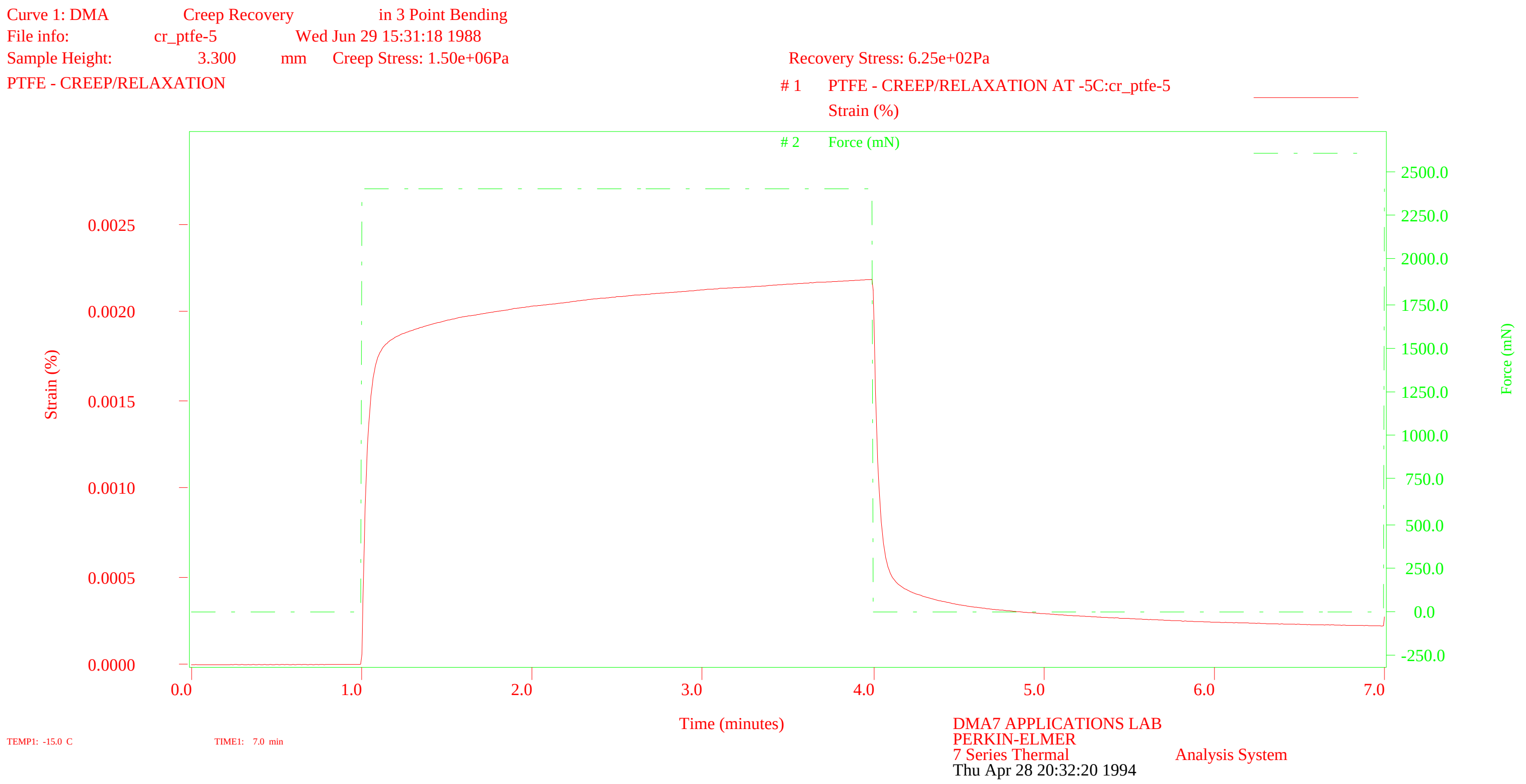
For example, two hot melt adhesives...

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 (%)
2 Force (mN)

TEMP1: -15.0 C
TIME1: 7.0 min

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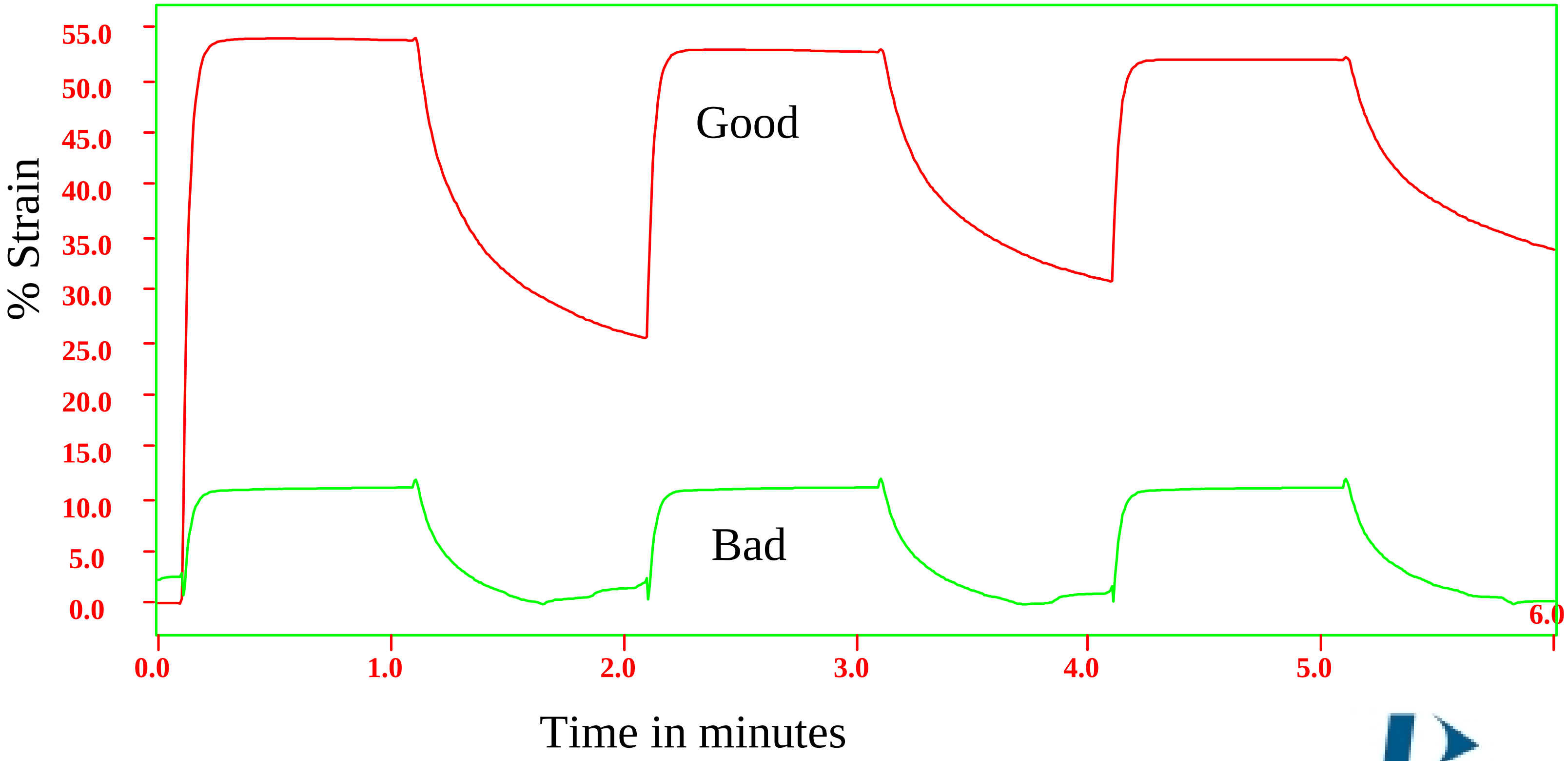
cyclic application of loads,

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.



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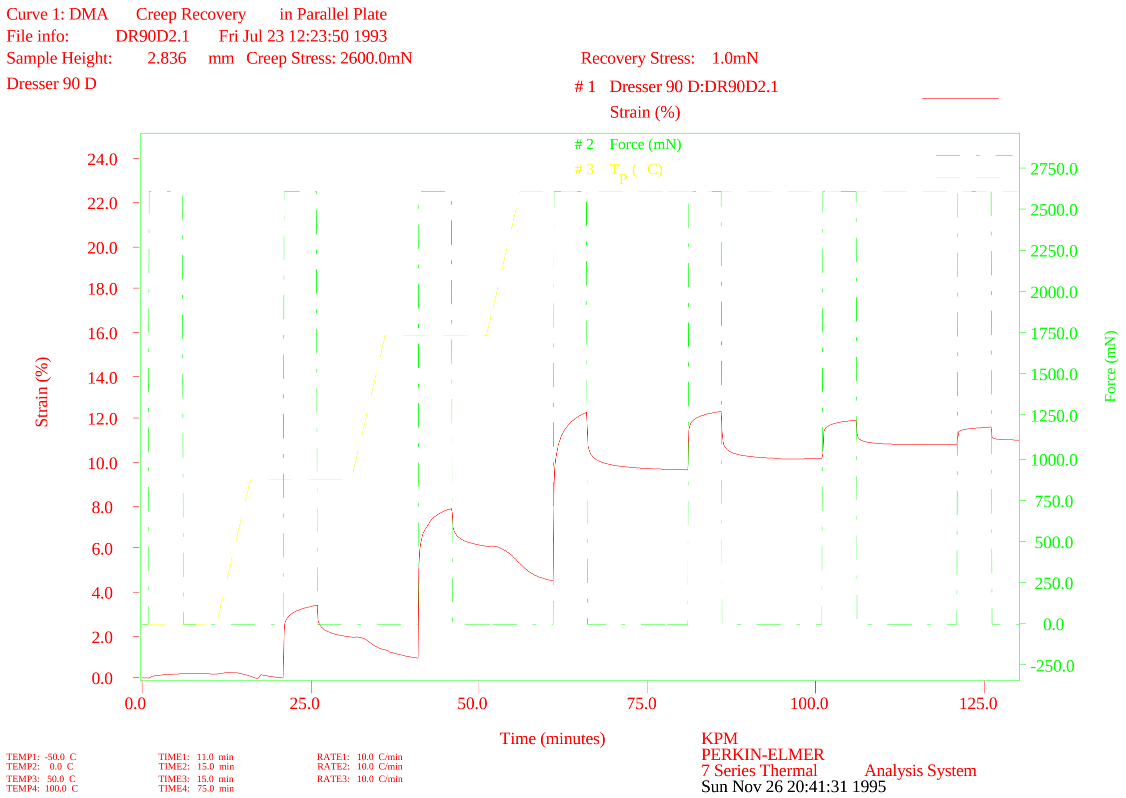
and with varying temperatures.



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
Recovery Stress: 1.0mN
Dresser 90 D

TEMP1: -50.0 C
TEMP2: 0.0 C
TEMP3: 50.0 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

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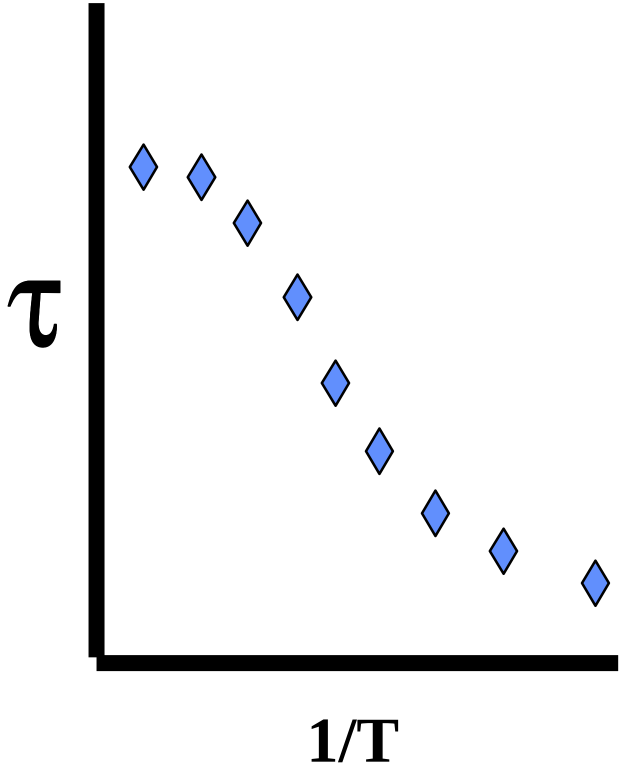
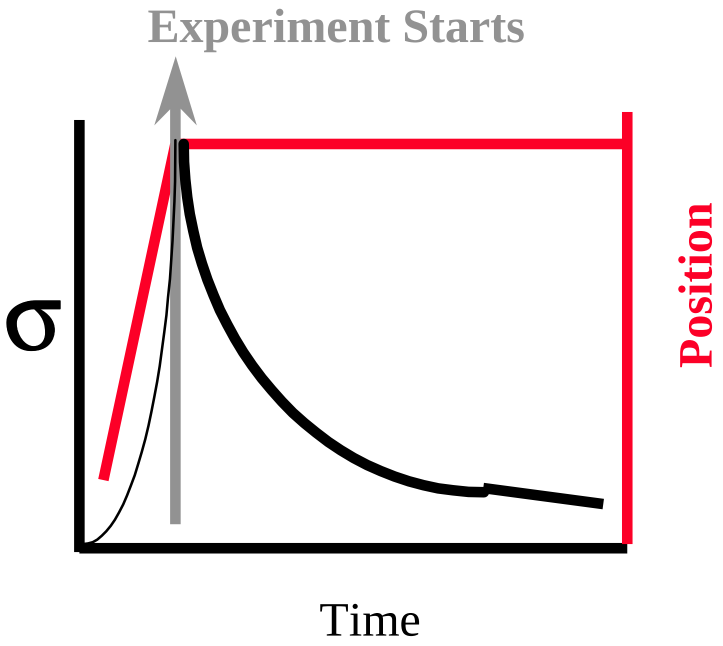
And you can tabulate this stuff graphically...



- 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.

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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

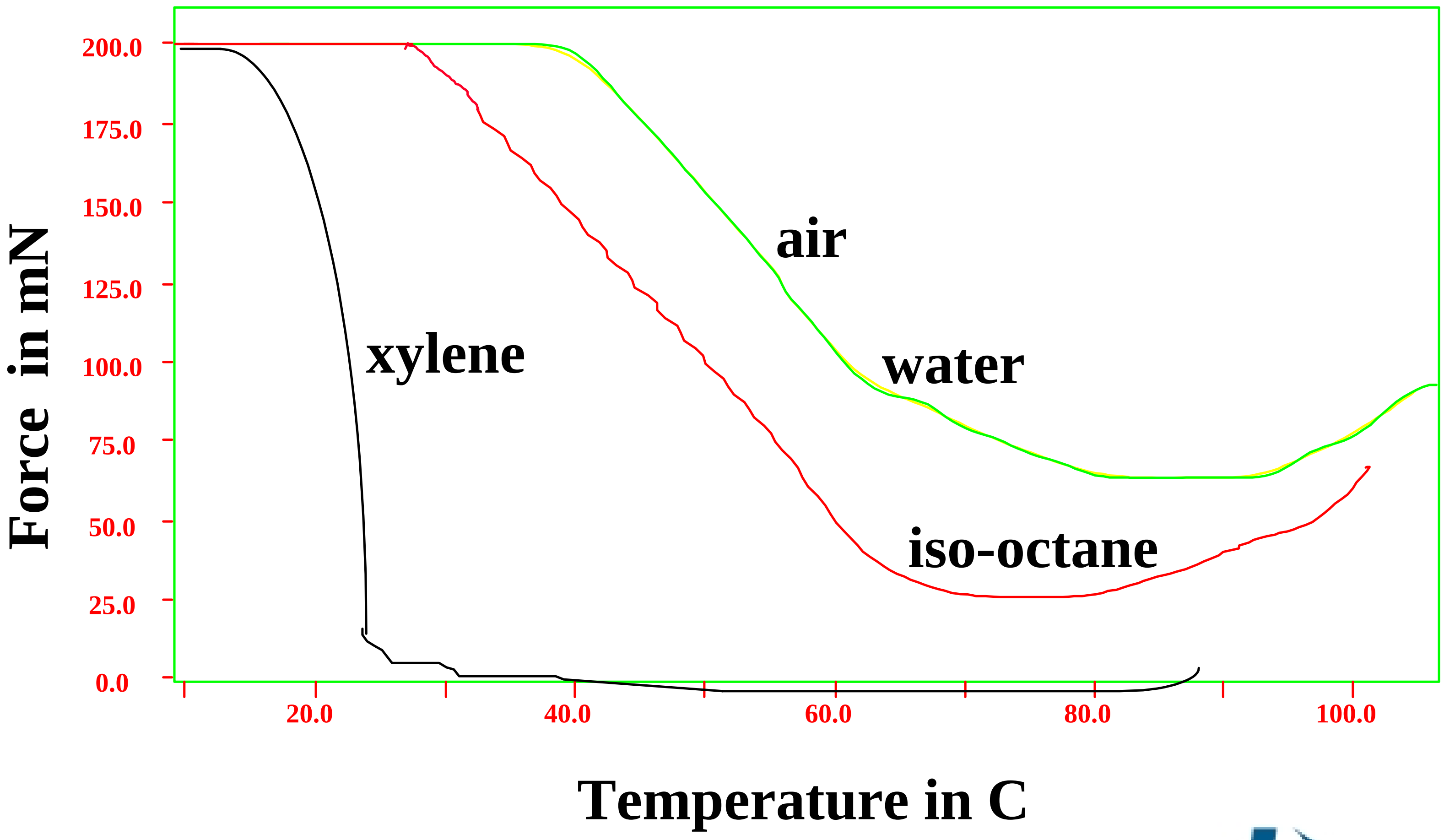
Tests in Solution

Microscopic DMA

Photo DMA

DMA-?

PP fibers in solvent



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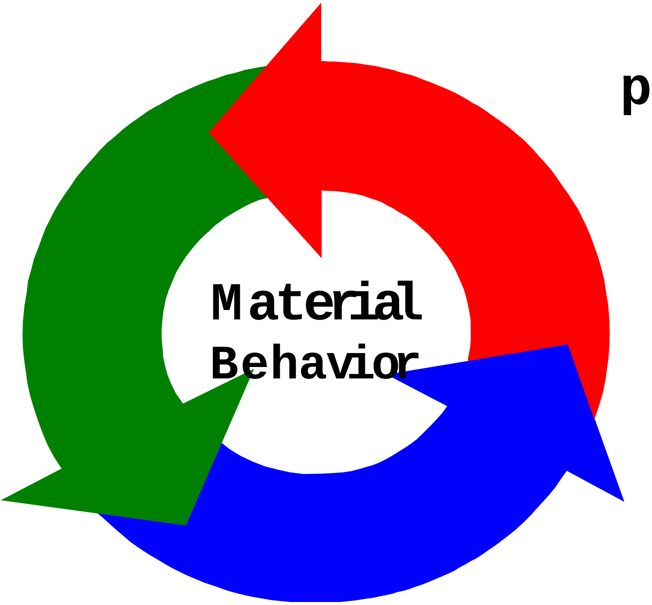
To Review, DMA ties together...

molecular structure

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



Material Behavior

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

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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.**

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