

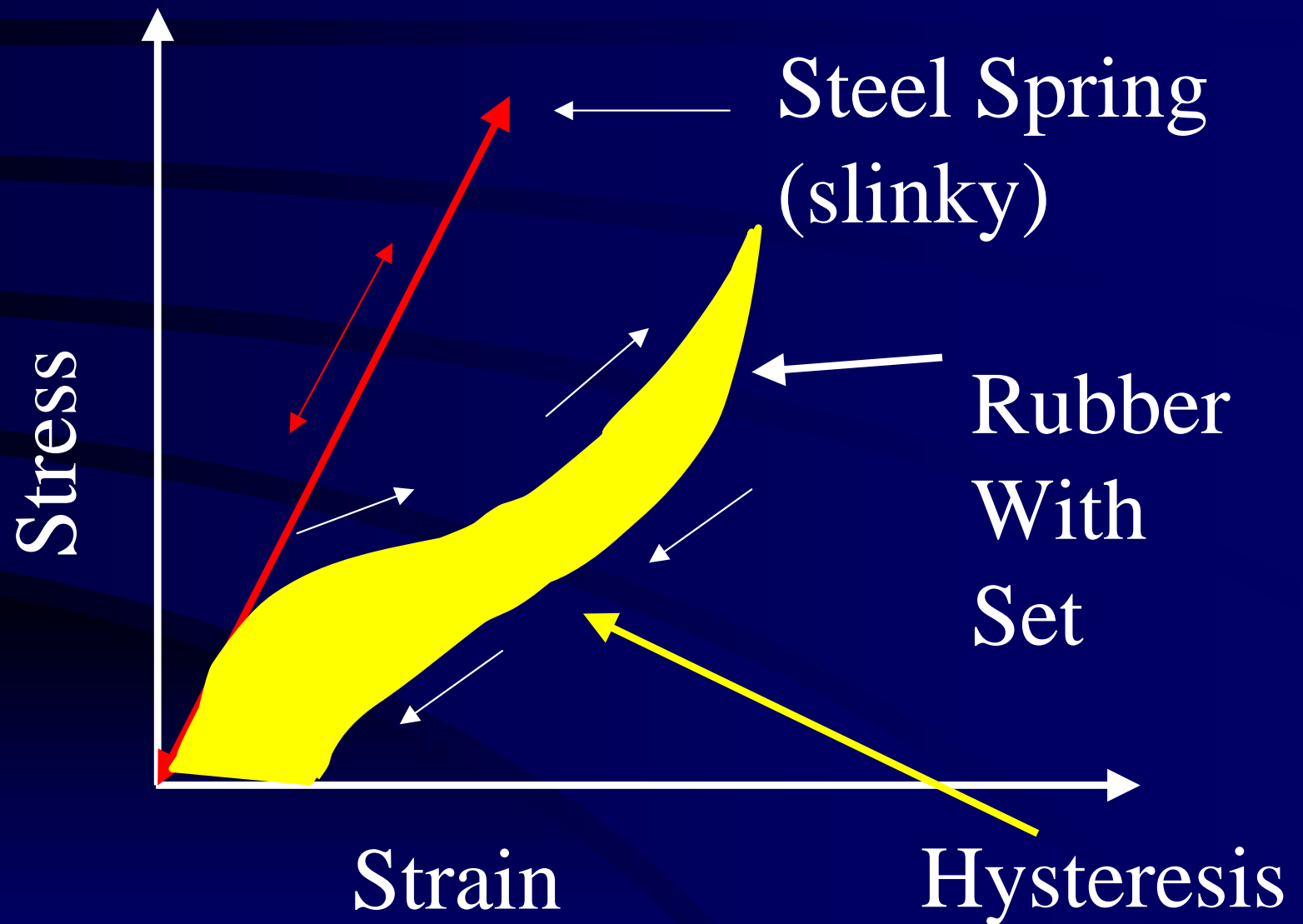
What defines an elastomer?

Properties:

Snappy and nearly
complete recovery after
deformation

Low modulus

Hysteresis



Traditional Definition of Elastomer

- An elastomer can be stretched 300% without breaking, and when released returns to within 10% of the original gauge length within 10 seconds
- Excludes many useful products (e.g., ACM, FKM)

What IS an Elastomer

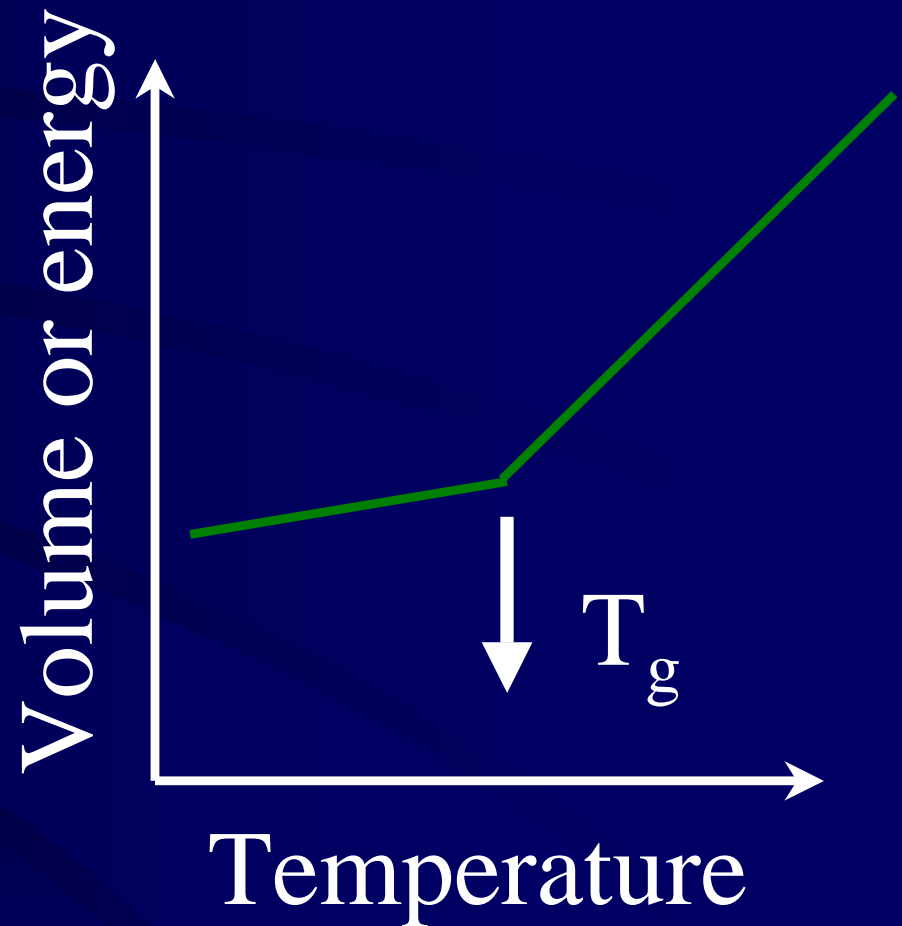
- Any low-crystallinity or amorphous, high molecular weight polymer with sufficiently flexible chains can in principle be made into an elastomer by crosslinking the chains. Such a polymer gel is an elastomer at 20+ kelvins above its glass temperature T_g .
- Crosslinks can be chemical (thermoset elastomers) or physical (TPEs)

Show Shrink Wrap Tubing Demo

- An elastomer is always defined as having a limited range of useful temperatures.
- Chains were quenched in an extended state. When T_g is reached micro-Brownian motion begins and the entropic forces pull the chains back to a less extended <more random> state and the tube shrinks in length and thickens.

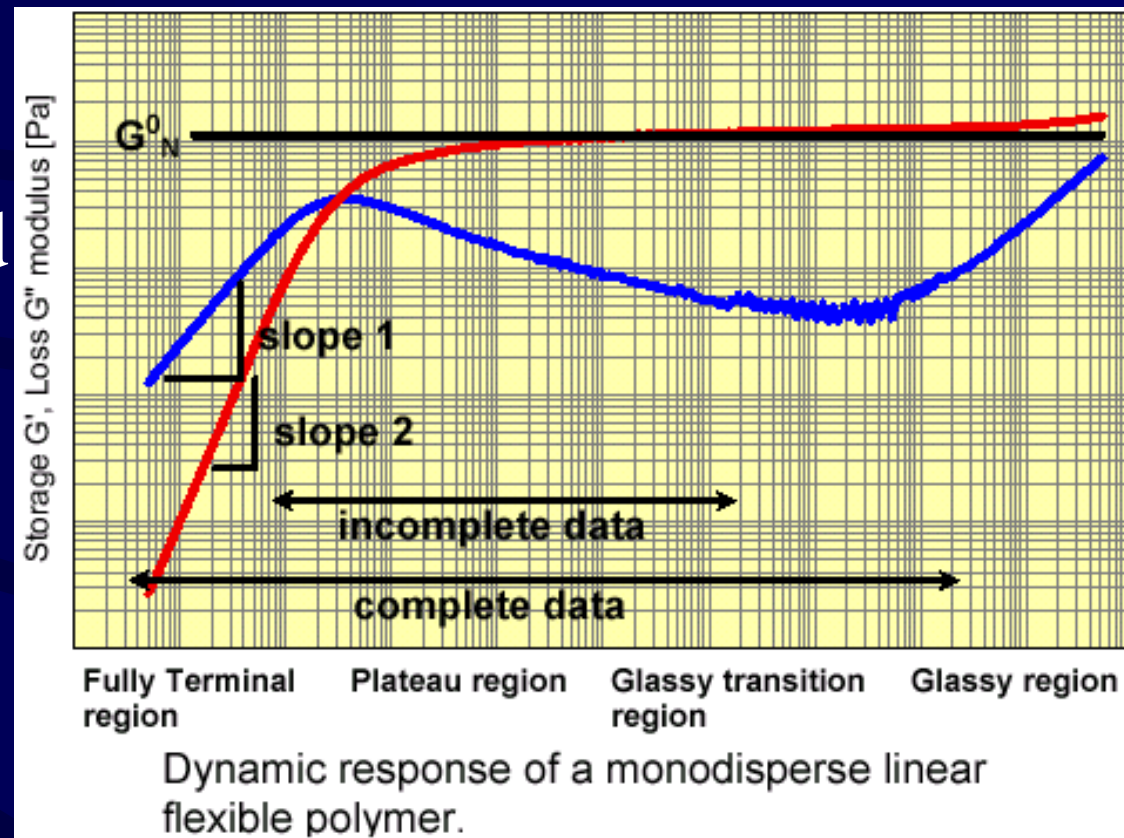
What is T_g ?

- The onset temperature for micro-brownian motion.
- A second order transition (no change in energy)



Stress Relaxation & Creep

- Many applications depend on sealing force being maintained for long periods
- Creep is rarely a problem per se
- Compression set is the standard method to gage compression relaxation

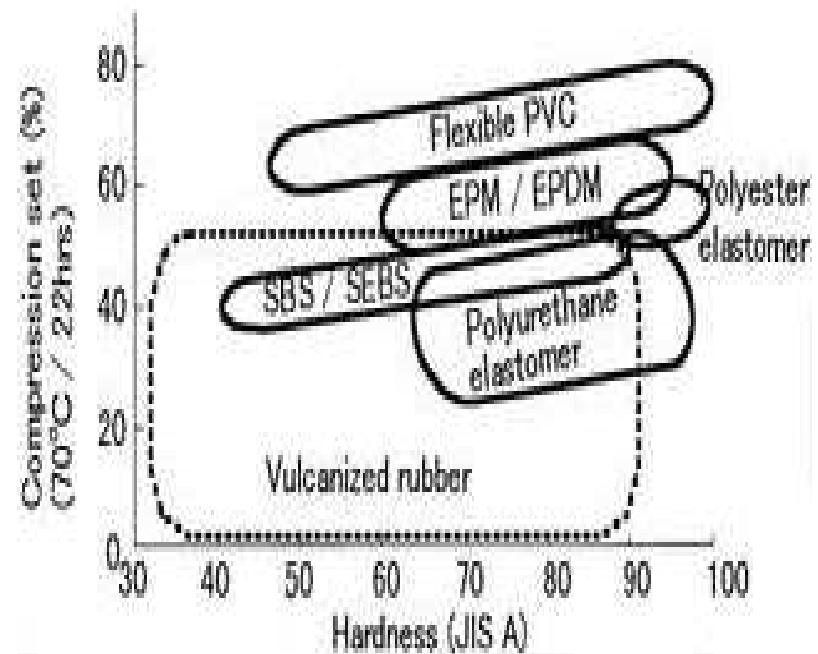


Rheometrics sales literature

Compression Set & Hardness Window

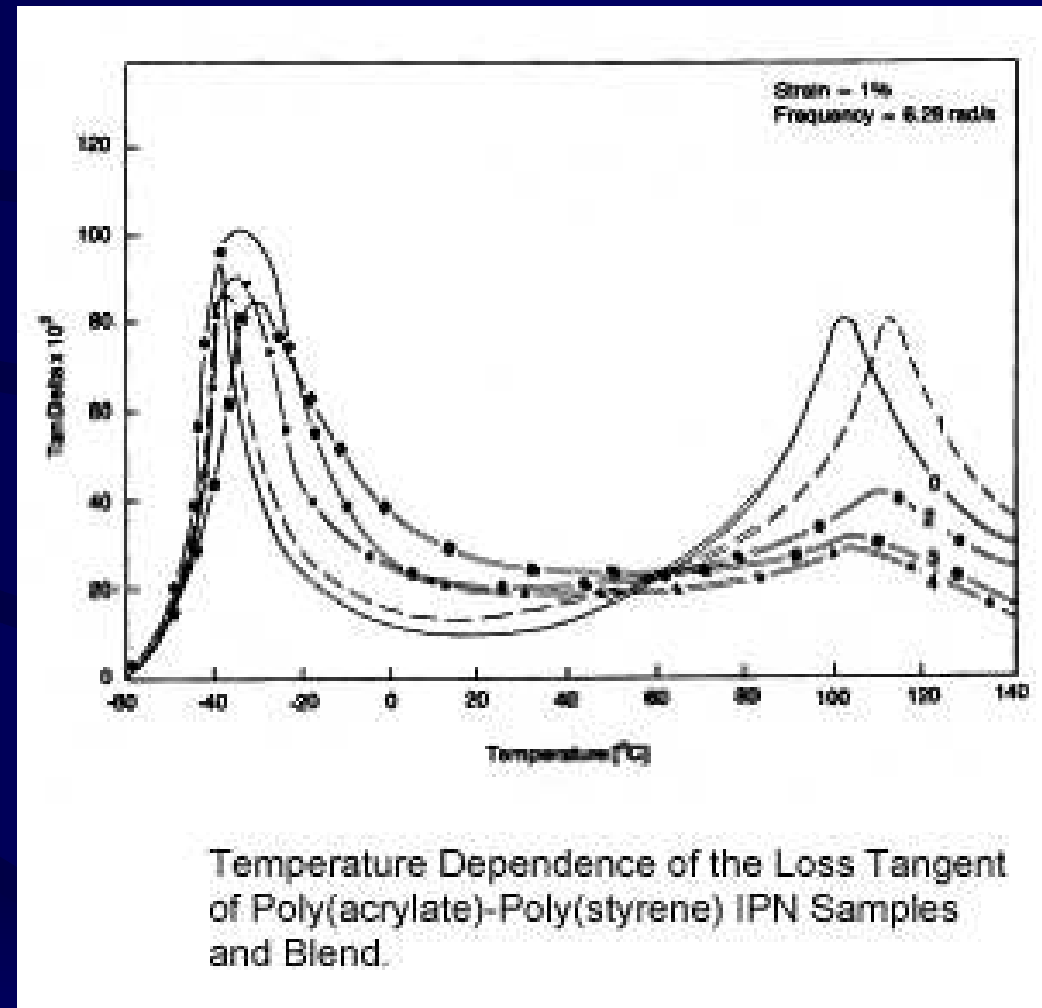
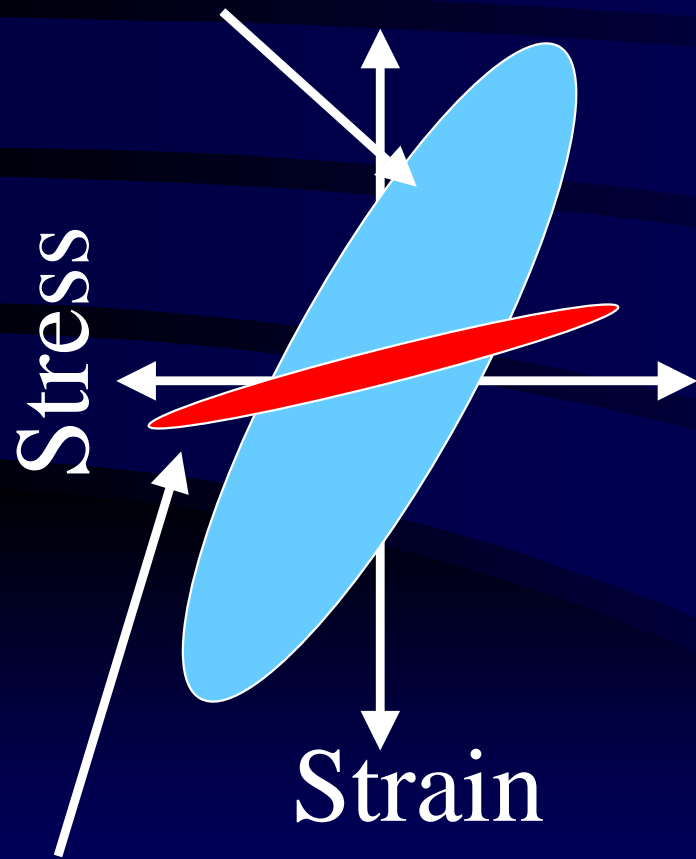
- Advantages of X-linked rubber include the largest working area for set and hardness.

Relation of hardness and compression set of elastomers.



Hysteresis and Temperature

Near Tg



Use Temp.

Importance of Elastomer Crystallinity

- Low crystallinity at zero strain essential
- Low Temperature Crystallization of NR, Neoprene can interfere with processing
- Reduction in Crystallinity after X-linking: nucleation prevented (neoprene shoes)
- Crystals can form physical crosslinks in multiblock polymer TPEs
- Strain induced crystallization leads to reinforcement at high strain

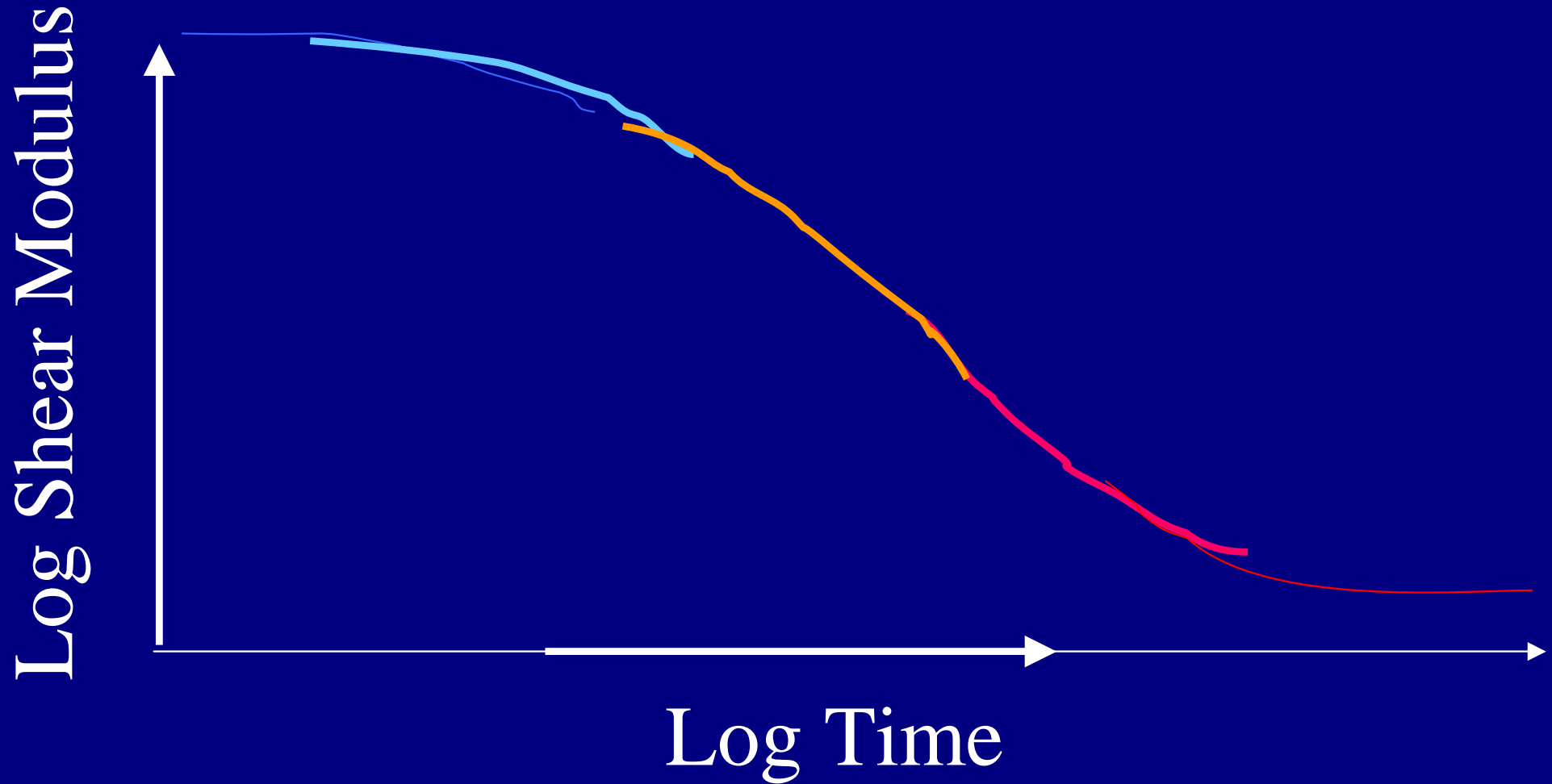
WLF Concept

- The molecular mobility at any temperature depends primarily on the remaining free volume.
- Rates for events (e.g. shear and bulk deformations etc.) can be expressed in terms of fractional free volume rather than Temperature as the independent variable.

Time-Temperature Superposition

- A series of frequency sweeps for a oscillatory deformation is repeated at various temperatures, in such a way (i.e. auto strain adjustments, degradation prevented via N2 blanket etc., overlapping modulus values in each trace) the plots may be used to form a master curve
- Elastomers upper end service temperature are limited by thermo-oxidative degradation
- State of the art method for long-term predictions of polymer behavior

WLF Experimental



WLF equation

The horizontal shifts a_T are tied directly to fractional free volume:

$$\log a_T = \frac{(B/2.303 f_0)(T - T_0)}{f_0/\alpha_f + T - T_0}$$

where

$$f = \frac{v_f}{v}$$

Size Distribution and Mobility of the Holes

- The size distribution of free volume packets has been probed with noble gases
- The dynamic & rapid movement of holes has a large effect on diffusivity, causing elastomers to be far more permeable than rigid plastics of similar chemistry.
- Permeability varies significantly between polymers in a way not explainable by simple models; may be due to hole size distribution

Time/temp superposition Elastomeric Region

- Relaxation rate fundamental
- Always several different relaxations (physical & chemical processes)
- Stiffness varies with measurement time (Shore A durometer example)
- Wide differences between polymers
- Viscosity \sim intermolecular friction \sim cohesive energy density (CED)

Cohesive Energy

- Definition :
 - Is the increase in internal energy per mole (U , joules/mol) if all the **inter-**molecular force are eliminated

Cohesive Energy Density (CED)

Energy per unit volume (U/V , Joules/cm³)

Cohesive Energy Density

- For low MW solvents, CED = heat of vaporization/unit volume
- Trickier to define for polymers, several models available; based on swelling in different solvents
- Solvent swelling maximal for solvents with similar CED to polymer
- Oil & fluid resistance of elastomers vary with chemistry; universal solvent resistance is therefore impossible

Cohesive Energy

- Additive Group Contribution Property
- It Need not match low molecular analogs
- Energetic adhesive forces (H-bonding & dipoles,) increase viscosity at equivalent molecular weight

Cohesive Energy

Material	CE (kJ/mol)
Poly Tetrafluoroethylene	8.0
Poly Epichlorohydrin	25.7
Poly Chloroprene (neoprene)	20.1-25.5
Poly Isoprene	19.9-31.8
Poly Isobutylene	17.1-18.4
Poly Butadiene	16.7-18.8

Effects of CED

- High CED ~ high viscosity
- High CED ~ high strength (fast testing)
- Low solubility in alkanes
- H-bonding makes for very high CED, not too common in elastomers, exception: polyurethanes (strongest elastomers)

Simplest Elastomer

- Sulfur...at elevated temperatures $>300^{\circ}\text{C}$, sulfur polymerizes to S_x , can be quenched to yield polysulfur elastomer
- Great wide-spectrum solvent resistance
- Reverts to normal S_8 form after a few days
- First synthetic elastomer (polysulfide) discovered via trying to stabilize S_x

Random walk model of chains.

- Similar to diffusion
- Volume exclusion & bond angle restrictions ignored
- Successful at low strain only Present simplest equation relating retractive force to deformation.
- Root mean square end-to-end distance proportional to bond length and to $\frac{1}{2}$ power of # of links

$$\left\langle R^2 \right\rangle^{\frac{1}{2}} = l n^{\frac{1}{2}}$$

Statistical Links

- Random walk beaded necklace model
- A statistical link or element is not a single C-C bond but a short section of chain.
- The length is chosen so that both it's end may be regarded as completely free joints in the chain removing some numerical difficulties in the analysis.

Statistical Links

- Length of freely rotating section varies with chain flexibility...about 7 carbon bonds for NR, less for silicone, more for most other elastomers
- High flexibility correlates mainly with rotatability of bonds in the main chain.
- Oxygen links in the main chain, as in VMQ, FVMQ, CO, ECO, and perfluoropolyethers (e.g. Sifel) lead to low hysteresis elastomers with relatively short freely rotating segments.

Entropic nature of the retractive force

- Metal spring lengthens with increasing temperature and a rubber band contracts.
- Deformation orients the chains, reducing entropy
- Increasing temperature \sim increasing retractive force (Gough 1805)
- Metal springs: deformation of crystals

Stress-Strain Curve for Freely Jointed Chain

Chain ends Probability Density Function

$$W(r)dr = Ke^{-\int_0^r L^*(r/r_m)dr/l} 4\pi r^2 dr$$

Entropy change is calculated from $W(r)$
and elastic retractive force from change in entropy
Good up to maximum extension!

$$L(u) = \coth(u) - 1/u$$

Rubber Elasticity in Tension

Using Gaussian assumptions

$$\sigma = RT \left(1 / \bar{v} M_c \right) \left(1 - 2 M_c / M \right) \left(\alpha^2 - 1 / \alpha \right)$$

Where:

$$\alpha = L / L_0$$

Matches Mooney Rivlin empirical form

$$\sigma = \left(2C_1 + 2 \frac{C_2}{\alpha} \right) \left(\alpha^2 - 1 / \alpha \right)$$

Strain-induced crystallinity

Effects

- creates very high strengths when elastomers deformed within appropriate temperature range
- crack tip reinforcement
- Sudden, dramatic strength reduction above melting temperature

Preventing Crystallization I

- Essential so that flexible-chain polymers can be elastomers
- elastomers can be from a single monomer that forms weakly crystallizable repeat structures (NR & cis-IR, cis-BR, CR)
- cis-neoprene (not available commercially, but I assume DuPont has done work on it).

Preventing Crystallization II

An irregular repeat structure

- Either from a single monomer that polymerizes several different ways (show polybutadiene structural options),
- Else from a mixture of monomers (show EPR, SBR, NBR, FKM), that can polymerize in several ways
 - NR & cis-IR vs trans-IR vs random IR
 - Non-tactic repeat structure (atactic & isotactic PP)
 - Other elastomers (e.g. PPO, CO) where a randomized chiral center prevents crystallization. where a random tacticity can prevent crystallization

General Purpose Rubbers

Natural	NR		
Polyisoprene	IR		
Styrene- butadiene	SBR		
Butyl	IIR		
Ethylene- Propylene	EPDM		
Polybutadiene	BR		

Solvent Resistant Rubbers

Polysulfides	T		
Nitrile	NBR		
Neoprene (polychloroprene)	CR		
Polyurethanes -polyesters -polyethers	AU EU		
Epichlorohydrin			
Epichlorohydrin ethylene Oxide	ECO		

Heat Resistant Rubbers

Silicone	MQ		
Chlorosulfonate d-Polyethylene	CSM		
Polyacrylates	ACM		
Fluororubbers	CFM		

Application to Rollers

- What are frequencies and temperatures of interest?
- Has the process had a spectrum analysis?
 - In time and linear output domains?
- Are characteristics of materials known in these ranges
- Pre-oriented surface encapsulated rubber to reduce hysteresis and improve hardness?