Cross-linked Polymers and Rubber Elasticity

Chapter 9 (Sperling)

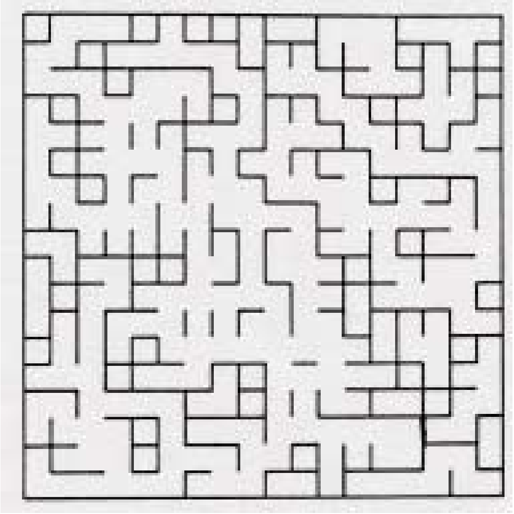
- Definition of Rubber Elasticity and Requirements
- Cross-links, Networks, Classes of Elastomers (sections 1-3, 16)
- Simple Theory of Rubber Elasticity (sections 4-8)
  - Entropic Origin of Elastic Retractive Forces
  - The Ideal Rubber Behavior
- Departures from the Ideal Rubber Behavior (sections 9-11)
  - Non-zero Energy Contribution to the Elastic Retractive Forces
  - Stress-induced Crystallization and Limited Extensibility of Chains (How to make better elastomers: High Strength and High Modulus)
  - Network Defects (dangling chains, loops, trapped entanglements, etc..)
  - Semi-empirical Mooney-Rivlin Treatment (Affine vs Non-Affine Deformation)

Definition of Rubber Elasticity and Requirements

- Definition of Rubber Elasticity:
  Very large deformability with complete recoverability.

- Molecular Requirements:
  - **Material must consist of polymer chains.**
    Need to change conformation and extension under stress.
  - **Polymer chains must be highly flexible.**
    Need to access conformational changes (not w/ glassy, crystalline, stiff mat.)
  - **Polymer chains must be joined in a network structure.**
    Need to avoid irreversible chain slippage (permanent strain).
    One out of 100 monomers must connect two different chains.
    Connections (covalent bond, crystallite, glassy domain in block copolymer)

Cross-links, Networks and Classes of Elastomers



- Chemical Cross-linking Process:
  Sol-Gel or Percolation Transition

- Gel Characteristics:
  - Infinite Viscosity
  - Non-zero Modulus
  - One giant Molecule
  - Solid Polymer Network

- Step Polymerization (isocyanates, oxirane)
- Chain Polymerization (styrene with divinylbenzene)
- Post-polymerization Reactions (vulcanization with sulfur)

- Cross-linked and Gels in the Food/Health Care Industry:
  Globular protein example: the egg white ! (S_2 bridges)
  Jello®, contact lenses, liquid soaps, shampoos (proteins, polysaccharides)

Cross-links, Networks and Classes of Elastomers

- Differentiate Thermosets and Elastomers:
  Concerned only with Elastomers (Why ? $\boxed{T > T_g}$)
- Historical Development:
  - Christopher Columbus, 1492
  - Gough, 1805
    - Stretching an elastomer leads to its …. **warming up**

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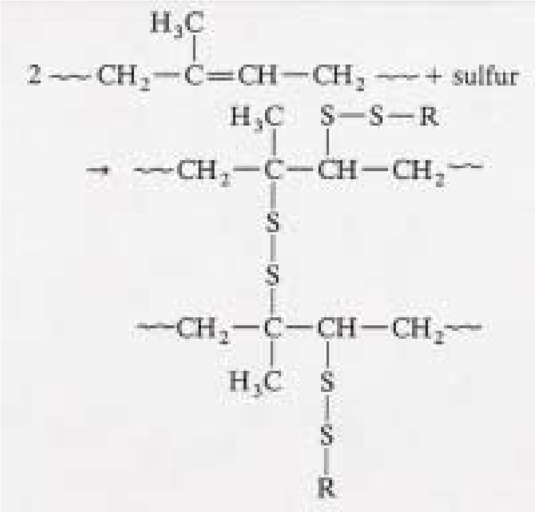
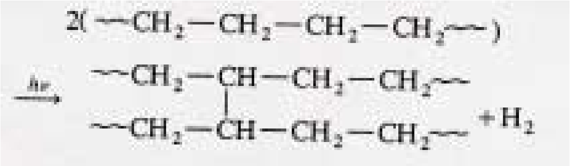
- Why cross-linking ?
  - Dimensional stability, creep reduction is required in manufactured goods!!!!

Cross-links, Networks and Classes of Elastomers

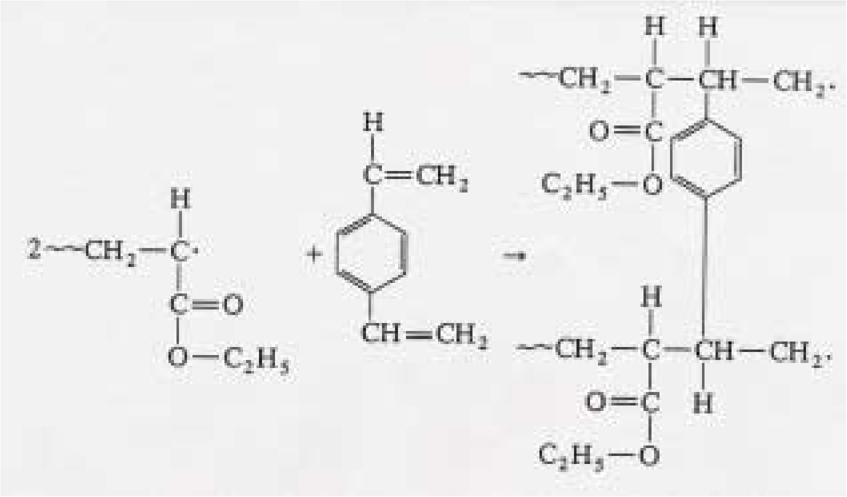
- Sulfur Vulcanization:



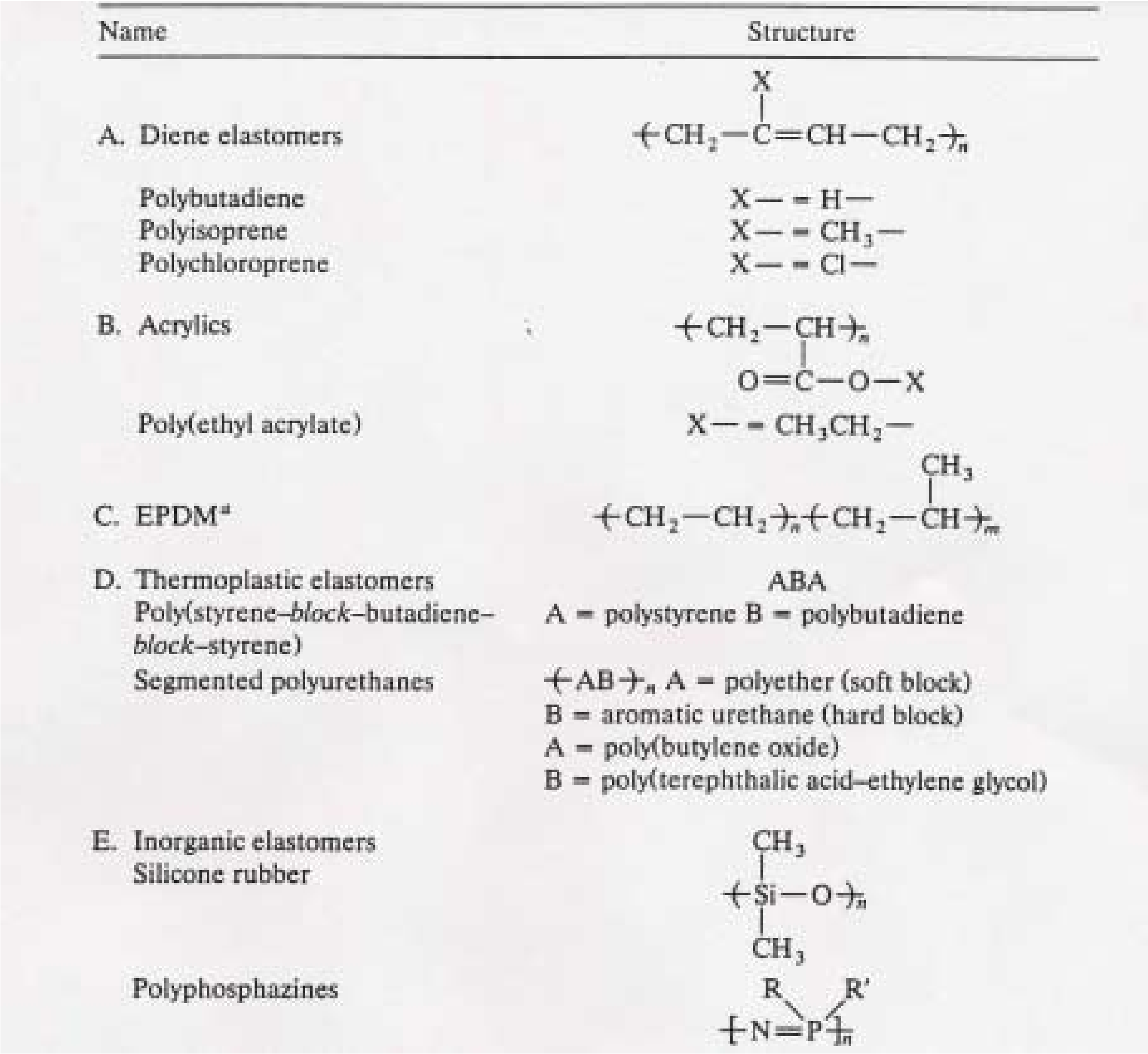
- Electron or γ Irradiation



- Chain Polymerization with a Tetrafunctional Comonomer



Cross-links, Networks and Classes of Elastomers



Name	Structure
A. Diene elastomers	$\left(CH_2-\overset{X}{\overset{\mid}{C}}=CH-CH_2\right)_n$
Polybutadiene	X— = H—
Polyisoprene	X— = CH_3—
Polychloroprene	X— = Cl—
B. Acrylics	$\left(CH_2-\underset{O=\overset{\mid}{C}-O-X}{CH}\right)_n$
Poly(ethyl acrylate)	X— = CH_3CH_2—
C. EPDM[a]	$\left(CH_2-CH_2\right)_n\left(CH_2-\overset{CH_3}{\overset{\mid}{CH}}\right)_m$
D. Thermoplastic elastomers	ABA
Poly(styrene–*block*–butadiene–*block*–styrene)	A = polystyrene B = polybutadiene
Segmented polyurethanes	$(AB)_n$ A = polyether (soft block) B = aromatic urethane (hard block) A = poly(butylene oxide) B = poly(terephthalic acid–ethylene glycol)
E. Inorganic elastomers Silicone rubber	$\left(\underset{\underset{CH_3}{\mid}}{\overset{\overset{CH_3}{\mid}}{Si}}-O\right)_n$
Polyphosphazines	$\left(N=\overset{R\ \ R'}{P}\right)_n$

Commercial Products

NBR, SBR

Butyl Rubber & EPDM
ca. add 2% of diene.

Block and Segmented Copolymers
Kraton®, Lycra®, Spandex®, Hytrel®

Caulking, gaskets,
O-rings, high T elastomers

Cross-links, Networks and Classes of Elastomers

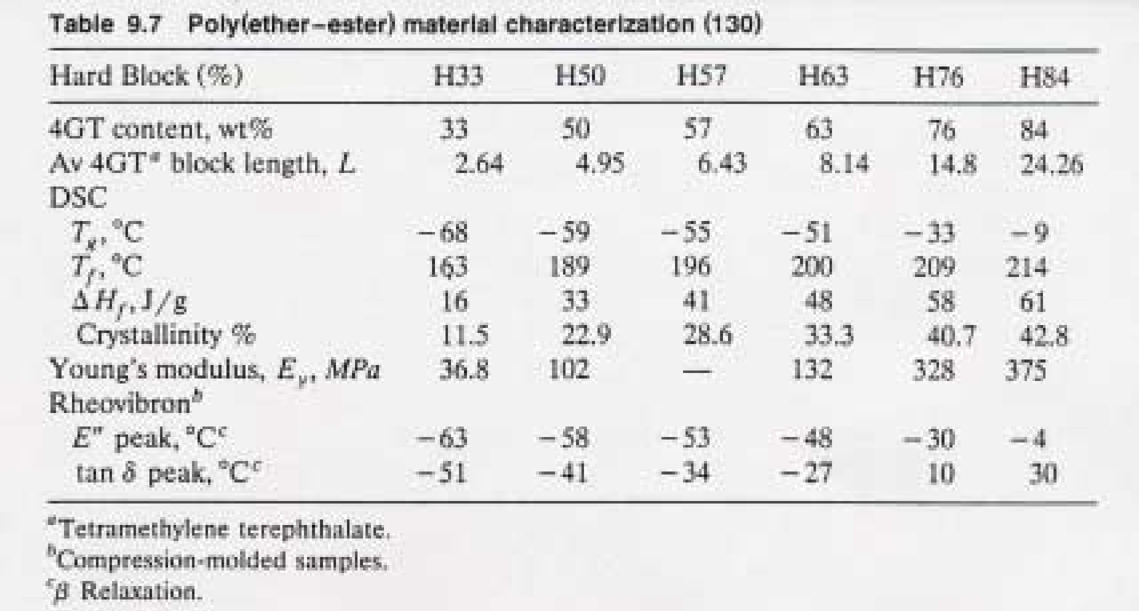


Table 9.7 Poly(ether–ester) material characterization (130)

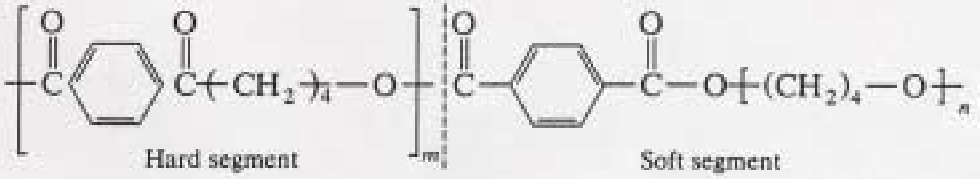
Hard Block (%)	H33	H50	H57	H63	H76	H84
4GT content, wt%	33	50	57	63	76	84
Av 4GT[a] block length, *L*	2.64	4.95	6.43	8.14	14.8	24.26
DSC						
T_g, °C	−68	−59	−55	−51	−33	−9
T_f, °C	163	189	196	200	209	214
ΔH_f, J/g	16	33	41	48	58	61
Crystallinity %	11.5	22.9	28.6	33.3	40.7	42.8
Young's modulus, E_y, *MPa*	36.8	102	—	132	328	375
Rheovibron[b]						
E'' peak, °C[c]	−63	−58	−53	−48	−30	−4
tan δ peak, °C[c]	−51	−41	−34	−27	10	30

[a] Tetramethylene terephthalate.

[b] Compression-molded samples.

[c] β Relaxation.

(129–131):



Segmented Copolymers:

Example: Hytrel® (DuPont)

Hard segment: m = 1, 2

Soft segment: n = 40-60

Cross-links, Networks and Classes of Elastomers

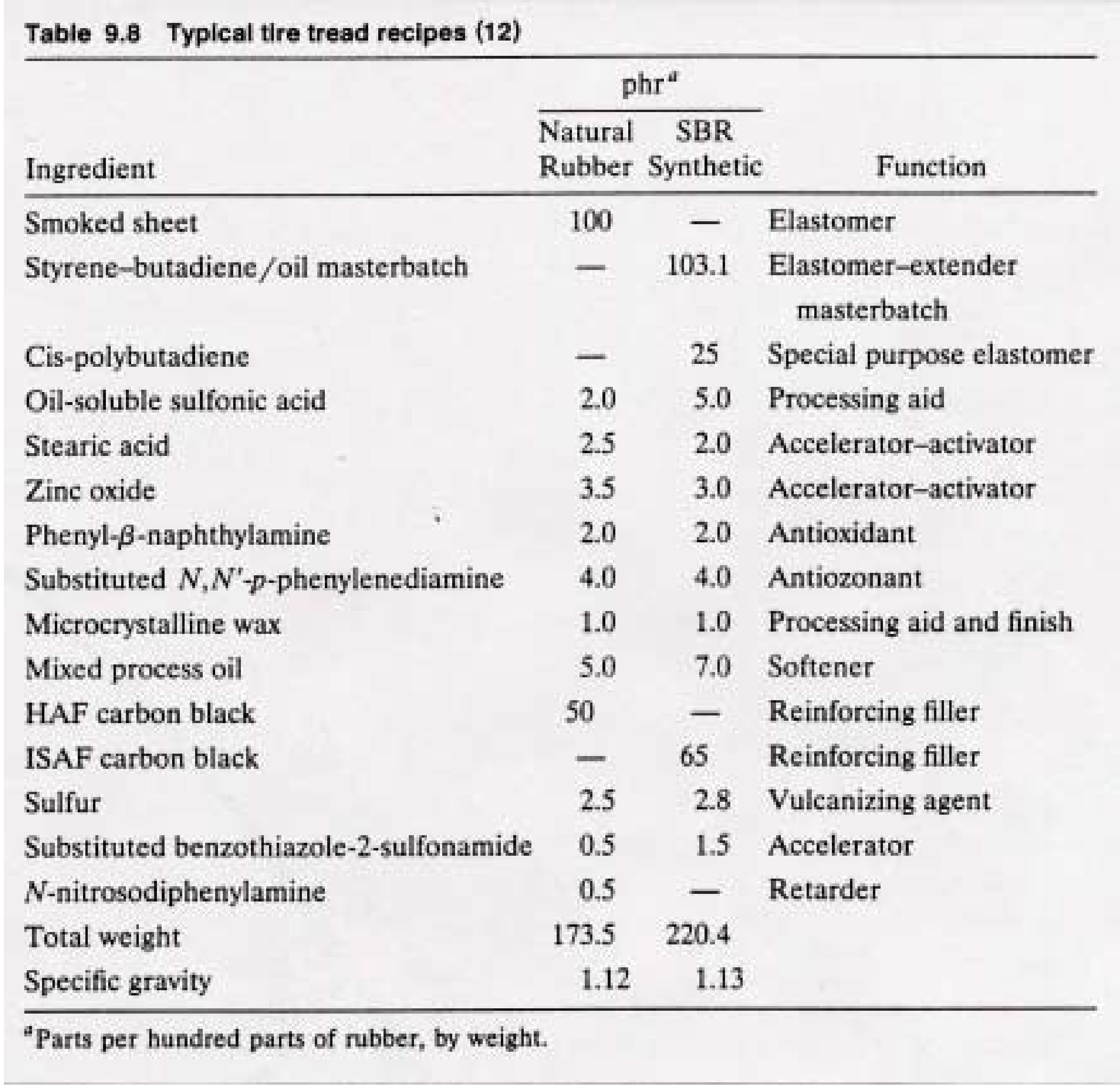


Table 9.8 Typical tire tread recipes (12)

Ingredient	phr[a] Natural Rubber	phr[a] SBR Synthetic	Function
Smoked sheet	100	—	Elastomer
Styrene–butadiene/oil masterbatch	—	103.1	Elastomer–extender masterbatch
Cis-polybutadiene	—	25	Special purpose elastomer
Oil-soluble sulfonic acid	2.0	5.0	Processing aid
Stearic acid	2.5	2.0	Accelerator–activator
Zinc oxide	3.5	3.0	Accelerator–activator
Phenyl-β-naphthylamine	2.0	2.0	Antioxidant
Substituted *N*,*N*′-*p*-phenylenediamine	4.0	4.0	Antiozonant
Microcrystalline wax	1.0	1.0	Processing aid and finish
Mixed process oil	5.0	7.0	Softener
HAF carbon black	50	—	Reinforcing filler
ISAF carbon black	—	65	Reinforcing filler
Sulfur	2.5	2.8	Vulcanizing agent
Substituted benzothiazole-2-sulfonamide	0.5	1.5	Accelerator
N-nitrosodiphenylamine	0.5	—	Retarder
Total weight	173.5	220.4	
Specific gravity	1.12	1.13	

[a] Parts per hundred parts of rubber, by weight.

Theory of Rubber Elasticity

- Thermodynamics, Statistical Mechanics and Chain Statistics (Kelvin, Kuhn, Guth, Mark, James, Treloar and Flory)

- Second Law of Thermodynamics:
  - **What happens if you release the stress applied to a cross-linked coil?**
  - A1: Deformation is a Constant Volume Process ($\nu \approx ½$)
  - A2: Helmholtz Free Energy ($F = A = U – TS$) should be minimized
  - A3: Assume the Internal Energy (U) is independent of deformation
  - Final Answer: **the Entropy must be maximized….**

- IN PLAIN LANGUAGE:
  - Releasing the stress applied to a cross-linked rubber, leads to the coiling back of extended chains, since a retraction allows the chains to adopt higher entropy conformations.
  - RETRACTIVE FORCES ARE ENTROPIC IN NATURE IN RUBBERY MATERIALS… What about metals ?

Theory of Rubber Elasticity

- Approach and Results:
  - Consider the Gaussian statistics for the distribution of end to end distances.
  - Calculate S, the entropy per chain in terms of <r_0^2>.
  - Calculate ΔF, the free energy change due to deformation (-TΔS).
  - Assume local and macroscopic deformations are the same (affine deformation).
  - Assume the volume does not change during deformation.
  - Rubbery materials are non-Hookean

$$F = U - TS = U - kT\ln\Omega(r,T)$$

$$f = \left(\frac{\partial F}{\partial r}\right)_{T,V} = -kT\left(\frac{\partial \ln\Omega(r,T)}{\partial r}\right)_{V,T} = \frac{3kTr}{\bar{r}_0^2}$$

$$\Delta F = -W = \frac{3nRT}{\bar{r}_0^2}\int_{\bar{r}_i^2}^{\bar{r}^2} r\,dr = \frac{nRT}{2}\frac{\bar{r}_i^2}{\bar{r}_0^2}\left(\alpha^2 + \frac{2}{\alpha} - 3\right)$$

$$\sigma = \left(\frac{\partial \Delta F}{\partial \alpha}\right) = nRT\frac{\bar{r}_i^2}{\bar{r}_0^2}\left(\alpha - \frac{1}{\alpha^2}\right)$$

$$E = 3nRT\frac{\bar{r}_i^2}{\bar{r}_0^2}$$

$$G = \frac{E}{2(1+\nu)} = nRT\frac{\bar{r}_i^2}{\bar{r}_0^2}$$

$$\sigma = G\left(\alpha - \frac{1}{\alpha^2}\right)$$

n = # active chains per unit volume
α: elongation ratio

Ideal Rubber Behavior

Theory of Rubber Elasticity

Comparison of Experiment and Theory

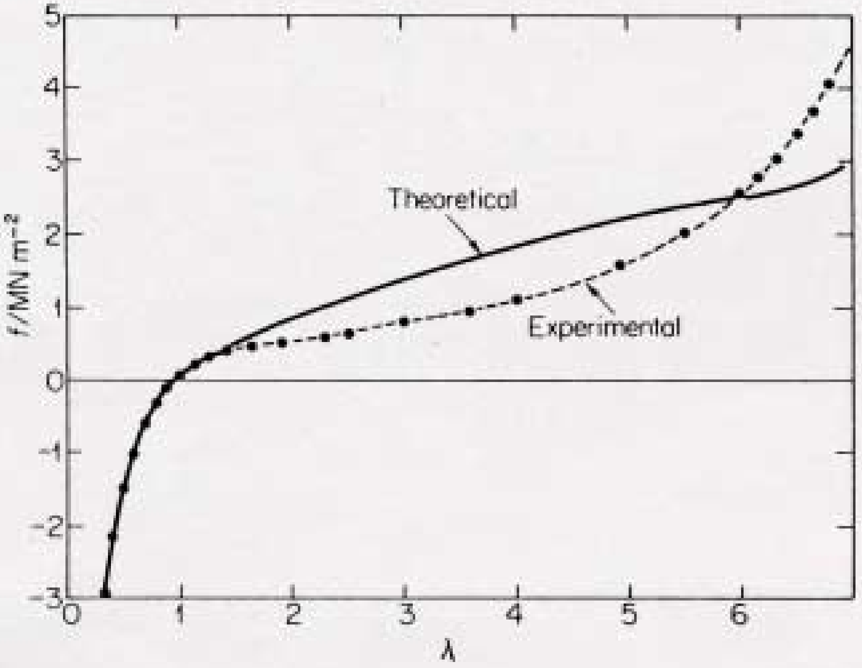


FIGURE 14.6. Extension or compression ratio λ as a function of the tensile or compressive force f for a rubber vulcanizate. Theoretical curve is derived from equation (14.21) using $G = 0.392 \text{ MN m}^{-2}$. (From data by Treloar, 1944.)

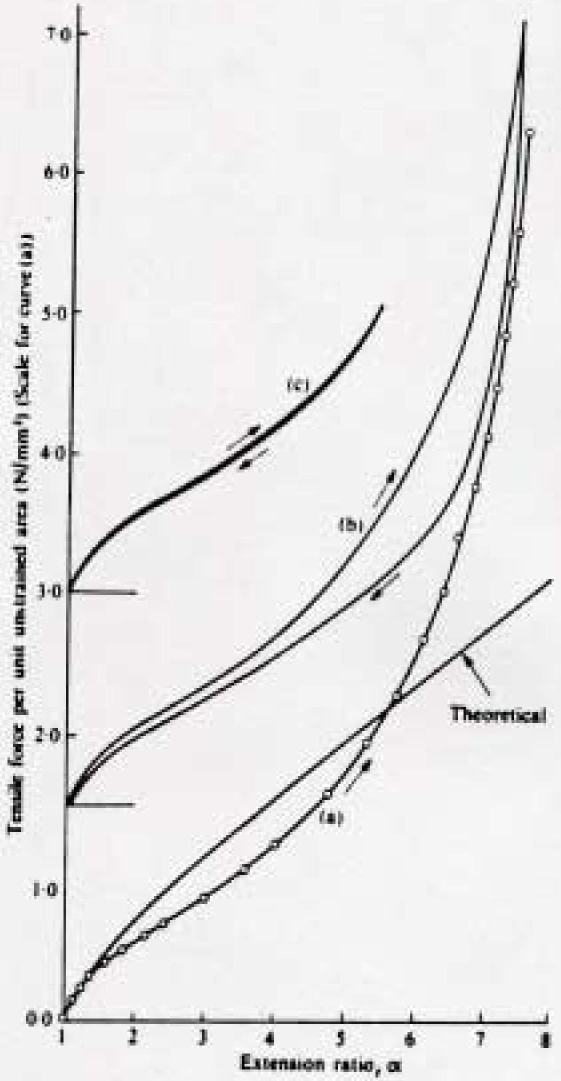


Figure 9.5 Stress – strain behavior of lightly cross-linked natural rubber at 50°C. Curve (*a*), experimental. Theoretical is equation (9.4). Curve (*c*) illustrates the reversible nature of the extension up to $\alpha = 5.5$. At higher elongations, curve (*b*), hysteresis effects become important. The theoretical curve has been fitted to the experimental data in the region of small extensions, with $nRT = 0.39 \text{ N} / \text{mm}^2$ (37, 38).

Theory of Rubber Elasticity

Typical Calculation

Assume an elastomer of 0.1 x 0.1 x 10 cm^3 is stretched to 25 cm length at 35°C, a stress of 2 10^7 dynes/cm^2 being required.
What is the concentration of active network chains and what is the magnitude of the shear modulus?

$$n = \frac{\sigma}{RT\left(\alpha - \frac{1}{\alpha^2}\right)}$$

$$G = nRT$$

n = 3.3 10^{-4} mol/cm^3 G = 0.86 J/cm^3 or G = 0.86 MPa

Theory of Rubber Elasticity

Ideal Rubber Equation of State

$$dU = dw + dq$$

$$dU = -pdV + fdL + TdS = fdL + TdS$$

$$F = U - TS$$

$$dF = dU - TdS - SdT$$

$$dF = fdL - SdT \Rightarrow f = \left(\frac{\partial F}{\partial L}\right)_{V,T}$$

$$f = \left(\frac{\partial F}{\partial L}\right)_{V,T} = \left(\frac{\partial U}{\partial L}\right)_{V,T} - T\left(\frac{\partial S}{\partial L}\right)_{V,T} - \cancel{S\left(\frac{\partial T}{\partial L}\right)_{V,T}}$$

$$dF = fdL - SdT \Rightarrow \left(\frac{\partial S}{\partial L}\right)_{V,T} = -\left(\frac{\partial f}{\partial T}\right)_{V,L}$$

$$f = \left(\frac{\partial U}{\partial L}\right)_{V,T} + T\left(\frac{\partial f}{\partial T}\right)_{V,L}$$

$$f_e = \left(\frac{\partial U}{\partial L}\right)_{V,T}$$

$$f_S = T\left(\frac{\partial f}{\partial T}\right)_{V,L} = -T\left(\frac{\partial S}{\partial L}\right)_{V,T}$$

Ideal Rubber EoS

$$\boxed{\begin{array}{l} f = T\left(\dfrac{\partial f}{\partial T}\right)_{V,L} \\[2ex] f_e = \left(\dfrac{\partial U}{\partial L}\right)_{V,T} = 0 \end{array}}$$

Theory of Rubber Elasticity

Rubber Thermoelastic Behavior

Stress required to achieve a given strain at a fixed temperature

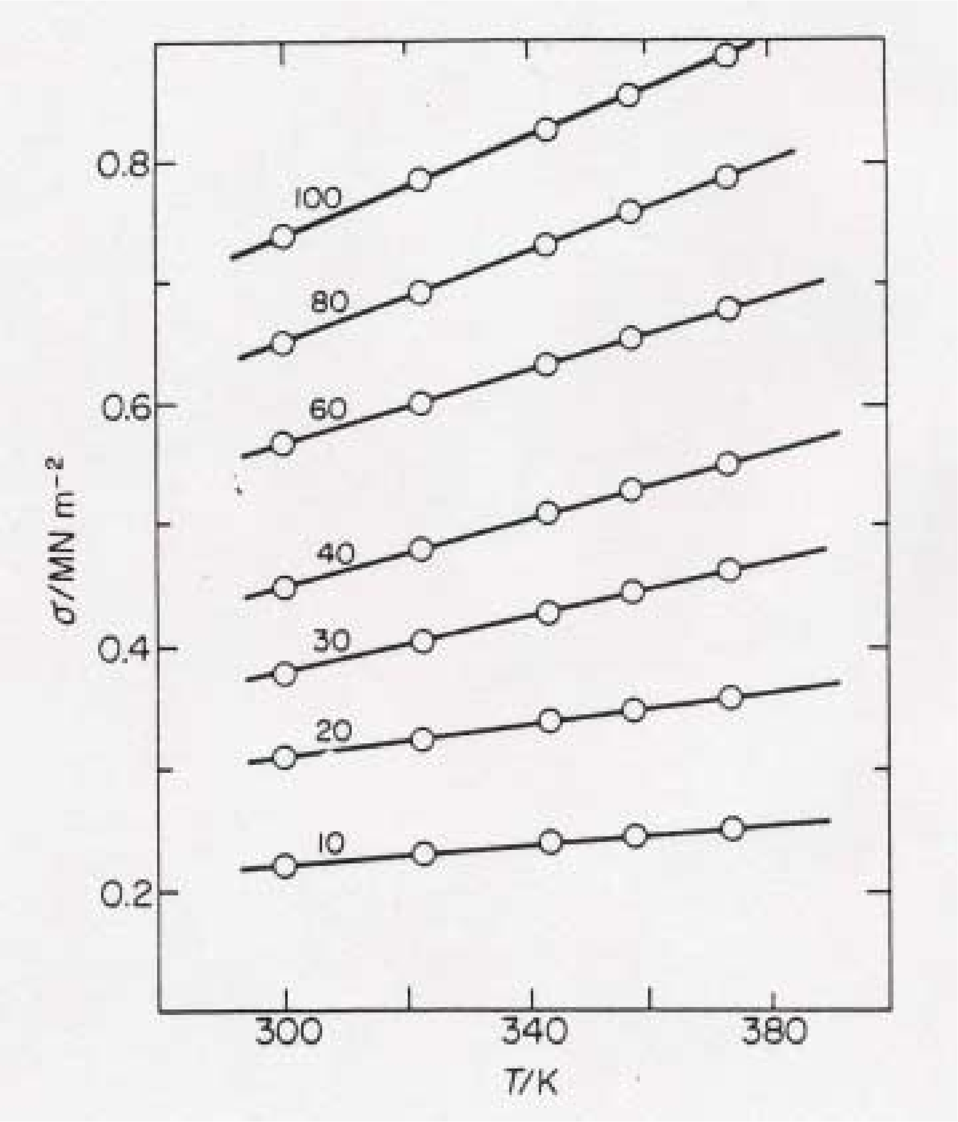
Rubber sample at different percentage strains.

$$\sigma = nRT\frac{\overline{r}_i^{\,2}}{\overline{r}_0^{\,2}}\left(\alpha - \frac{1}{\alpha^2}\right)$$

$$f = f_e + f_S$$

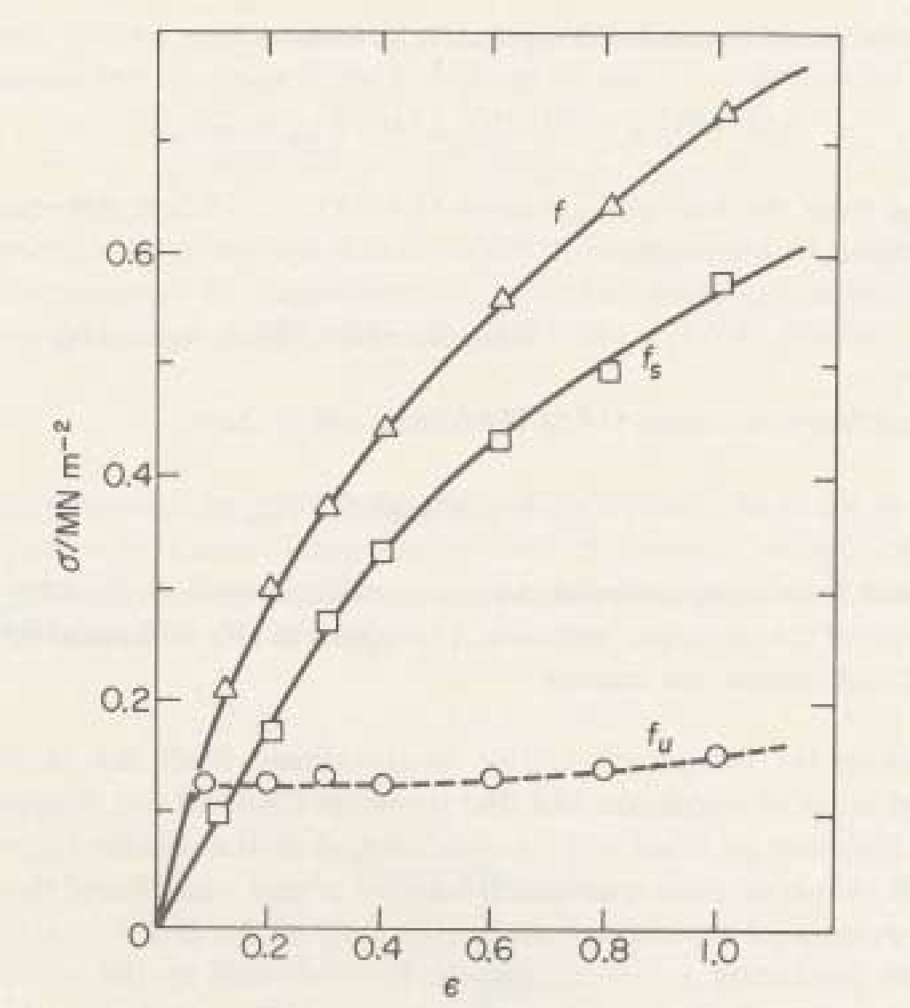
$$f_S = T\left(\frac{\partial f}{\partial T}\right)_{L,V}$$

$$f_e = \left(\frac{\partial U}{\partial L}\right)_{T,V} = f - T\left(\frac{\partial f}{\partial T}\right)_{L,V}$$



Theory of Rubber Elasticity

- Is the behavior of a real elastomer truly ideal ?
- How do we explain the observation made by Gough (strain leads to a rise in temperature)?



$$f = f_e + f_S$$

$$f_S = T\left(\frac{\partial f}{\partial T}\right)_{L,V}$$

$$f_e = \left(\frac{\partial U}{\partial L}\right)_{T,V} = f - T\left(\frac{\partial f}{\partial T}\right)_{L,V}$$

$$\left(\frac{\partial T}{\partial L}\right)_{S,p} = -\left(\frac{\partial T}{\partial S}\right)_{L,p}\left(\frac{\partial S}{\partial L}\right)_{T,p} = \frac{T}{C_{p,L}}\left(\frac{\partial f}{\partial T}\right)_{L,p}$$

Departure from Ideal Rubber Behavior

- Departures from the Ideal Rubber Behavior
  - Non-zero Energy Contribution to Elastic Retractive Forces (previous slide)
  - Stress-induced Crystallization
  - Limited Extensibility of Chains
    (better elastomers with high strength and high modulus can be obtained when bimodal networks with long and short chain segments are used)
  - Network Defects
    They must be accounted for in the calculation of the modulus.
    How do we get the true "n" ?

Departure from Ideal Rubber Behavior

- Non-zero Energy Contribution to Elastic Retractive Forces

$$f_e = \left(\frac{\partial U}{\partial L}\right)_{T,V} = f - T\left(\frac{\partial f}{\partial T}\right)_{L,V}$$

$$\frac{f_e}{f} = \frac{1}{T}\frac{d\ln\langle r_o^2\rangle}{dT}$$

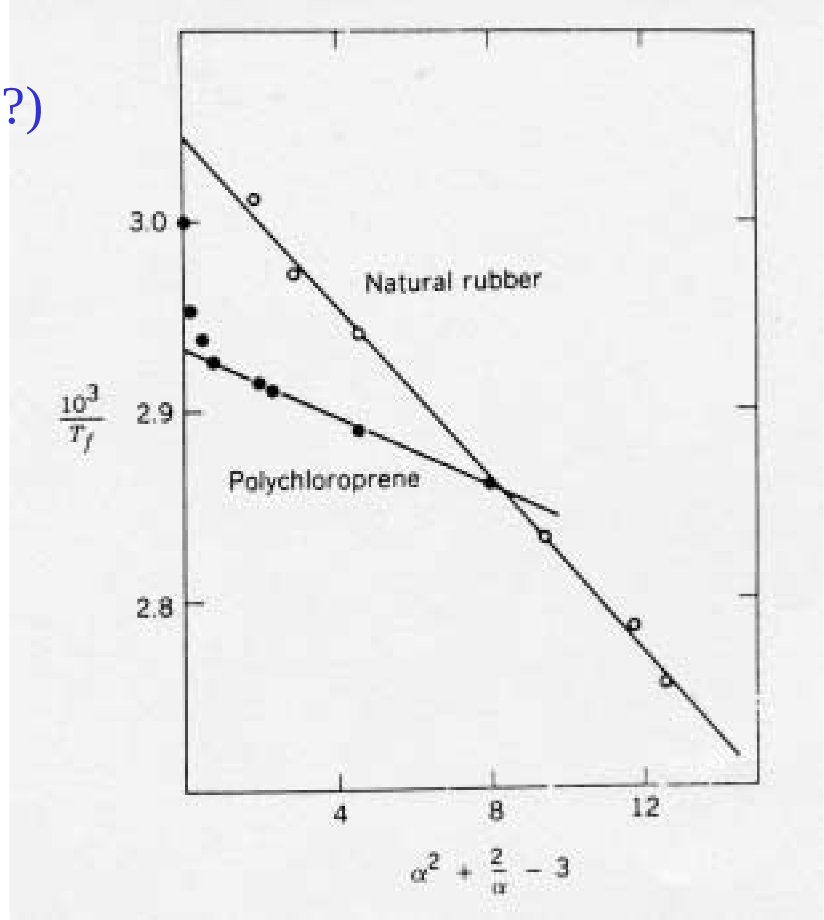
$$[\eta] = \phi\left(\frac{\langle r_o^2\rangle}{M}\right)^{3/2} M^a$$

$$\frac{d\ln\langle r_o^2\rangle}{dT} = \frac{2}{3}\frac{d\ln[\eta]}{dT}$$

Polymer	f_e / f
natural rubber	0.12
t-poly(isoprene)	0.10
cis poly(butadiene)	0.17
poly(ethylene)	-0.42
poly(ethyl acrylate)	-0.16
poly(dimethyl siloxane)	0.15

Departure from Ideal Rubber Behavior

- Stress-Induced Crystallization
  - One of the two possible reasons for up-swing of stress at high strains
  - Modulus increases rapidly as crystals act as new cross-links !
  - Only for crystallizable chains !
  - Melting point increases with stress (why ?)



$$\frac{1}{T_m} = \frac{1}{T_m^0} - \frac{R}{2N_u \Delta H_f^0}\left(\alpha^2 + \frac{2}{\alpha} - 3\right)$$

Departure from Ideal Rubber Behavior

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

- Limited Chain Extensibility
  - As chains extend significantly, the Gaussian Statistics approximation no longer holds.
  - Mooney-Rivlin-Saunders semi-empirical theory allows to extend the predicted stress-strain curves from low to moderate extensions (not high extensions, $\alpha < 2.5$ see fig. 9-18).
  - How can we make better elastomers (high strengths, high modulus) ?
  - $C_1 = 2 – 6$ kg/cm^2, $C_2 = 2$ kg/cm^2
  - $2C_2/C_1$ measures looseness of network (Flory)

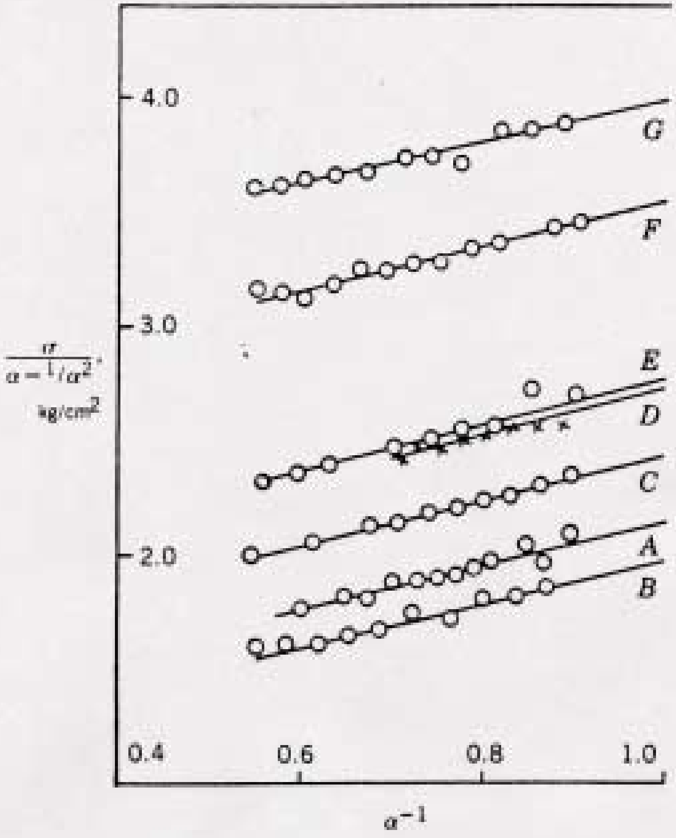
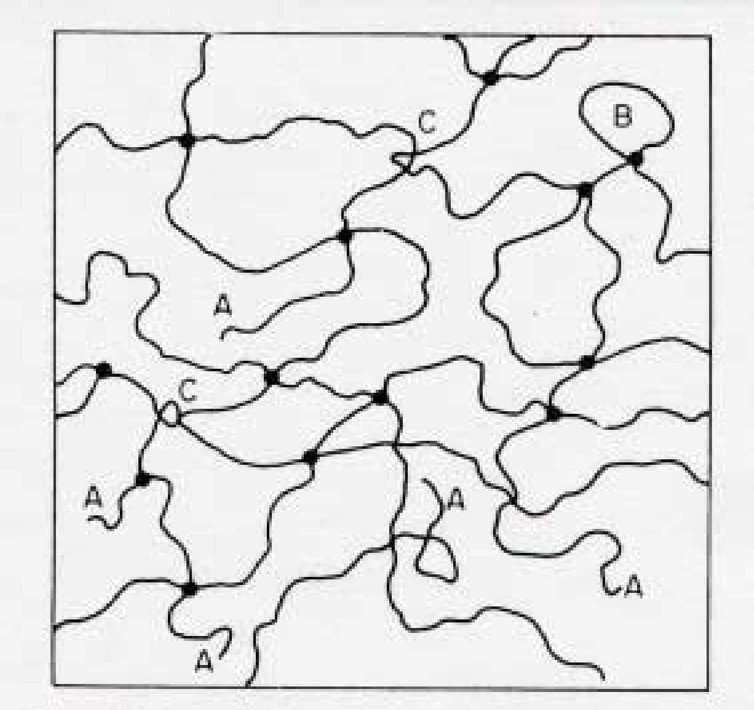


Figure 9.15 Plot of $\sigma / (\alpha - 1/\alpha^2)$ versus α^{-1} for a range of natural rubber vulcanizates. Sulfur content increases from 3 to 4%, with time of vulcanization and other quantities as variables (48).

Departure from Ideal Rubber Behavior

- Network Defects
  - Loose Chain Ends (A.), Intramolecular Loops (B.), Entangled Chain Loops (C.)
  - The quantity n in the Rubber Elasticity Theory is the true density of active chain sections between cross-links. It could be calculated from stress-strain curves.
  - This number can also be estimated from the extent of swelling. The larger n, the lower the extent of swelling. Swelling is the isotropic expansion of the network as solvent molecules diffuse in the network.

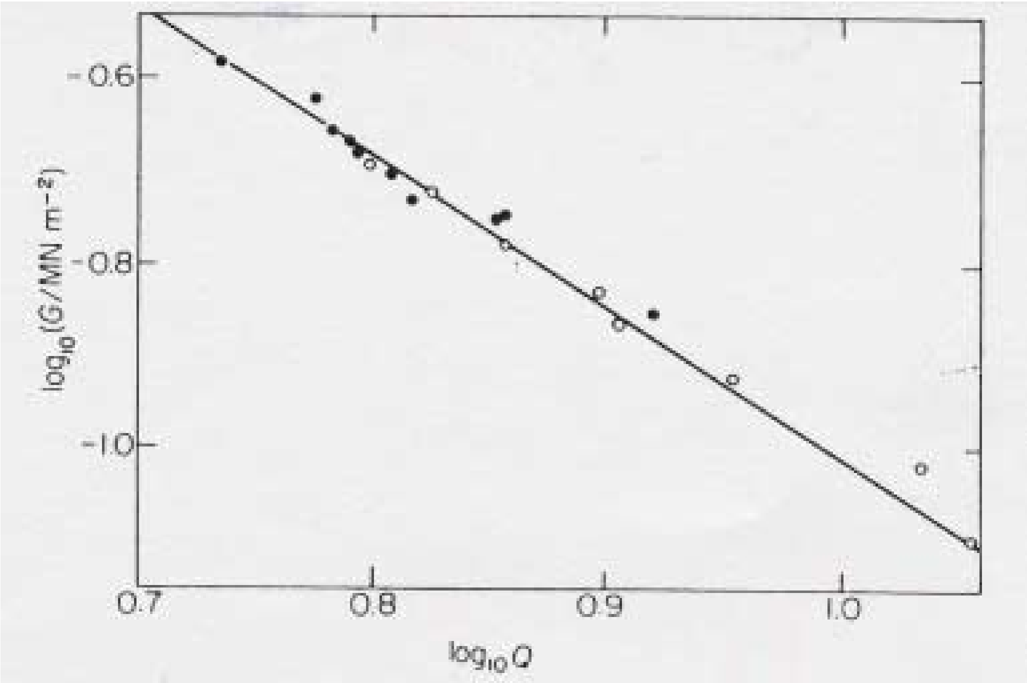


$$\sigma = \left[n_C \left(1 - \frac{2M}{M_C} \right) + n_P \right] RT \frac{\overline{r}_i^2}{\overline{r}_0^2} \left(\alpha - \frac{1}{\alpha^2} \right)$$

Accounts qualitatively for the effect of chain ends and entanglements

Swelling of Elastomers

Density of Active Network Chains
Swelling vs. Shear Modulus



Flory-Rehner Equation

$\Delta G_{SWEL} = \Delta G_{MIX} + \Delta G_{ELAST}$

$$\Delta G_{elas} = \frac{3}{2} nRT\left[\frac{1}{v_2^{2/3}} - 1\right]$$

$$-\left(\ln[1-v_2] + \chi_1 v_2^2 + v_2\right) = nV_1\left(v_2^{1/3} - \frac{v_2}{2}\right)$$

Flory-Rehner and
Rubber Elasticity
Theories

A: Constant
Q: Swelling Ratio

$$G = \frac{ART}{V_1 Q^{5/3}}$$

$$Q = \frac{V}{V_0} = \frac{1}{v_2}$$