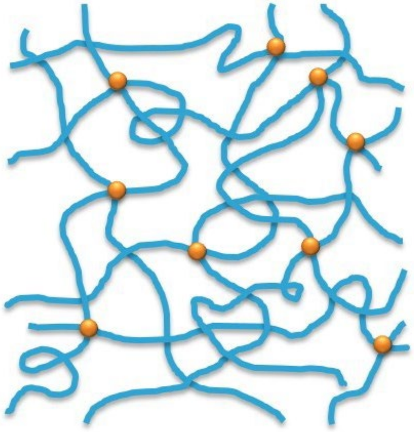
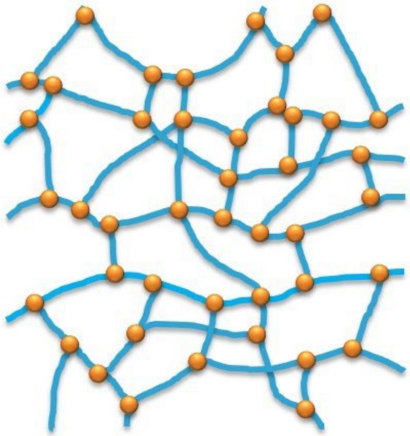
Course: Physical Chemistry of Polymeric Materials

Networks and Rubber Elasticity



Elastomer



Duroplast

Outline

Formation of Networks – Crosslinking Strategies

Structure of Networks

Theory of Elasticity

Thermodynamics of Elasticity

The Carnot Cycle

Swelling of Polymer Networks

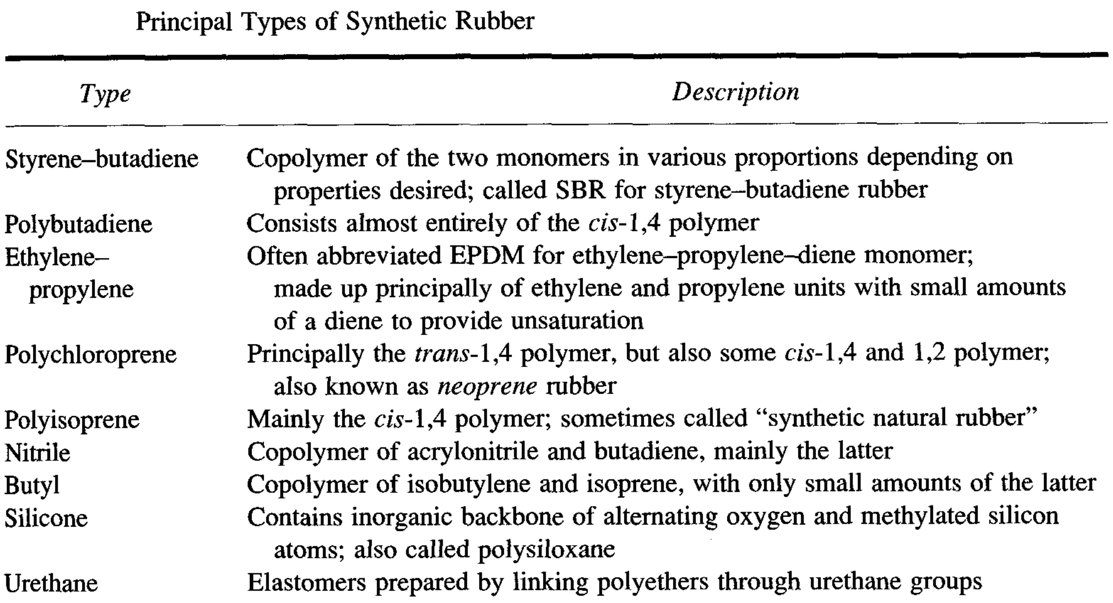
Paul J. Flory, Molecular Theory of Rubber Elasticity, Polymer Journal, 1985, 17, 1-12.
T.-S. Lin et al. , revisiting the elasticity theory for real gaussian phantom networks, Macromolecules, 2019, 52, 2685-1694.

Rubbers / Elastomers

Rubber: natural polymer
Elastomer: synthetic material

Usually both are used interchangeably

- Easily undergo very large reversible elongations (≤ 500-1000 %) at relatively low stresses
- Are covalently crosslinked, three dimensional networks
- T_g well below room temperature → solid, soft and deformable

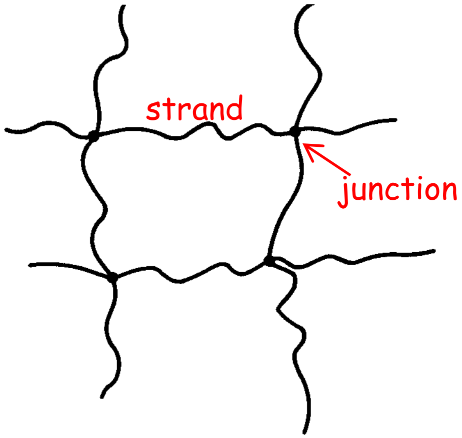


Principal Types of Synthetic Rubber

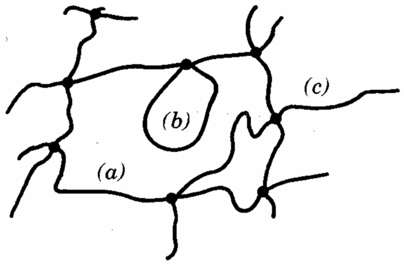
Type	*Description*
Styrene–butadiene	Copolymer of the two monomers in various proportions depending on properties desired; called SBR for styrene–butadiene rubber
Polybutadiene	Consists almost entirely of the *cis*-1,4 polymer
Ethylene–propylene	Often abbreviated EPDM for ethylene–propylene–diene monomer; made up principally of ethylene and propylene units with small amounts of a diene to provide unsaturation
Polychloroprene	Principally the *trans*-1,4 polymer, but also some *cis*-1,4 and 1,2 polymer; also known as *neoprene* rubber
Polyisoprene	Mainly the *cis*-1,4 polymer; sometimes called "synthetic natural rubber"
Nitrile	Copolymer of acrylonitrile and butadiene, mainly the latter
Butyl	Copolymer of isobutylene and isoprene, with only small amounts of the latter
Silicone	Contains inorganic backbone of alternating oxygen and methylated silicon atoms; also called polysiloxane
Urethane	Elastomers prepared by linking polyethers through urethane groups

Thermoplastic elastomers: behave as rubbers, but can be melt processed

Formation of Networks by Cross-Linking



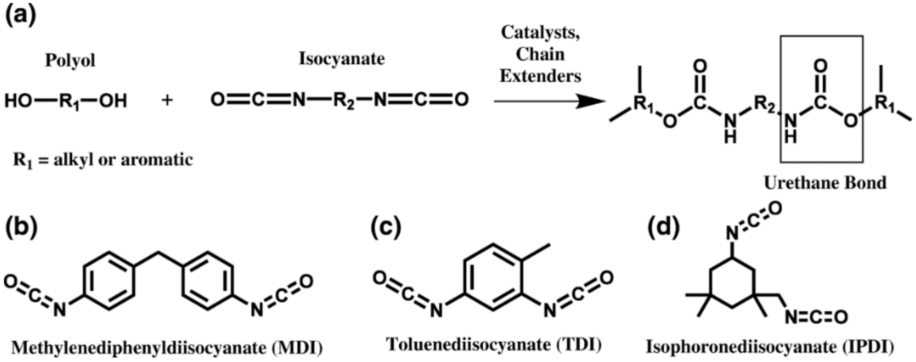
Idealized structure of a cross-linked polymer. Wavy lines, polymer chains; circles, cross-links.

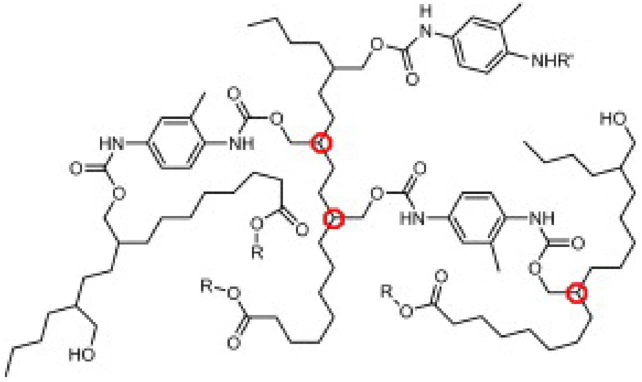


Network structure and defects. (*a*) Elastically active chain; (*b*) loop; (*c*) dangling chain end.

Crosslinking Strategies (1):

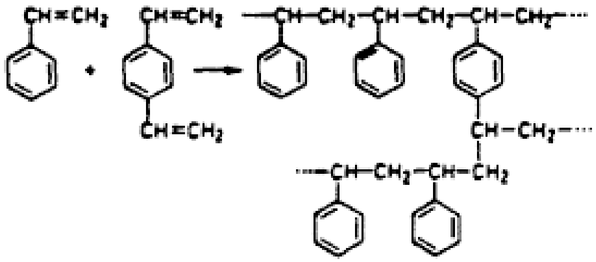
1. **Step polymerization**: small molecules with functionality greater than two to form short, branched chains.
   epoxied (oxiranes) with amines or isocyanates with polyols.
   Schematically:





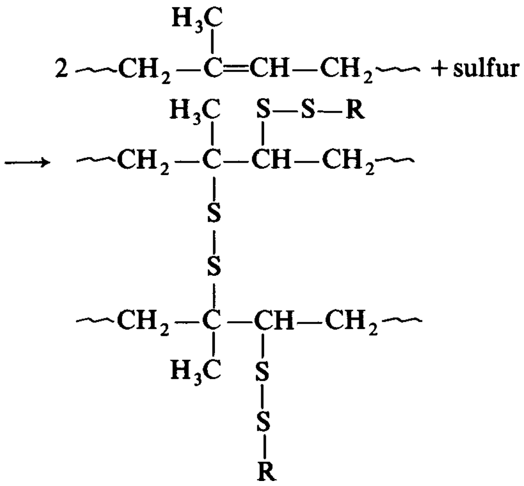
M. Carme Coll Ferrer et a. ,Polymer, Volume 49, issue 15, 2008, 3279-3287

2. **Chain polymerization** with multi(≥ 2)functional molecules present
   ex.: styrene polymerized with divinyl benzene

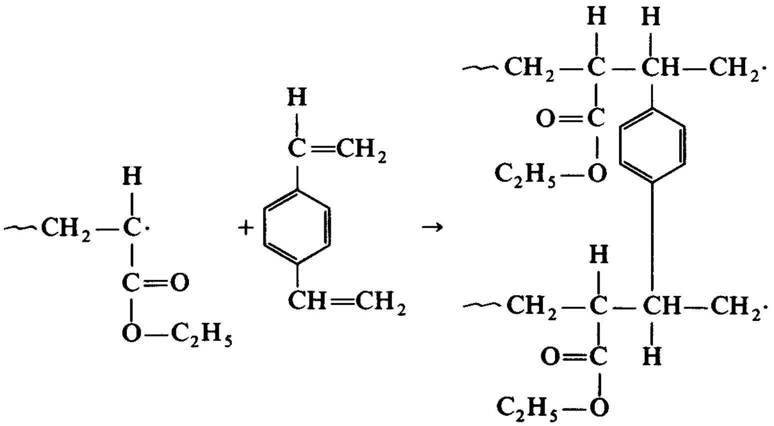


Crosslinking Strategies (2):

3. **Postpolymerization** reactions, where a linear or branched polymer is crosslinked after synthesis is complete
   ex.: Vulcanization of rubber with sulfur

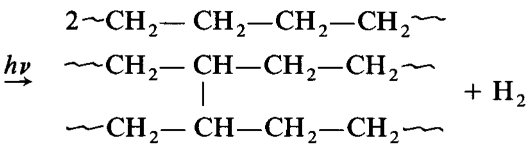


4. Use of multifunctional monomer in the **simultaneous polymerization** and crosslinking of polymers



Crosslinking Strategies (3):

5. **Radiation crosslinking** with an electron beam or gamma irradiation

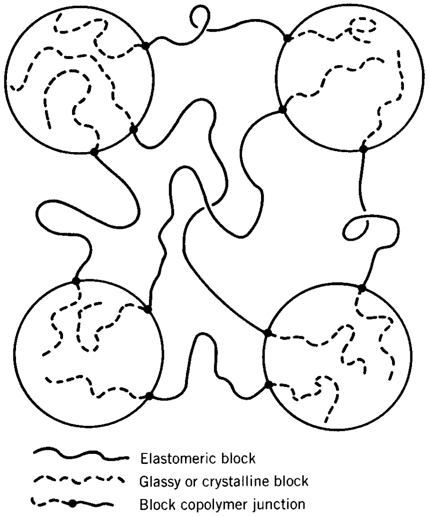


$$2\sim\mathrm{CH_2-CH_2-CH_2-CH_2}\sim \xrightarrow{h\nu} \begin{array}{c}\sim\mathrm{CH_2-CH-CH_2-CH_2}\sim \\ | \\ \sim\mathrm{CH_2-CH-CH_2-CH_2}\sim\end{array} + \mathrm{H_2}$$

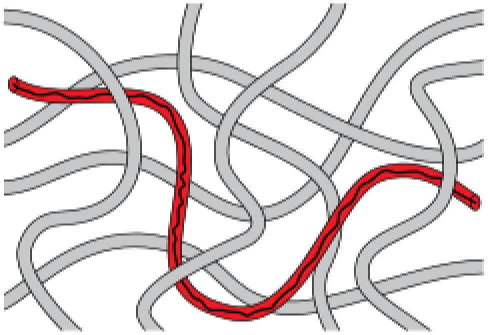
6. **Physical** (= non-covalent) **crosslinking**:

- thermoplastic elastomers
- semi-crystalline polymers at $T > T_g$

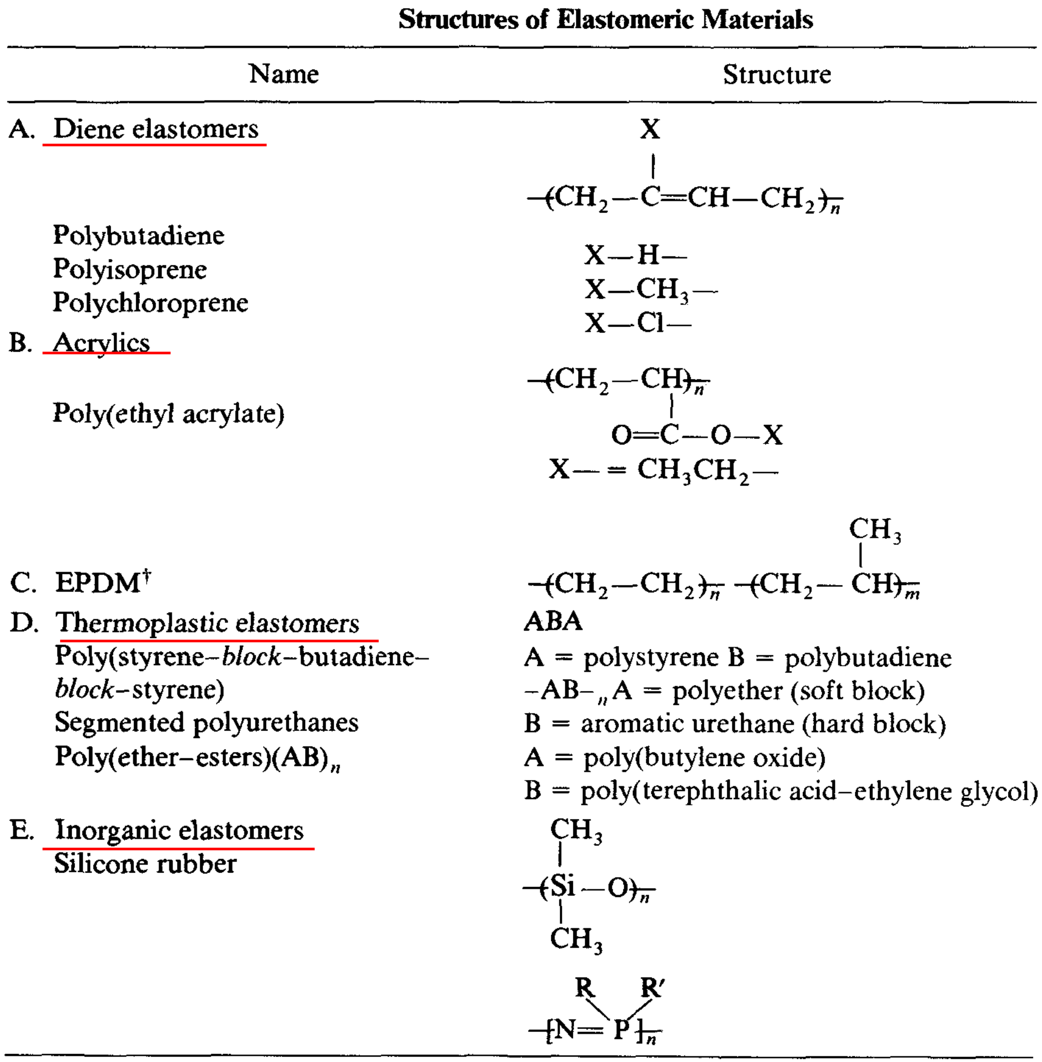
(• amorphous polymers of high MW)



Idealized triblock copolymer thermoplastic elastomer morphology.



Classes of Elastomers



Structures of Elastomeric Materials

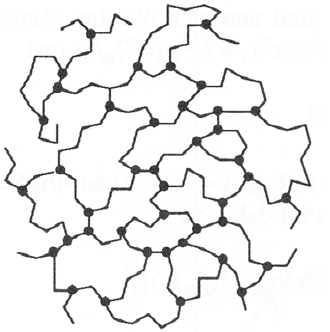
Name	Structure
A. Diene elastomers	$-\!(CH_2-\overset{X}{\overset{\vert}{C}}=CH-CH_2)_n-$
Polybutadiene	X—H—
Polyisoprene	X—CH_3—
Polychloroprene	X—Cl—
B. Acrylics	
Poly(ethyl acrylate)	$-\!(CH_2-\underset{O=C-O-X}{\underset{\vert}{CH}})_n-$ X— = CH_3CH_2—
C. EPDM†	$-\!(CH_2-CH_2)_n-(CH_2-\overset{CH_3}{\overset{\vert}{CH}})_m-$
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)
Poly(ether–esters)$(AB)_n$	A = poly(butylene oxide) B = poly(terephthalic acid–ethylene glycol)
E. Inorganic elastomers	
Silicone rubber	$-\!(\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{Si}}}}-O)_n-$
	$-[N=P(R)(R')]_n-$

†EPDM: ethylene-propylene diene monomer

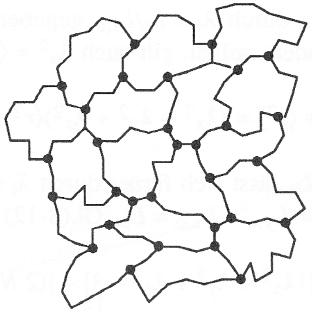
Structure of Networks

Networks with trifunctional junction

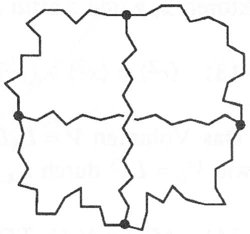
reality → model



Network with different strand lengths and mesh sizes and dangling ends

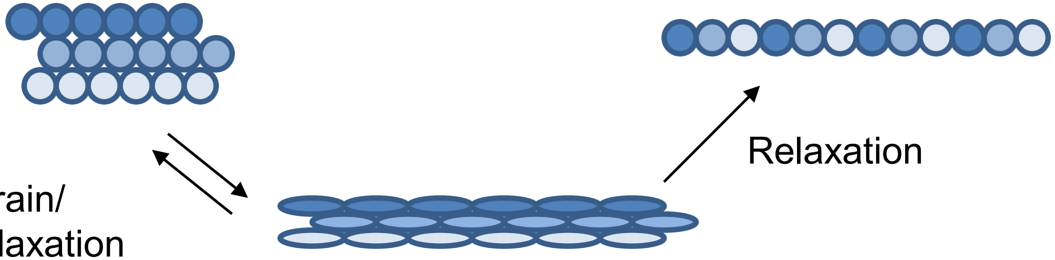


Network with different strand lengths but similar mesh size (14 segments); no dangling ends



Perfect network with equal strand lengths (15 segments), no ends, loops and entanglements

Elasticity



strain/
relaxation

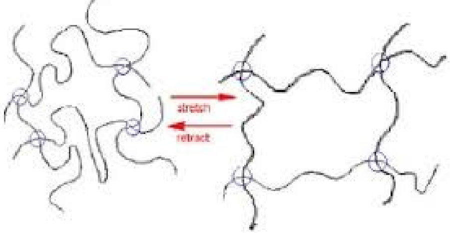
Relaxation

	enthalpic elasticity	entropic elasticity
Reversible deformation	small (ca. 0.1%)	high (more than 100%)
Young’s Modulus E	high	low
Temp. change on strain	cooling down	heating up
Change of length on heating	elongation	contraction
Example	steel	rubber band

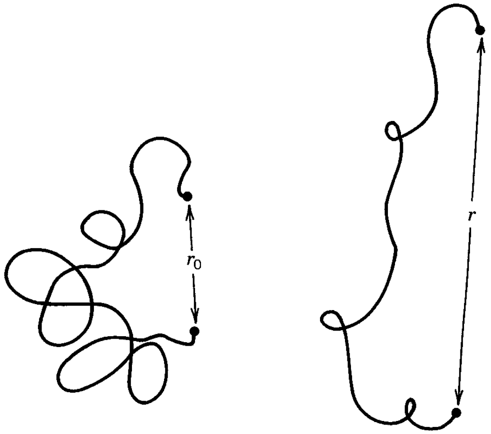
Theory of Rubber Elasticity

Rubber elasticity is entropy driven

Changes to the Rubber Network upon stretching

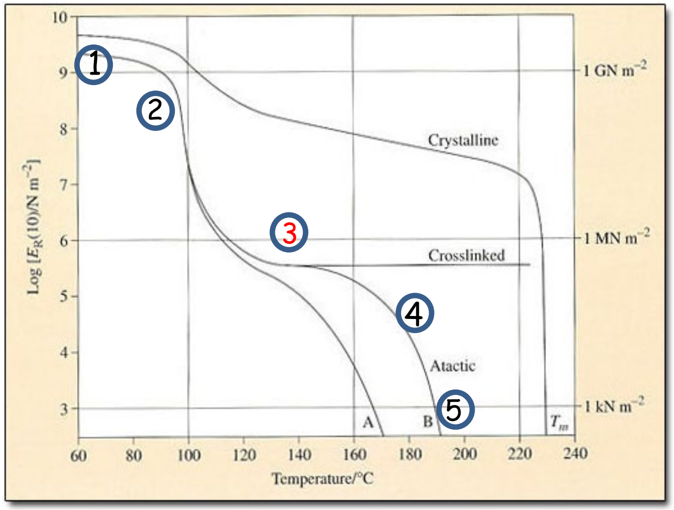


between 2 junction points



(a) (b)

A network chain segment. (*a*) Relaxed, with a random coil conformation, and (b) extended, owing to an external stress.



rubber elasticity refers to region 3

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

(non-linear: cf. Hooke‘s Law)

σ = retractive stress
α = extension ratio (= L/L_0)
n = number of active network segments per unit volume (= ρ/M_c)
[M_c: number average molecular weight between cross-links]
R = 8,31x10^7 (dyn cm)/(mol K)

Thermodynamics of Elasticity

for entropy elastic bodies

Equation of state for an Elastomer

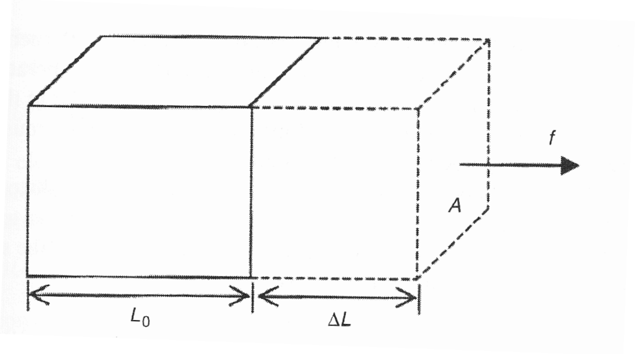
$$f = \left(\frac{\delta G}{\delta L}\right)_{T,p} = \left(\frac{\delta H}{\delta L}\right)_{T,p} - T\left(\frac{\delta S}{\delta L}\right)_{T,p}$$

for ideal elastomer $\left(\frac{\delta H}{\delta L}\right)_{T,p} = 0$

$$f = \left(\frac{\delta A}{\delta L}\right)_{T,V} = \left(\frac{\delta U}{\delta L}\right)_{T,V} - T\left(\frac{\delta S}{\delta L}\right)_{T,V}$$

for ideal elastomer $\left(\frac{\delta U}{\delta L}\right)_{T,V} = 0$

f = retractive force
S = entropy
A = Helmholtz free energy (sometimes as F)
G = Gibbs free energy
U = internal energy
H = enthalpy



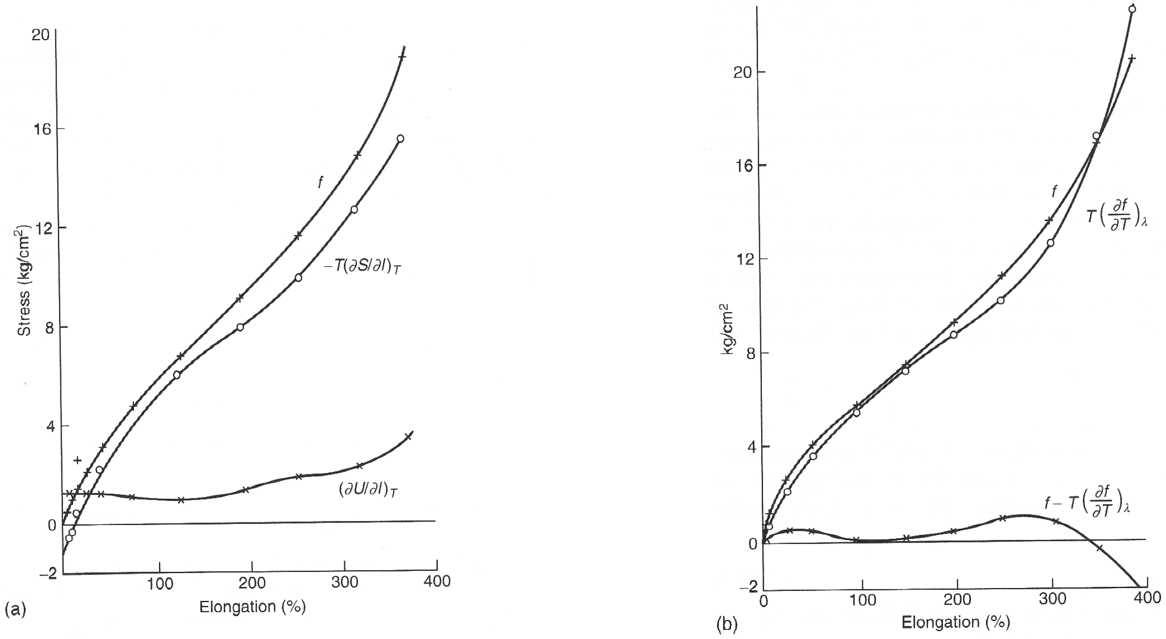
Stress – Strain Curves

relationship between the entropy and the retractive force is given as:

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

$$\rightarrow \quad \boxed{f = \left(\frac{\delta U}{\delta L}\right)_{T,V} + \mathrm{T}\left(\frac{\delta f}{\delta T}\right)_{L,V}}$$

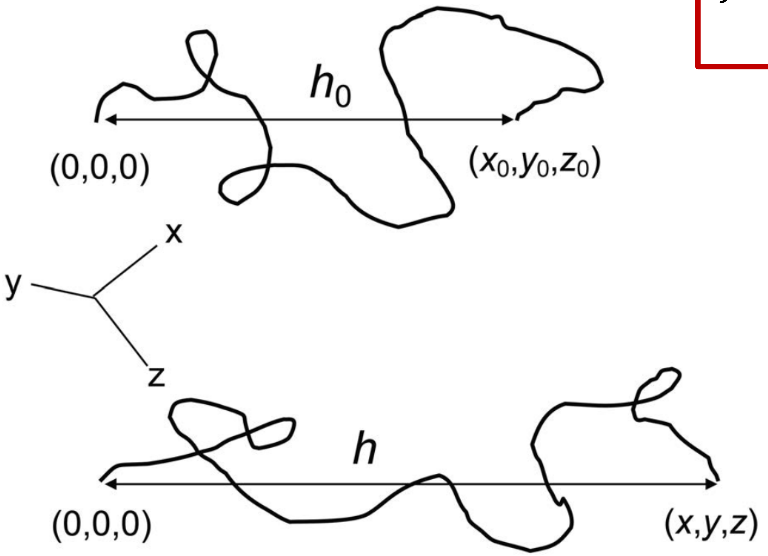
Stress versus elongation for natural rubber, resolved into internal energy and entropic contributions at
(a) constant temperature (b) constant strain



Statistical Thermodynamic of Rubber Elasticity

Equation of state for a single Gaussian chain:

$$f = -T\left(\frac{\delta \Delta S_{chain}}{\delta h}\right) = \left(\frac{3kT}{\overline{h^2}}\right)h = \left(\frac{3kT}{Nb^2}\right)h$$



Extension of a single Gaussian chain from initial end-to-end distance h_0 to final end-to-end distance h.

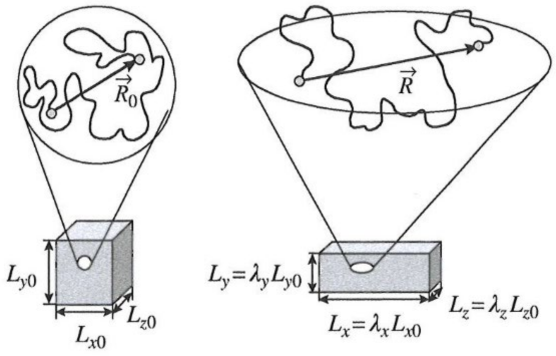
f is the force to extend the chain to h
Stretching of a random walk chain the retractive force depends on the segment length b.
The smaller b (= the larger the flexibility of a chain), the larger is f at given stress

Single Gaussian chain behaves like a Hook's law spring with a spring constant $\frac{3kT}{\overline{h^2}}$ and a zero rest length. The spring stiffer as the temperature increases based on entropic nature.

Affine Network Model

Equation of state for a macroscopic network: ideal network of Gaussian strands

(affine network)



$$\sigma = \left(\frac{\delta F}{\delta \alpha}\right)_{T,V} = nRT\,\frac{\overline{h_i^2}}{\overline{h_0^2}}\left(\alpha - \frac{1}{\alpha^2}\right)$$

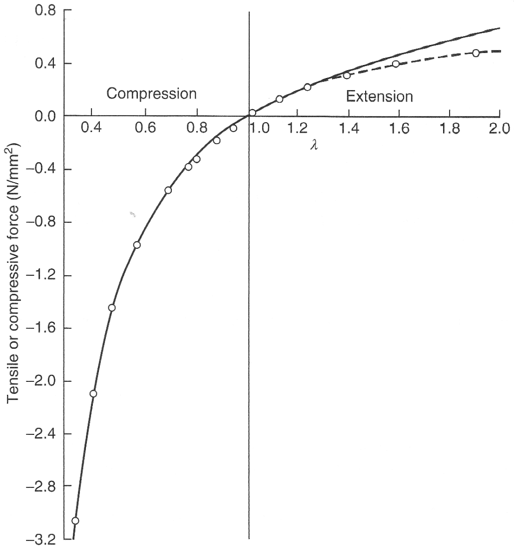


Figure 10.12 Stress for cross-linked natural rubber in compression and extension. (Data from Treloar, L.R.G., *Trans. Faraday Soc.*, 40, 59, 1944. With permission.)

σ:	stress
$\frac{\overline{h_i^2}}{\overline{h_0^2}}$:	front factor,
$\overline{h_i^2}$:	isotropic unstrained end-to-end distance in the network
$\overline{h_0^2}$:	isotropic end-to-end distance for a free, relaxed chain
$\alpha = L/L_0$	extension ratio
n:	number of active network chains per unit volume

Modulus of the Macroscopic Network:

Young’s Modulus: $E = L\left(\frac{\delta\sigma}{\delta L}\right)_{T,V} = nRT\frac{\overline{h_i^2}}{\overline{h_0^2}}\left(2\alpha^2 + \frac{1}{\alpha}\right) \approx 3nRT\frac{\overline{h_i^2}}{\overline{h_0^2}}$

Shear Modulus: $G = nRT\frac{\overline{h_i^2}}{\overline{h_0^2}} = \frac{\rho RT}{M_x}$ M_x molecular weight between crosslinks

stress-strain relationships and the modulus of an ideal elastomer:

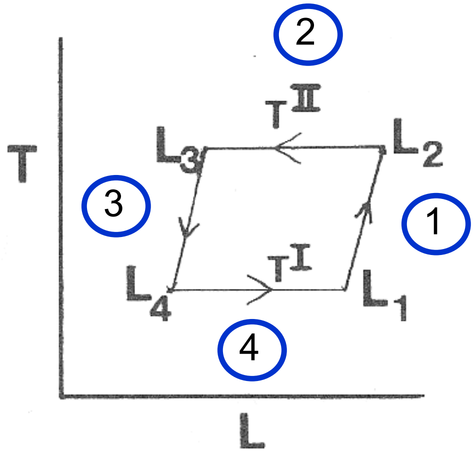
$$\sigma = G\left(\alpha - \frac{1}{\alpha^2}\right)$$

Conclusions:

1. The modulus increases with temperature, just as with the spring constant of a single chain, due to is entropic origin.
2. The modulus increases as a function of crosslinks density, because M_x decreases; a ‘tighter’ network is ‘stiffer’.
3. The modulus is independent of the functionality of crosslinks.
4. The extensional stress is not a linear function of the strain

The “Carnot Cycle” for Elastomers

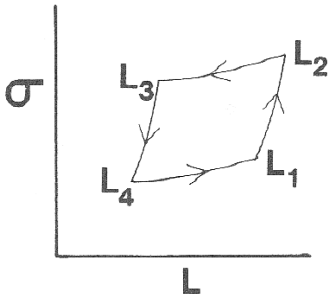
Carnot Cycle = production of useful work by a gas in a heat engine



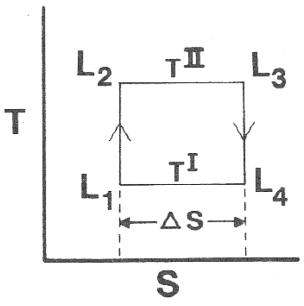
(a)

Stress – length steps, two adiabatically and two isothermally

1. At L_1 and T_I a stress is applied stretching the elastomer adiabatically to L_2
   → heating up to T_{II}
2. At T_{II}, isotherm contraction to L_3 adsorbing heat from surrounding
3. Adiabatic contraction to L_4 cooling to T_I
4. Increasing length from L_4 to L_1 isothermally, and heat is given off to its surrounding



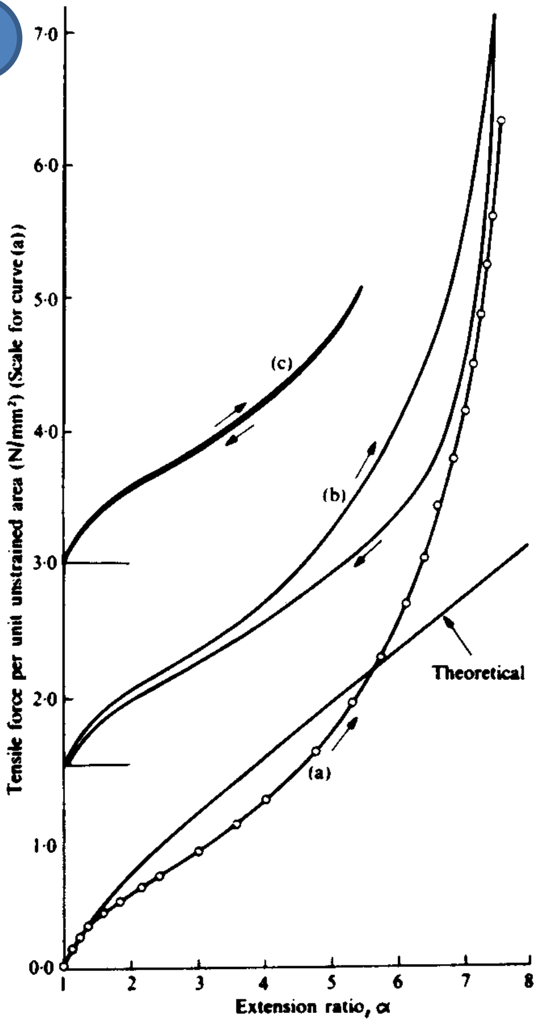
(b)



(c)

Tests of the Theory

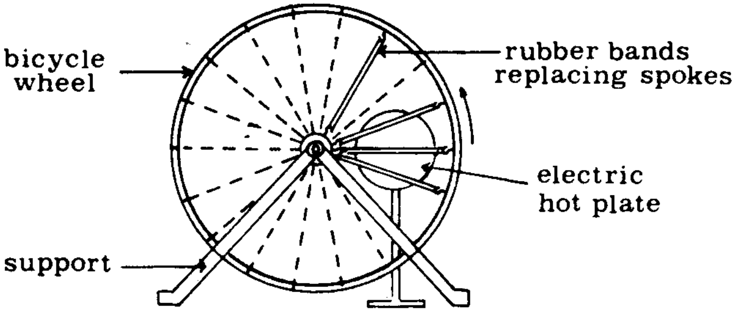
A



Stress–strain behavior of lightly cross-linked natural rubber at 50°C. Curve (*a*), experimental. Theoretical is equation (7.4). 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 $nRT = 0.39\ N/\text{mm}^2$ (27, 28).

B

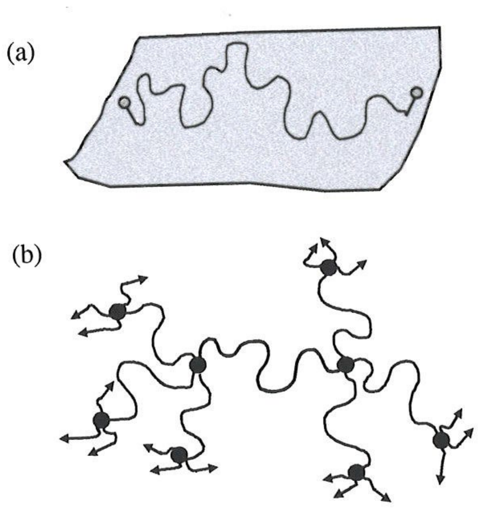
A bicycle wheel is mounted on a stand, with a source of heat on one side only. Stretched rubber bands replace the spokes. On heating, the stress that the stretched rubber bands exert is increased, so that the center of gravity of the wheel is displaced toward 9 o'clock in the drawing. The wheel then rotates counter-clockwise



A thermally rotated wheel, employing an elastomer as the working substance

Phantom Network

In the bulk of the network the junction points are free to fluctuate about their mean position.
→ reduction of the net stress



(a) In the affine network model, the ends of each network strand are pinned to an elastic background. (b) In the phantom network model, the ends of network strands are joined at crosslink junctions that can fluctuate. Circles are crosslink junctions and arrows denote attachments to the rest of the macroscopic network.

Assumption:
network has a treelike topology,
every strand bear the same stress when a macroscopic strain is applied

Modulus: $G = \frac{\nu_e}{V}\left(\frac{f-2}{f}\right)kT$

f: functionality
ν_e: number of elastically effective strands

When the end-to-end distance becomes an appreciable fraction of the contour length the Gaussian distribution can be not longer applied. Kuhn and Grün derived a distribution function including the so-called inverse Langevin function.

The Mooney – Rivilin Model

Considering elastomer as a continuum, based on symmetrical consideration following semi-empirical equation of Mooney-Rivlin was found.

$$\sigma = 2C_1\,(\alpha - 1/\alpha^2) + 2C_2\,(1 - 1/\alpha^3)$$

C_1, C_2 parameter of the material, but not function of the deformation

The following form of this equation suggests plotting the following quantity versus $1/\alpha$:

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

which should give a straight line with intercept $2C_1$ and slope $2C_2$.

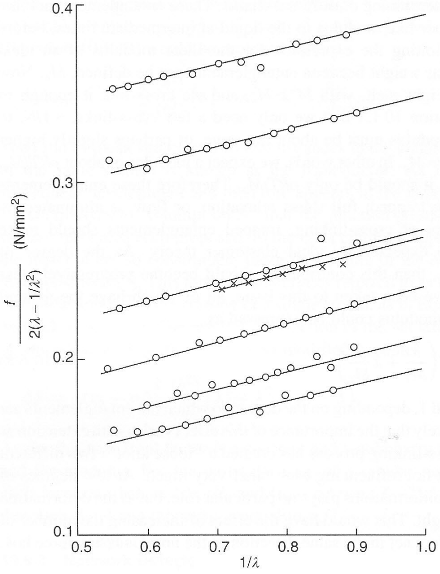


Figure 10.15 A "Mooney plot" for various rubbers in simple extension. (Data from Gumbrell, S.M., Mullins, L., and Rivlin, R.S., *Trans. Faraday Soc.*, 49, 1495, 1953. With permission.)

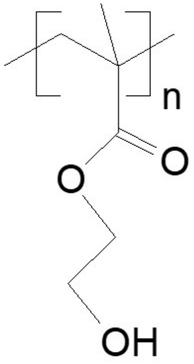
Swelling of Polymer Networks

Lightly crosslinked polymer material is able to imbibe and retrain a large volume of solvent

Examples:

-Hot melt adhesives. The glue is applied as a liquid at high temperature and solidifies upon cooling. A typical formulation could include about 30% of a PS-PI-PS triblock copolymer. At low temperature PS segregates from PI to form roughly spherical styrene aggregates that acts as crosslinks. At high temperature the segregation is disrupted and the polymer flows. The remaining 70% of the material consists of low-molecular weight species → diluting the PI and softening the resulting gel, and plasticizing and decreasing T_g of PS

-Soft Contact Lenses. They are a hydrogel network in which the polymer (largely cross-inked poly(hydroxymethyl methacrylate) is either water soluble or at least water compatible.



Questions:

1. How changes the expression for the modulus of an ideal elastomer when solvent is incorporated?
2. How much solvent can a network take up?

Swelling of Polymer Networks

1. Modulus of a swollen rubber:

The stress in the swollen network is reduced by a factor $\nu_2^{1/3}$ compared to the original network, and the modulus is reduced by the same factor when computed for constant cross-sectional area

$$\boxed{\sigma = kT\frac{\nu_e}{V_0}\,\nu_2^{1/3}\left(\alpha - \frac{1}{\alpha^2}\right)}$$

$\nu_2 = V_0/V$ volume fraction of polymer in resulting gel
V_0 network volume
V network swollen with solvent to a new volume
ν_e number of elastically effective strands

2. Swelling Equilibrium

It can be understood as a simple balance between the osmotic drive to dilute the polymer and the entropic resistance to strand extension.

→ at equilibrium a determination of χ and the molecular weight between crosslinks is possible

Swelling of Polymer Networks

Equilibrium swelling theory of Flory and Rehner, basic consideration:

1. Entropy change due to mixing of polymer and solvent. This entropy change is positive and favors swelling
2. Swelling reduces the number of possible chain conformations. The corresponding entropy change is negative and opposes swelling
3. Heat of mixing (ΔH) of polymer and solvent: can be positive, negative or zero. Usually slightly positive, which opposes mixing

Flory-Rehner equation:

$$\boxed{-\left[ln(1 - \nu_2) + \nu_2 + \chi_1 \nu_2^2\right] = V_1 n \left[\nu_2^{1/3} - \frac{\nu_2}{2}\right]}$$

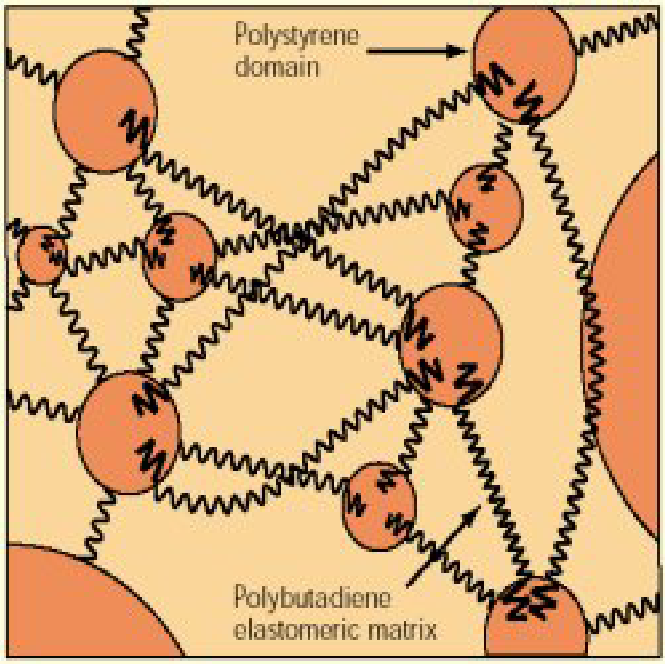
ν_2 = polymer volume fraction V_0/V
V_1 = molar volume of solvent
χ_1 = Flory-Huggins interaction parameter
n = number of active network segments / unit volume

Utility: determine n / M_c from swelling experiments

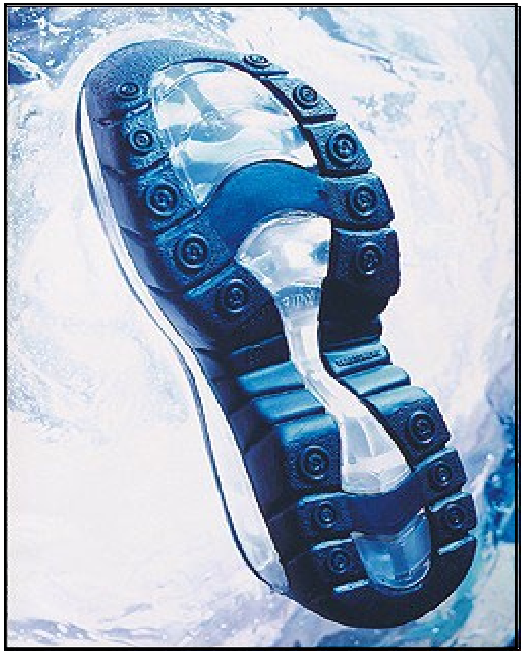
Thermoplastic Elastomers

Styrene-isoprene-styrene and styrene-1,2-butadiene-styrene ABA triblock copolymers with short styrene blocks are useful as thermoplastic elastomers (*Cariflex*, *Kraton*, *Soloprene*, *Stereon*)

Thermoplastic elastomers behave as elastomers at ambient temperatures but are thermoplastic at elevated temperatures ($T > T_{g,PS}$), where theycan be molded and remolded



The polystyrene blocks aggregate to form glassy (hard) domains that physically crosslink the rubbery (soft) polydiene blocks



http://www.kraton.com/

Summary

1. Analysis of rubber elasticity via macroscopic thermodynamics is relatively straightforward, the main new ingredient being the incorporation of the work of deformation into the free energy. An ideal elastomer is defined as one for which the force resisting deformation is entirely entropic, which is a reasonable approximation for many rubber materials.

2. The molecular basis of rubber elasticity rests in the reduction of conformational degrees of freedom when a single Gaussian chain is extended. A single Gaussian chain acts as a Hooke's law spring, with a stiffness that is proportional to absolute temperature.

3. Straightforward expressions for the force required to deform an ideal elastomer are obtained by modeling the network as a collection of Gaussian strands and be making an assumption as to how the macroscopic deformation is transmitted to each strand. The resulting shear and extensional moduli are proportional to the number of strands per unit volume.

4. Networks or gels are often capable of absorbing more than 100 times their own weight in solvent, a phenomenon that is central to many applications, and that can be understood as a simple balance between the osmotic drive to dilute the polymer and the entropic resistance to strand extension.