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! (S₂ 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 \( T > T_g \))

• Historical Development:
  – Christopher Columbus, 1492
  – Gough, 1805
    • Stretching an elastomer leads to its … warming up
Cross-links, Networks and Classes of Elastomers

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    • Stretching followed by cooling leads to loss of retractive power and density rise
Cross-links, Networks and Classes of Elastomers

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  – Christopher Columbus, 1492
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    • Stretching an elastomer leads to its …. **warming up**
    • Under constant load, heating leads to…. **shrinkage**
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  – Raincoat story, ca. early 19th century
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Cross-links, Networks and Classes of Elastomers

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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 $\gamma$ Irradiation

• Chain Polymerization with a Tetrafunctional Comonomer
## Cross-links, Networks and Classes of Elastomers

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A. Diene elastomers</strong></td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td>Polybutadiene</td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td>Polyisoprene</td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td>Polychloroprene</td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td><strong>B. Acryliks</strong></td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td>Poly(ethyl acrylate)</td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td><strong>C. EPDM</strong></td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td><strong>D. Thermoplastic elastomers</strong></td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td>Poly(styrene–block–butadiene–block–styrene)</td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td>Segmented polyurethanes</td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td><strong>E. Inorganic elastomers</strong></td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td>Silicone rubber</td>
<td><img src="" alt="Structure" /></td>
</tr>
<tr>
<td>Polyphosphazenes</td>
<td><img src="" alt="Structure" /></td>
</tr>
</tbody>
</table>

### 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

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)

<table>
<thead>
<tr>
<th>Ingredient</th>
<th>phr&lt;sup&gt;a&lt;/sup&gt;</th>
<th>Natural Rubber</th>
<th>SBR Synthetic</th>
<th>Function</th>
</tr>
</thead>
<tbody>
<tr>
<td>Smoked sheet</td>
<td>100</td>
<td>—</td>
<td>103.1</td>
<td>Elastomer—extender masterbatch</td>
</tr>
<tr>
<td>Styrene–butadiene/oil masterbatch</td>
<td>—</td>
<td>20.0</td>
<td>103.1</td>
<td>Elastomer—extender masterbatch</td>
</tr>
<tr>
<td>Cis-polybutadiene</td>
<td>25</td>
<td>5.0</td>
<td>25</td>
<td>Special purpose elastomer</td>
</tr>
<tr>
<td>Oil-soluble sulfonic acid</td>
<td>3.0</td>
<td>3.0</td>
<td>3.0</td>
<td>Processing aid</td>
</tr>
<tr>
<td>Stearic acid</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>Accelerator—activator</td>
</tr>
<tr>
<td>Zinc oxide</td>
<td>3.5</td>
<td>3.5</td>
<td>3.5</td>
<td>Accelerator—activator</td>
</tr>
<tr>
<td>Phenyl-β-naphthylamine</td>
<td>2.0</td>
<td>2.0</td>
<td>2.0</td>
<td>Antioxidant</td>
</tr>
<tr>
<td>Substituted (N,N'p)-phenylenediamine</td>
<td>4.0</td>
<td>4.0</td>
<td>4.0</td>
<td>Antiozonant</td>
</tr>
<tr>
<td>Microcrystalline wax</td>
<td>1.0</td>
<td>1.0</td>
<td>1.0</td>
<td>Processing aid and finish</td>
</tr>
<tr>
<td>Mixed process oil</td>
<td>5.0</td>
<td>7.0</td>
<td>7.0</td>
<td>Softener</td>
</tr>
<tr>
<td>HAF carbon black</td>
<td>50</td>
<td>—</td>
<td>65</td>
<td>Reinforcing filler</td>
</tr>
<tr>
<td>ISAF carbon black</td>
<td>65</td>
<td>—</td>
<td>65</td>
<td>Reinforcing filler</td>
</tr>
<tr>
<td>Sulfur</td>
<td>2.5</td>
<td>2.5</td>
<td>2.5</td>
<td>Vulcanizing agent</td>
</tr>
<tr>
<td>Substituted benzothiazole-2-sulfonamide</td>
<td>0.5</td>
<td>1.5</td>
<td>1.5</td>
<td>Accelerator</td>
</tr>
<tr>
<td>(N)-nitrosodiphenylamine</td>
<td>0.5</td>
<td>—</td>
<td>0.5</td>
<td>Retarder</td>
</tr>
<tr>
<td>Total weight</td>
<td>173.5</td>
<td>220.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Specific gravity</td>
<td>1.12</td>
<td>1.13</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<sup>a</sup>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 \( (\nu \approx \frac{1}{2}) \)
  - 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 $\Delta F$, the free energy change due to deformation ($-T\Delta S$).
  - Assume local and macroscopic deformations are the same (affine deformation).
  - Assume the volume does not change during deformation.
  - Rubbery materials are non-Hookean

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

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

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

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

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

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

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

$n = \# \text{ active chains per unit volume}$  
$\alpha: \text{ elongation ratio}$  

Ideal Rubber Behavior
Theory of Rubber Elasticity
Comparison of Experiment and Theory

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 $nRT = 0.39$ N/mm² (37, 38).

Figure 14.6: Extension or compression ratio $\lambda$ as a function of the tensile or compressive force $f$ for a rubber vulcanize. Theoretical curve is derived from equation (14.21) using $G = 0.392$ MN m⁻². (From data by Treloar, 1944.)
Assume an elastomer of $0.1 \times 0.1 \times 10$ cm$^3$ is stretched to 25 cm length at 35°C, a stress of $2 \times 10^7$ dynes/cm$^2$ being required. What is the concentration of active network chains and what is the magnitude of the shear modulus?

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

$$G = nRT$$

$n = 3.3 \times 10^{-4}$ mol/cm$^3$  \hspace{1em} G = 0.86$ J/cm$^3$ or $G = 0.86$ MPa
Theory of Rubber Elasticity

Ideal Rubber Equation of State

dU = dw + dq

\[ dU = -pdV + fdL + TdS = fdL + TdS \]

\[ F = U - TS \]

\[ dF = dU - TdS - SdT \]

\[ dF = fdL - SdT \implies f = \left( \frac{\partial F}{\partial L} \right)_{v,T} \]

\[ f = \left( \frac{\partial F}{\partial L} \right)_{v,T} = \left( \frac{\partial U}{\partial L} \right)_{v,T} - T \left( \frac{\partial S}{\partial L} \right)_{v,T} - S \left( \frac{\partial T}{\partial L} \right)_{v,T} \]

\[ dF = fdL - SdT \implies \left( \frac{\partial S}{\partial L} \right)_{v,T} = -\left( \frac{\partial f}{\partial T} \right)_{v,L} \]

\[ f = \left( \frac{\partial U}{\partial L} \right)_{v,T} + T \left( \frac{\partial f}{\partial T} \right)_{v,L} \]

\[ f_e = \left( \frac{\partial U}{\partial L} \right)_{v,T} \]

\[ f_s = T \left( \frac{\partial f}{\partial T} \right)_{v,L} = -T \left( \frac{\partial S}{\partial L} \right)_{v,T} \]

Ideal Rubber EoS

\[ f = T \left( \frac{\partial f}{\partial T} \right)_{v,L} \]

\[ f_e = \left( \frac{\partial U}{\partial L} \right)_{v,T} = 0 \]
Theory of Rubber Elasticity

Rubber Thermoelastic Behavior

Stress required to achieve a given strain at a fixed temperature

Rubber sample at different percentage strains.

\[ \sigma = nRT \frac{r_i^2}{r_0^2} \left( \alpha - \frac{1}{\alpha^2} \right) \]

\[ f = f_e + f_s \]

\[ f_s = T \left( \frac{\partial f}{\partial T} \right)_{L,V} \]

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

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

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

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

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

<table>
<thead>
<tr>
<th>Polymer</th>
<th>( f_e ) / ( f )</th>
</tr>
</thead>
<tbody>
<tr>
<td>natural rubber</td>
<td>0.12</td>
</tr>
<tr>
<td>t-poly(isoprene)</td>
<td>0.10</td>
</tr>
<tr>
<td>cis poly(butadiene)</td>
<td>0.17</td>
</tr>
<tr>
<td>poly(ethylene)</td>
<td>-0.42</td>
</tr>
<tr>
<td>poly(ethyl acrylate)</td>
<td>-0.16</td>
</tr>
<tr>
<td>poly(dimethyl siloxane)</td>
<td>0.15</td>
</tr>
</tbody>
</table>
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

• 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) ?

− \( C_1 = 2 – 6 \text{ kg/cm}^2, \ C_2 = 2 \text{ kg/cm}^2 \)

− \( 2C_2/C_1 \) measures looseness of network (Flory)

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

\[
\sigma = n_c \left( 1 - \frac{2M}{M_c} \right) + n_p \left[ RT \frac{r_i^2}{r_0^2} \left( \alpha - \frac{1}{\alpha^2} \right) \right]
\]

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

\[ \Delta G_{SWEL} = \Delta G_{MIX} + \Delta G_{ELAST} \]

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

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

Flory-Rehner and Rubber Elasticity Theories

A: Constant
Q: Swelling Ratio

\[ G = \frac{ART}{V_1Q^{5/3}} \]

\[ Q = \frac{V}{V_0} = \frac{1}{v_2} \]