Chapter 3 Rubber Elastic State

3.1 Introduction

Natural rubber : A latex from Hevea Braziliensis
cf. rubber : material to remove marks from paper (지우개)

Elastomer : A polymer which exhibits rubber elastic properties

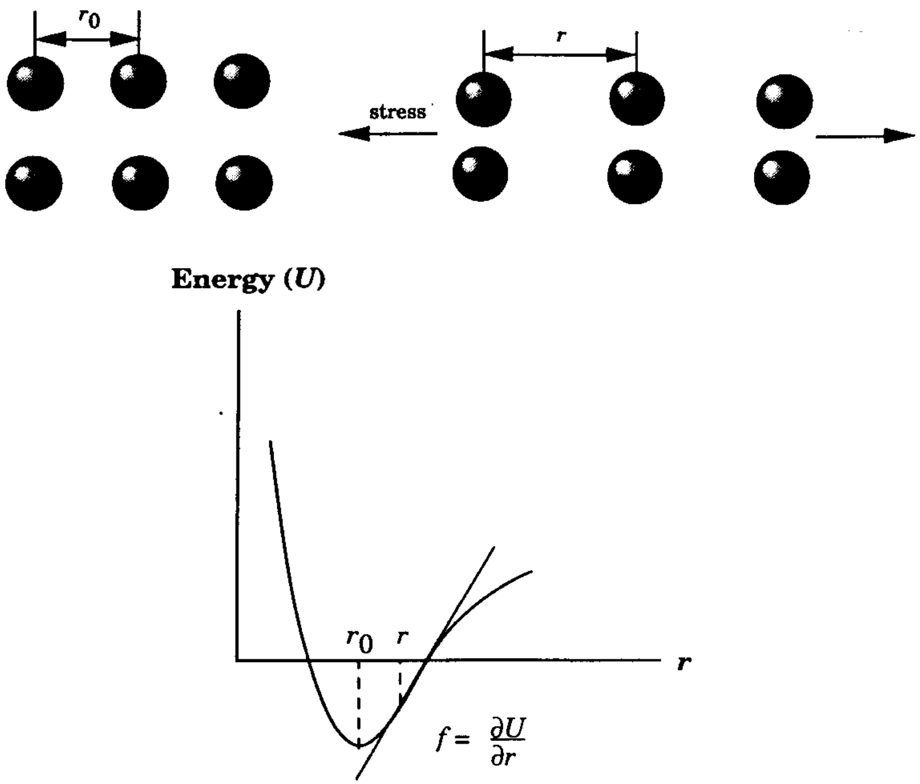
※ Rubber band experiment

100% strain by hanging a dead load

→ (heating) → suddenly decrease

• *Metals or highly crystalline materials*

→ Hookean elastic behavior (typically ε < 0.2 %)



$$U \approx C(r - r_0)^2$$

C : constant
r_0 : equilibrium bond length

$$f = \frac{\partial U}{\partial r} = 2C(r - r_0)$$

f : elastic force

$$\sigma = \frac{2C}{A}(r - r_0) = E\varepsilon$$

$E = 2Cr_0/A$

$$\varepsilon = \frac{r - r_0}{r_0}$$

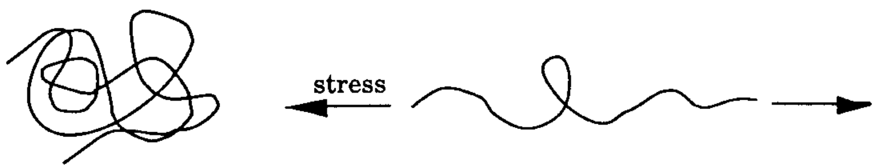
==> Hooke's law (energy-driven elasticity)

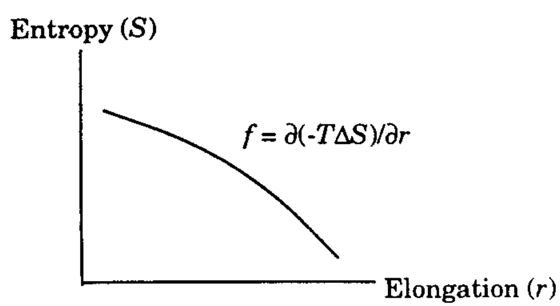
← U가 최소되는 상태 선호

- *Rubbers* (entropy-driven elasticity) ← S 가 최대되는 상태 선호

The entropy of the rubber decreases on stretching.

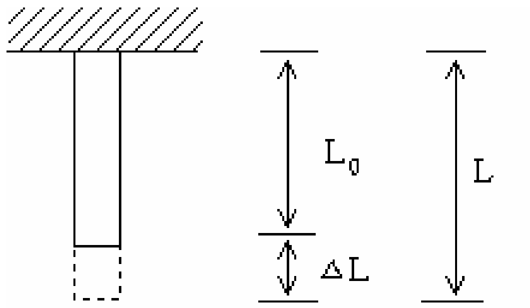
(Due to changes in the conformational entropy)





$$f = \frac{\partial(-T\Delta S)}{\partial r}$$

3.2 Thermodynamics of rubber elasticity



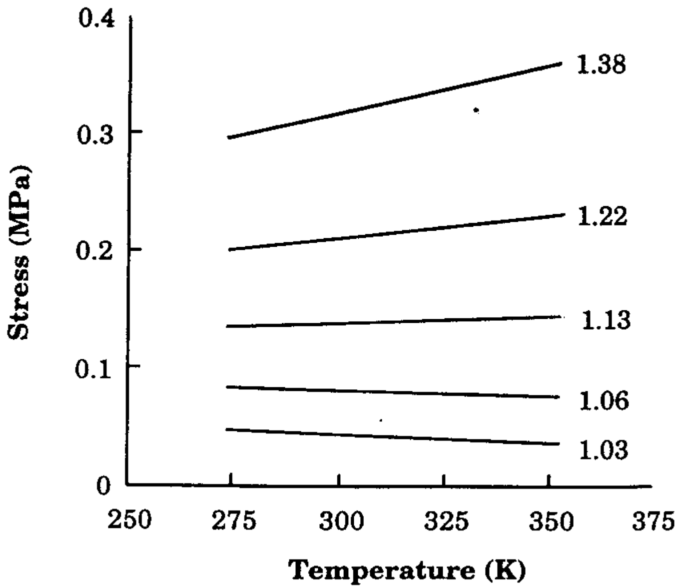
constant strain

Measuring σ with various temperature

$\lambda = L/L_0 < 1.1 \rightarrow \sigma \downarrow$ with T$\uparrow$

〃 $> 1.1 \rightarrow \sigma \uparrow$ with T$\uparrow$

"*thermo-elastic inversion*"



From the thermodynamic laws,

$$\underbrace{dE}_{\text{Internal energy change}} = \underbrace{TdS}_{dQ} \underbrace{- pdV + fdL}_{dW} \quad \text{: reversible process}$$

fdL: Work done by deformation

$$G = H - TS$$

$$= E + pV - TS \qquad \text{(미분하면)}$$

$$dG = fdL + Vdp - SdT$$

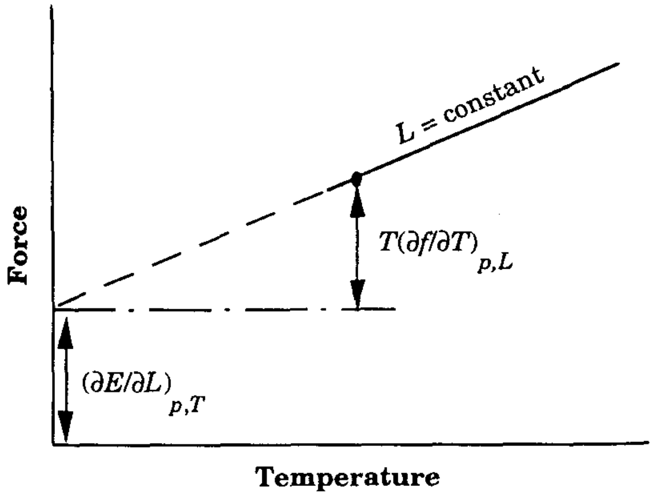
$$\left(\frac{\partial G}{\partial L}\right)_{T,p} = f, \qquad \left(\frac{\partial G}{\partial T}\right)_{p,L} = -S$$

G : *state function* (exact differential) 즉, 미분순서에 상관없음

$$\left(\frac{\partial f}{\partial T}\right)_{L,p} = -\left(\frac{\partial S}{\partial L}\right)_{p,T}$$: *Maxwell relation*

정리하면,

$$\Rightarrow \quad f = \underbrace{\left(\frac{\partial E}{\partial L}\right)_{p,T}}_{\text{Energetic component}} + \underbrace{T\left(\frac{\partial f}{\partial T}\right)_{p,L}}_{\text{Entropic component}}$$



Analogous expression for constant V conditions

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

Energetic force component

(f_e)

Entropic force component

(Natural rubber인 경우 80-85% 정도 차지)

Fraction of energetic force component

$$\frac{f_e}{f} = 1 - \frac{T}{f}\left(\frac{\partial f}{\partial T}\right)_{V,L}$$

f_e/f of PE : -0.42 $\Rightarrow$ extended conformation requires lower energy

f_e/f of natural rubber : 0.15 - 0.2

Table 3.1 Energetic stress ratio of a few polymers

Polymer	Diluent	v_2[a]	f_e/f
Polyethylene	none	1.00	−0.42
Polyethylene	n-$C_{30}H_{62}$	0.50	−0.64
Polyethylene	n-$C_{32}H_{66}$	0.30	−0.50
Natural rubber	none	1.00	0.17
Natural rubber	n-$C_{16}H_{34}$	0.34–0.98	0.18
Natural rubber	decalin	0.20	0.14
Poly(dimethyl siloxane)	none	1.00	0.25
Trans (1,4-polyisoprene)	none	1.00	−0.10
Trans (1,4-polyisoprene)	decalin	0.18	−0.20

Source: Mark (1984).
[a] Volume fraction of polymer in network.

3.3 Statistical theory of rubber elasticity

Affine network model *vs.* Phantom network model

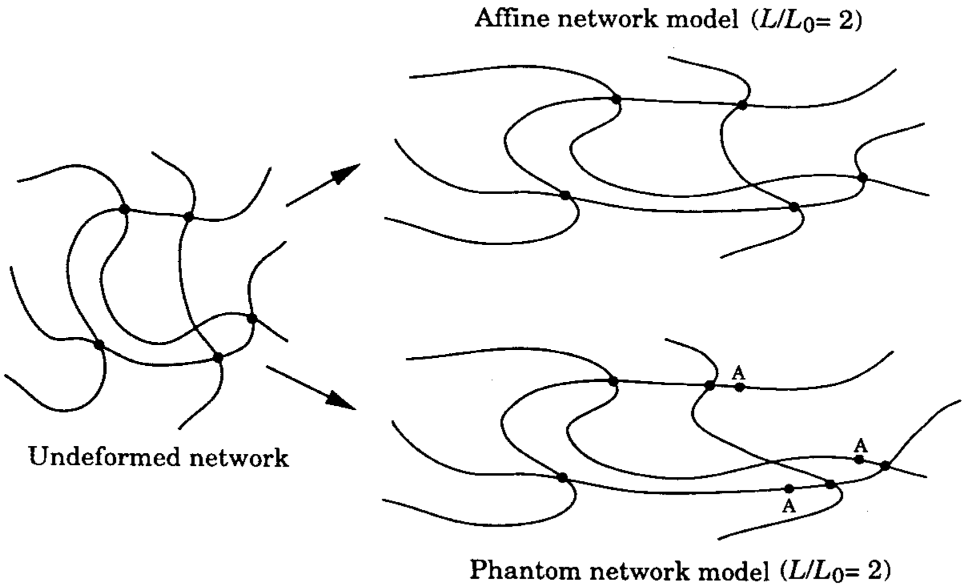


Figure 3.10 Schematical representation of the deformation of a network according to the affine network model (upper) and the phantom network model (lower). The points marked with an A indicate the position of the crosslinks assuming affine deformation.

Affine network model

Assumptions

- Chain segments are represented by Gaussian statistics
- S (entropy) of the network = Σ of S of the individual chains
- All different conformational states have the same energy
- Deformation is affine (균일 변형)
- Isotropic network at rest state
- Incompressible during deformation

Distribution of the end-to-end vectors

$$P(x,y,z)dxdydz = \left(\frac{3}{2\pi\langle r^2\rangle_0}\right)^{3/2} \exp\left(-3(x^2+y^2+z^2)/2\langle r^2\rangle_0\right)dxdydz$$

$\overline{r_0} = (x_0, y_0, z_0)$: unstressed state

$\overline{r} = (x, y, z)$: stressed state

$x = \lambda_1 x_0$

$y = \lambda_2 y_0$ $\lambda_1, \lambda_2, \lambda_3$: principal extension ratio (주 신장비)

$z = \lambda_3 y_0$

$S = k \ln P$: Boltzmann's entropy relationship

$\Delta G = \Delta H - T\Delta S$ 의 관계식을 이용하면,

ΔH = 0 : All conformational states have the same energy

→ $\Delta G = \frac{1}{2} nkT\left(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3\right)$

$nk = NR,\ R = N_A k$

n : # of Gaussian chain segments

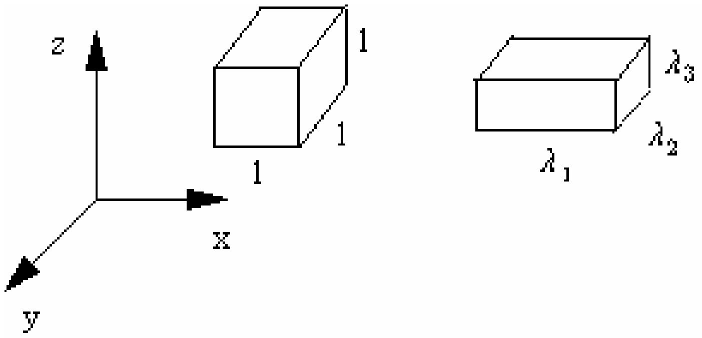
N : # of moles of Gaussian chain segments

* *Stress-strain equation for a uniaxial stress*

$$\lambda_1 = \lambda$$

$$\lambda_2 = \lambda_3 = \frac{1}{\sqrt{\lambda}} \quad \leftarrow \quad \lambda_1\lambda_2\lambda_3 = 1$$

$$\lambda = \frac{L}{L_0}$$



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

$$= \frac{nkT}{L_0}\left(\lambda - \frac{1}{\lambda^2}\right)$$

$$f = \sigma A = \sigma\left(\frac{A_0}{\lambda}\right) = \frac{NRT}{L_0}\left(\lambda - \frac{1}{\lambda^2}\right)$$

$$\therefore\ \sigma = \frac{NRT}{V_0}\left(\lambda^2 - \frac{1}{\lambda}\right)$$

$$\frac{N}{V_0} = \left(\frac{N\overline{M}_c}{V_0}\right)\left(\frac{1}{\overline{\overline{M}}_c}\right) = \left(\frac{m_0}{V_0}\right)\left(\frac{1}{\overline{\overline{M}}_c}\right) = \frac{\rho}{\overline{\overline{M}}_c}$$

$\overline{M}_c$: No. avg. MW of the Gaussian chain segments

$$\therefore\ \sigma = \frac{\rho RT}{\overline{\overline{M}}_c}\left(\lambda^2 - \frac{1}{\lambda}\right)$$

$$T\uparrow,\ \overline{M}_c\downarrow\ \rightarrow\ \sigma\uparrow$$

cf. Phantom network model

$$\sigma = \frac{\rho RT}{2\overline{\overline{M}}_c}\left(\lambda^2 - \frac{1}{\lambda}\right)$$: crosslink functionality가 4인 경우

3.5 Deviations from classical statistical theories

Loose chain ends do not contribute to the elastic force.

Modification of the stress-strain relationship

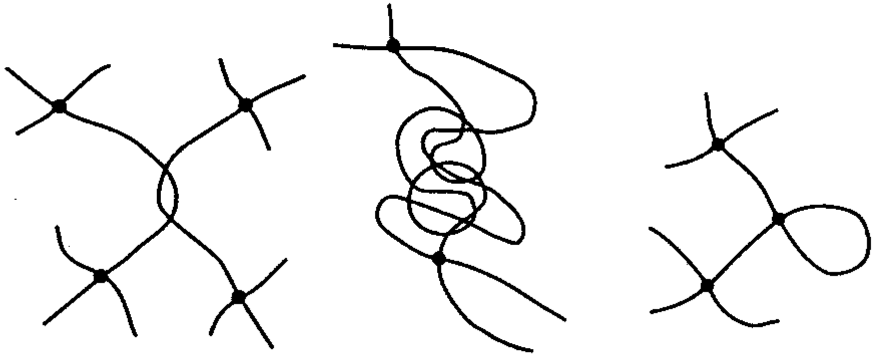
$$\sigma = \frac{\rho RT}{\overline{M}_c}\left(1 - \frac{2\overline{M}_c}{M}\right)\left(\lambda^2 - \frac{1}{\lambda}\right)$$

Other types of network defect :

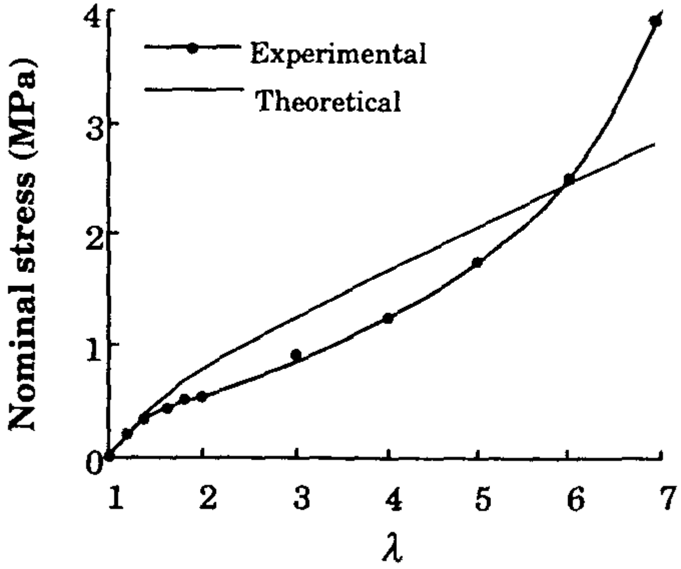
(a) permanent physical crosslinks

(b) temporary physical crosslinks

(c) intramolecular crosslink



(a) (b) (c)



Above λ = 4, positive curvature

Possible causes :

1) non-Gaussian behavior

2) crystallization

3.7 Theory of Mooney & Rivlin

(based on *continuum mechanics*)

· For a uniaxially stressed specimen,

Basis: Rubber is incompressible
Isotropic
Hookean behavior in simple shear

Mooney-Rivlin equation:

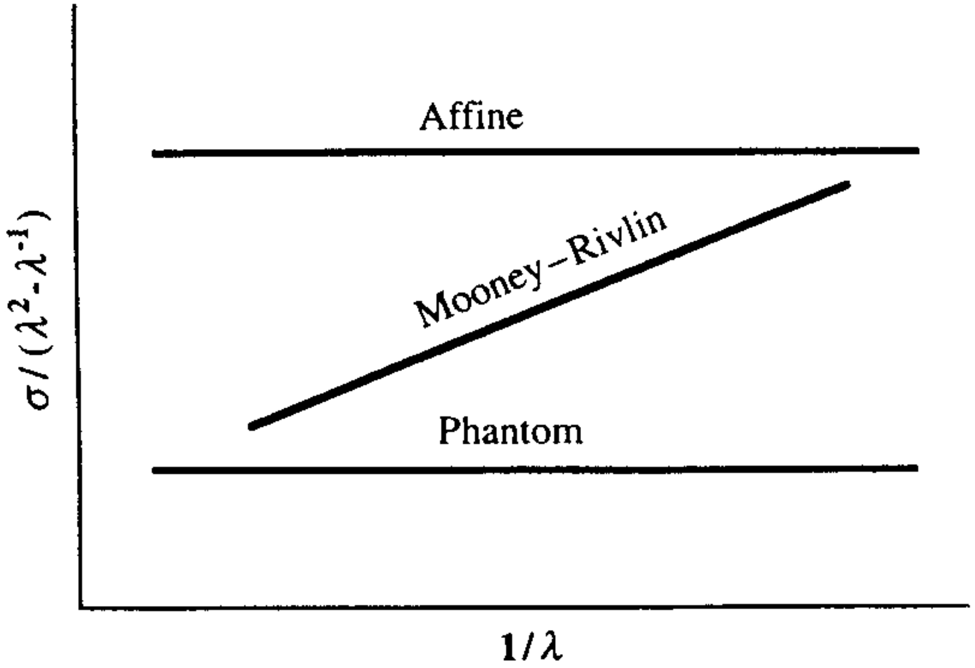
$$\sigma = 2\left(C_1 + \frac{C_2}{\lambda}\right)\left(\lambda^2 - \frac{1}{\lambda}\right)$$

C_1, C_2 : material constants

. Related to the looseness with which the crosslinks are imbedded in the structure.

. Solvent content $\uparrow \rightarrow C_2 \downarrow$

· $v_2 \leq 0.2 \rightarrow C_2 \approx 0$


Affine
Mooney–Rivlin
Phantom
$\sigma/(\lambda^2-\lambda^{-1})$
$1/\lambda$