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Course Notes of Chapter 4.1

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1. Introduction: Basic Mechanical Behavior

Slide 211 shows **the evolution of Young's modulus E of an amorphous polymer as a function of temperature.** This curve reflects the mechanical response of the material at **small deformation**, below and above the glass transition temperature T_g. As we have already discussed, the "transition zone" shifts toward higher temperatures when the measurement speed increases, due to the time-temperature equivalence principle.

At low temperatures, the material is in the **glassy regime**, where polymer chains cannot change their segmental conformations during deformation. Under stress, the deformation primarily changes the intermolecular distances rather than the conformations, increasing the enthalpic contribution to the cohesive energy E_{coh}. In this regime, $E \approx K$ (bulk modulus) ≈ 1–2 GPa, which is a relatively high value, since deformation primarily changes interatomic distances rather than conformations. Similar values are found for glassy semicrystalline polymers or semicrystalline polymers with a low T_g, provided their degree of crystallinity remains sufficiently high.

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Upon increasing the temperature, we enter **the transition zone**, where the elastic modulus drops by several orders of magnitude, and the response becomes highly sensitive to both temperature and strain rate. The material exhibits viscoelastic behavior, which we will describe in Chapter 4.2 of the class.

Finally, above T_g, we reach the **rubbery plateau**. Unlike conventional liquids, amorphous polymers maintain a nearly constant modulus (a few MPa) over a broad temperature range. Although E slightly increases with T in this regime, this variation is not visible on the logarithmic scale of the plot. For very low molar mass polymers, the plateau disappears and the material behaves like a viscous liquid immediately above T_g. For **elastomers** (crosslinked polymers of effectively infinite molar mass), the plateau persists up to the degradation temperature, with $E \approx 1$ MPa.

The goal of this week's lecture (and the first week after the semester break) is to describe and explain the elastomeric behavior observed in this plateau region.

1.1 Rubber Elasticity

The elasticity of glassy and semi-crystalline polymers arises primarily from cohesive interactions (E_{coh}), and is almost time-independent. At larger deformations, these materials typically exhibit plasticity or fracture, rather than reversible elasticity.

In contrast, **rubbers and elastomers can undergo large, reversible deformations**, often up to several hundred percent true strain. Three molecular features are essential for this behavior (Slide 215):

- **long and flexible chains**, capable of adopting a vast number of conformations.
- **weak intermolecular forces**, small compared to the forces involved in stretching the chains.
- **local anchoring points** (either chemical crosslinks or topological entanglements) that prevent irreversible flow.

Thus, rubber elasticity is a phenomenon **unique to polymers in the rubbery state**, i.e. above their T_g. Polymers exhibiting rubbery behavior at room temperature are typically low-T_g, flexible polymers with little or no crystallization tendency. Typical examples include random aliphatic copolymers, polymers based on dienes (such as natural rubber, with C=C double bonds), or heteroatomic main chains (such as polysiloxanes).

While C=C double bonds might suggest restricted rotation, in polyisoprene the neighboring carbons are only monosubstituted, and the smallest substituents (H or CH_3) actually facilitate rotation around adjacent C–C bonds because steric hindrance is minimal. Likewise, the Si–O and Si–Si bonds in heteroatomic chains exhibit low rotational barriers, contributing to high chain flexibility.

1.2 Elastomers or Rubbers?

By definition, **a rubber is an amorphous polymer in the rubbery state**, i.e. used at $T > T_g$ within the rubbery plateau. An **elastomer is a lightly crosslinked polymer** (chemically or physically) whose service temperature lies within this rubbery regime.

While rubbers can be uncrosslinked, the crosslinking in elastomers prevents viscous flow and ensures permanent elasticity. The crosslinks serve as permanent junction points that help returning the network to its original dimensions after unloading. The entanglement plateau that appears in non-crosslinked polymers at sufficiently high molar mass will be discussed later (Chapter 4.2 of the class). This week, and at the beginning of next week, we focus primarily on elastomers.

2. Phenomenology

2.1 Rubbery Behavior

The compression modulus

$$K = \frac{8E_{coh}}{V_0} \quad , \tag{1}$$

remains nearly constant with T, around 5 GPa, both below and above T_g (think of liquid water: perfectly fluid, yet almost incompressible – jumping from the Golden Gate Bridge would feel like hitting concrete due to the high K of water).

In contrast, the **Young's modulus $\boldsymbol{E}$ decreases by roughly three orders of magnitude above $\boldsymbol{T_g}$.** As a consequence, a relatively small force can produce large uniaxial deformations. Since K remains large, the volume change during deformation is, however, small, and the material behaves as effectively incompressible (Slide 219).

This can be expressed through the **Poisson's ratio $\boldsymbol{v}$** which is defined as the ratio between transverse contraction and longitudinal extension under uniaxial load. The relative volume change during elongation Δl is given by:

$$\frac{\Delta \mathrm{V}}{V_0} = (1-2v)\frac{\Delta l}{l_0} \equiv (1-2v)\varepsilon \quad , \tag{2}$$

and

$$v = \frac{1}{2}\left(1 - \frac{E}{3K}\right) \quad . \tag{3}$$

For rubbery materials, since $K \gg E$, one finds $v = 0.5$. Hence, **rubbers and elastomers are often treated as incompressible solids.**

2.2 Thermodynamics of the Deformation of an Elastomer

As early as 1802, John Gough and later James Prescott Joule measured the elastic force f as a function of T at constant stretching l by heating or cooling stretched rubber samples. They observed that, above T_g:

$$f \propto T \quad , \tag{4}$$

indicating that the restoring force increases linearly with temperature at constant extension. This implies that $(\partial U/\partial l)_{T,V} \approx 0$. Hence, **the deformation does not significantly alter the internal energy (enthalpic) of the system. Therefore, the elastic force arises almost entirely from entropy changes** (entropic elasticity, Slides 220–222). For a detailed thermodynamic description of rubber elasticity, see the Reader on Rubber Elasticity.

Below T_g, conformational changes are frozen, the deformation modifies E_coh and thus the internal energy U, leading to enthalpic elasticity. **Above T_g, barriers to conformational changes vanish, and the internal energy remains constant during stretching. Deformation then reduces the entropy of the system, as stretched chains have fewer conformational possibilities. This entropy decrease corresponds to an increase in the Helmholtz free energy, generating a restoring force that drives the system back to its most probable (maximum entropy) state upon unloading** (Slides 222 and 223)**.**

This entropic nature of the restoring force explains the counterintuitive temperature behavior of rubbers (Slide 214):

- the **modulus increases with T** ($f \propto T$),
- rubbers **contract when heated** under tension (the Gough-Joule effect),
- and they **heat up during rapid stretching**, as entropy decreases faster than heat can be exchanged with the environment.

3. Molecular Theory of Rubber Elasticity

The molecular origin of rubber elasticity can be described quantitatively using **statistical thermodynamics**. In this framework, the restoring force of a stretched elastomer arises from the entropy change associated with deforming long, flexible polymer chains whose ends are constrained within a three-dimensional network, by chemical crosslinks or entanglements.

The analysis proceeds in two main steps (see the Reader on Rubber Elasticity for details):

1.) single-chain entropy:

Each network strand (a subchain between two crosslinks) **is modeled as an ideal freely jointed chain** with n segments of length a. The probability of finding such a chain with an end-to-end vector $\vec{R}_n$ follows a three-dimensional **Gaussian distribution**. From this, the conformational entropy of a single chain is obtained as

$$S^c = S_0 - \frac{3kR_n{}^2}{2na^2} \quad , \tag{5}$$

indicating that the entropy decreases quadratically as the chain is stretched. The most probable (and most entropic) state is the random coil, while stretched conformations are exponentially less probable.

2.) Network averaging (affine network model):

In the **affine network model** (Slide 225), the macroscopic deformation is transmitted directly to all strands. Averaging over an isotropic distribution of chains and summing over all strands (with N chains per unit volume) yields the total free-energy change:

$$\Delta A = \frac{NkT}{2}\left[\lambda_1{}^2 + \lambda_2{}^2 + \lambda_3{}^2 - 3\right] \quad . \tag{6}$$

where λ_i are the principal stretch ratios (Slide 229).

For **uniaxial tension** of an incompressible rubber ($\lambda_1 = \lambda,\ \lambda_2 = \lambda_3 = 1/\sqrt{\lambda}$), differentiation of this free energy with respect to the stretch ratio gives the tensile stress.

$$\sigma = NkT(\lambda - \lambda^{-2}) \quad . \tag{7}$$

For small deformations ($\varepsilon = \lambda - 1 \ll 1$), this simplifies to a linear relation:

$$\sigma \approx 3NkT\varepsilon \quad . \tag{8}$$

Hence, the **Young's modulus** is

$$E = \frac{\sigma}{\varepsilon} = 3NkT \quad , \tag{9}$$

and the corresponding **shear modulus** is

$$G = \frac{E}{3} = NkT \quad . \tag{10}$$

Physical implications (Slide 230)**:**

- **elasticity is entropic**: deformation alters the number of chain conformations, not the internal energy.
- $E \propto T$: **rubbers become stiffer when heated**, in contrast to most materials.
- $E \propto N$: **the modulus increases with crosslink density** (e.g., through vulcanization)
- chain characteristics cancel out: in the Gaussian limit, the modulus depends only on strand density, not on n or a.

Limitations (Slide 231):

- **finite extensibility**: at large stretches, the Gaussian assumption fails; chain stiffening can be described by using the **Langevin** function (Slide 232).
- **high crosslinking density**: when subchains become very short, and the Gaussian assumption becomes invalid.
- **network topology**: the affine model assumes all chains deform identically. Real networks exhibit non-affine deformations, especially near defects or dangling ends.
- **phantom network approximation**: chains are treated as if they can pass through one another, neglecting excluded-volume effects.
- **energetic contributions**: at large deformations or for stiff chains, internal energy changes become significant
- **strain-induced crystallization** is ignored.

4. Empirical Approaches

While Equations 7 and 9 describe the behavior of ideal rubbers remarkably well, practical materials often deviate from this simple model. To account for such effects, empirical models such as the Mooney-Rivlin equation are used (Slides 233 and 234). These models assume that the strain energy density is a scalar quantity that is independent of the coordinate system, and can therefore be expressed as a function of the **invariants** of the deformation tensor:

$$I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2, \quad I_2 = \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2, \quad I_3 = \lambda_1^2\lambda_2^2\lambda_3^2. \tag{11}$$

The use of **even powers** of the principal stretches reflects the **isotropic** nature and **incompressibility** of elastomers. Because the strain energy is proportional to the square of the deformation (as in a Hookean spring), we focus on the invariants I_1, I_2, and I_3.

For incompressible rubbers, $\lambda_1\lambda_2\lambda_3 = 1$, and the strain energy function can be expanded as

$$\Delta A = \mathrm{C}_{10}(I_1 - 3) + \mathrm{C}_{01}(I_2 - 3). \tag{12}$$

where C_{10} and C_{01} are empirical constants.

In the simplest case ($\mathrm{C}_{01} = 0$ and $\mathrm{C}_{10} = 1/2\, N\mathrm{k}T$), this expression reduces to the statistical theory prediction (Equation 6). Additional terms can be included to improve agreement with experimental stress-strain data.

5. Summary

- **elastomers can undergo very large, reversible deformations**: this behavior is unique to lightly cross-linked, flexible polymers above their T_g.

- the stress-strain behavior of elastomers is dominated by **entropic elasticity**, which can be explained by statistical mechanics: stretching lowers configurational entropy and generates an entropic restoring force that scales linearly with T.
- this restoring force arises because deformation decreases the number of accessible chain conformations, reducing entropy and increasing the free energy.
- the molecular theory predicts $\boldsymbol{E = 3N\mathrm{k}T}$, explaining why rubbers become stiffer when heated or more densely crosslinked.
- the theory applies primarily to **amorphous, non-crystallizing polymers in the rubbery state**, such as polybutadiene, *cis*-1,4-polyisoprene, neoprene, polyisobutylene, and various random copolymers (Slides 237–239).