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Course Notes of Chapter 4.1

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1. Introduction: Basic Mechanical Behavior

Slide 196 shows **the diagram which summarizes the evolution of the modulus (Young's modulus in this case) of an amorphous polymer as a function of temperature** and which therefore reflects **the behavior at small deformations** below and above the glass transition (the "transition zone", as we have already seen, moves towards higher temperatures, if we increase the speed of measurement).

1. At low temperatures, we can identify **the glassy regime**, where the molecules do not change their conformation during small deformations. By applying a stress to the material, rather the separation of molecules tends to increase and, hence, the enthalpic contribution to E_{coh}. The Young's modulus is therefore quite close to the compression modulus, K, i.e. on the order of 2 GPa. Similar values are also found in glassy semicrystalline polymers and also in semi-crystalline polymers with a low T_g, provided that the degree of crystallinity remains fairly high.

2. By increasing the temperature, we enter **the transition zone**, where the modulus decreases substantially. In this regime the behavior becomes very sensitive not only to the temperature but also to the measurement speed. We speak of a "viscoelastic" behavior, which we will phenomenologically describe next week (along with molecular models).
3. Finally, we enter the **rubbery state**. Unlike a conventional liquid, amorphous polymers show a more or less extended temperature plateau above T_g, depending on the molar mass, where the modulus remains approximately constant at a few MPa (in fact, we will see that it increases with T in this regime, but this is not seen on a logarithmic scale that covers several orders of magnitude). Thus, if the mass becomes very low, we find the behavior of a classical liquid and the elastic modulus tends towards zero immediately above T_g, while for an elastomer (crosslinked rubbery polymer with an effectively infinite mass), the modulus remains around 1 MPa until the degradation temperature.

The goal of this week's course is to describe and explain this "elastomeric" behavior.

1.1 Rubber Elasticity

The elasticity of glassy and semi-crystalline polymers depends essentially on E_{coh}, and generally little on the time scale of the measurement, whereas, as we will see later (Chapter 4.3), large deformations are in general permanent (plasticity or rupture). On the other hand, **rubbers and elastomers are materials capable of large elastic (reversible) deformations** ranging to several hundred percent. Three conditions are necessary for this:

- Long and flexible chains.
- Intermolecular forces that are globally weak compared to other forces that come into play during deformation.
- Local anchoring points (entanglements, cross-links).

The "rubbery" elasticity is therefore a phenomenon almost unique to organic polymers above their T_g. Polymers which show rubbery behavior at ambient temperature are typically low T_g flexible polymers which crystallize little or not at all. Often, these are random aliphatic copolymers, with catenary double bonds (dienes - *cf.* natural rubber) or heteroatomic chains (containing S, Si or O in addition to C). You may wonder whether a double bond will increase the stiffness of a polymer chain, because of the hindered rotation. However, the carbons are only monosubstituted, and in case of an attached H atom or some other small substituent, we facilitate the rotation of the C-C bonds on either side of the double bond. And the -Si- or -O- of a heteroatomic chain are even less bulky.

1.2 Elastomers or Rubbers?

By definition, a rubber is an amorphous polymer in the rubbery state, i.e. operated at a temperature above T_g within the rubbery plateau. An elastomer is a lightly crosslinked ("vulcanized") polymer whose use temperature corresponds to the rubbery state. We will discuss entanglement, the phenomenon that gives rise to a rubbery plateau in non-crosslinked polymers at another day. This week's discussion will focus on elastomers.

2. Phenomenology

2.1 Rubbery Behavior

The compression modulus

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

varies little with T, always being on the order of 5 GPa whether we are below or above T_g (think of liquid water for example, which is perfectly liquid, but almost incompressible – if you don't believe me, imagine that the immediate impact at the water surface after jumping from the Golden Gate Bridge will be similar like falling onto a floor of concrete). On the other hand, Young's modulus, E, decreases by a factor of 1000 above T_g. That implies that one needs a relatively small force to apply large uniaxial deformations to the material. As K remains high, the volume does not change much under these conditions and the material effectively becomes incompressible, even if K has not changed.

We can express this idea in terms of the Poisson's ratio v which is the ratio between the relative transverse shrinkage and relative longitudinal elongation when pulled. The change in volume during lengthening Δl is

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

and

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

is therefore close to 0.5 in the rubbery state, because $K >> E$. **Rubbery polymers and elastomers are often considered incompressible.**

2.2 Thermodynamics of the Deformation of an Elastomer

For a process proceeding under constant pressure, where volume changes are negligible, instead of

$$G = H - TS = U + pV - TS \tag{4}$$

we can employ the **Helmholtz free energy**

$$A = U - TS \qquad (5).$$

If the length of the sample changes by $\mathrm{d}l$ during the application of an external force f, the internal energy change will be:

$$\mathrm{d}U = \mathrm{d}Q - \mathrm{d}W = T\mathrm{d}S + f\mathrm{d}l \quad (6),$$

$$\mathrm{d}A = \mathrm{d}U - T\mathrm{d}S - S\mathrm{d}T = f\mathrm{d}l - S\mathrm{d}T \quad (7),$$

where $f\mathrm{d}l$ is the effort made by the system against the force f and $\mathrm{d}Q$ is the change in heat. From the identity (Equation 8), it follows for f:

$$\mathrm{d}F(x,y) = \left(\frac{\partial F}{\partial y}\right)_x \mathrm{d}y + \left(\frac{\partial F}{\partial x}\right)_y \mathrm{d}x \quad (8),$$

$$f = \left(\frac{\partial A}{\partial l}\right)_T, \quad -S = \left(\frac{\partial A}{\partial T}\right)_l \quad (9).$$

We are looking for an expression for the force, f, in terms of quantities that we can measure, and must therefore eliminate S. We therefore take the expressions we have just obtained, and we use the identity

$$\frac{\partial^2 F(x,y)}{\partial x \partial y} = \frac{\partial}{\partial x}\left(\left(\frac{\partial F}{\partial y}\right)_x\right)_y = \frac{\partial}{\partial x}\left(\left(\frac{\partial F}{\partial x}\right)_y\right)_x \quad (10).$$

$$\left(\frac{\partial f}{\partial T}\right)_l = -\left(\frac{\partial S}{\partial l}\right)_T \quad (11).$$

Now we can go back to Equation 9 and use Equation 11 to eliminate the entropy term:

$$f = \left(\frac{\partial A}{\partial l}\right)_T = \left(\frac{\partial U}{\partial l}\right)_T - T\left(\frac{\partial S}{\partial l}\right)_T = \left(\frac{\partial U}{\partial l}\right)_T + T\left(\frac{\partial f}{\partial T}\right)_l \quad (12).$$

This is the result we were looking for: an expression for f in terms of l that does not contain a term in S. What can be done with this result?

Already in 1802, John Gough (then James Prescott Joule later in the 1850s) determined f (or the stress) as a function of T for a constant l (by changing the temperature of an elastomer at constant strain, while measuring the force). **Joule was able to demonstrate that for a (large) constant deformation: $f \propto T$ for $T > T_g$** (Slide 207). If we compare this result with Equation 12, we see that this implies that the contribution of internal energy to f is negligible. **The response of a polymer to a force in the rubbery state is therefore dominated by the second term of Equation 12, i.e. by the entropic contribution.**

As a physical interpretation (Slide 208), **we admit that above T_g, the energetic barrier to changes in conformation is negligible** and therefore the chains can be stretched upon deformation without changing E_{coh}. Chain stretching changes entropy, (because the undeformed conformations correspond to the maximum entropy of the system), and therefore

A. If there is a change of A as a function of l, there is a force, f. The question now is how to calculate this force.

3. Molecular Theory of Rubber Elasticity

3.1 Entropy of a Chain

We start with the expression for the probability that the two ends of a freely jointed chain are separated by a distance r (Slide 211):

$$P(r)dr = 4\pi r^2 \left(\frac{3}{2\pi}\right)^{3/2} \left(\frac{1}{\sqrt{n}a}\right)^3 exp\left(-\frac{3r^2}{2na^2}\right) dr \qquad (13).$$

(n = number of links, a = length of a link).

We then obtain an expression for the probability $W(\vec{r})$ that one end of the chain is at $\vec{r} = \vec{x}, \vec{y}, \vec{z}$, if the other end is at (0,0,0) (Slide 211):

$$W(\vec{r})dr = \frac{P(r)dr}{4\pi r^2} = \left(\frac{3}{2\pi}\right)^{3/2} \left(\frac{1}{\sqrt{n}a}\right)^3 exp\left(-\frac{3r^2}{2na^2}\right) dr \qquad (14).$$

Then, we admit that the number of possible conformations $\Omega(\vec{r})$ for a chain whose two ends define $\vec{r}$ is proportional to $W(\vec{r})$. Thus, the conformational entropy of the chain is

$$S^c(\vec{r}) = kln[\Omega(\vec{r})] = C + kln[\mathrm{W}(\vec{r})] \qquad (15).$$

$$S^c(\vec{r}) = C + kln\left[\left(\frac{3}{2\pi}\right)^{\frac{3}{2}} \left(\frac{1}{\sqrt{n}a}\right)^3 exp\left(-\frac{3r^2}{2na^2}\right)\right] \qquad (16).$$

$$= C + k\left(ln\left[\left(\frac{3}{2\pi}\right)^{\frac{3}{2}} \left(\frac{1}{\sqrt{n}a}\right)^3\right] - \frac{3r^2}{2na^2}\right) \quad \Rightarrow S^c(\vec{r}) = S_0 - \frac{3r^2}{2na^2} \qquad (17).$$

3.2 Effect of a Deformation

We will now apply a deformation λ which has the effect of transforming $\vec{r} = \vec{x}, \vec{y}, \vec{z}$ into $\vec{r}(\lambda) = \lambda_1\vec{x}, \lambda_2\vec{y}, \lambda_3\vec{z}$ as shown in the diagram on Slide 213. The entropy change is

$$\Delta S^c = -\frac{3k(r(\lambda)^2 - r^2)}{2na^2} = -\frac{3k((\lambda_1^2-1)x^2 + (\lambda_2^2-1)y^2 + (\lambda_3^2-1)z^2)}{2na^2} \qquad (18).$$

Assuming that there is no change in internal energy during deformation, the change of free energy (Equation 5) is $\Delta A^c = -T\Delta S^c$ and hence

$$\Delta A^c = \frac{3kT((\lambda_1^2-1)x^2 + (\lambda_2^2-1)y^2 + (\lambda_3^2-1)z^2)}{2na^2} \qquad (19).$$

Consider a network of N freely jointed subchains per unit volume (equivalent to N crosslink points) with an average of n bonds per subchain. The mean square distance between the ends of these subchains in the absence of deformation is (as you know...):

$$\langle R_n^2 \rangle = na^2 \qquad \text{or} \qquad \langle x_n^2 \rangle + \langle y_n^2 \rangle + \langle z_n^2 \rangle = na^2 \tag{20}$$

Since the direction of $\vec{r}$ arbitrary,

$$\langle x_n^2 \rangle = \langle y_n^2 \rangle = \langle z_n^2 \rangle = \frac{na^2}{3} \tag{21}$$

So, **for a small deformation of an elastomer, such that all the subchains follow the macroscopic deformation because they are connected by N crosslinking points per unit volume**,

$$\langle \Delta A^c \rangle = \frac{3kT\left((\lambda_1^2 - 1)\langle x_n^2 \rangle + (\lambda_2^2 - 1)\langle y_n^2 \rangle + (\lambda_3^2 - 1)\langle z_n^2 \rangle\right)}{2na^2}$$
$$= \frac{kT\left((\lambda_1^2 - 1) + (\lambda_2^2 - 1) + (\lambda_3^2 - 1)\right)}{2} \tag{22}$$

The change in free energy per unit volume is thus

$$\Delta A = N\langle \Delta A^c \rangle = \frac{NkT(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3)}{2} \tag{23}$$

Now consider a uniaxial strain $\lambda_1 = \lambda$. As our elastomer is incompressible $\lambda_1\lambda_2\lambda_3 = 1$, and

$$\lambda_2 = \lambda_3 = \frac{1}{\sqrt{\lambda}} \tag{24}$$

So,

$$\Delta A = \frac{NkT(\lambda^1 + 2\lambda^{-1} - 3)}{2} \tag{25}$$

If we apply a change in length l to a unit volume of the elastomer, $\lambda = 1 + l$ and $\mathrm{d}\lambda = \mathrm{d}l$. So (Equation 12), the stress, σ, corresponding to $\mathrm{d}l$, i.e. force / unit area

$$\sigma = f = \left(\frac{\partial A}{\partial l}\right)_T = \left(\frac{\partial A}{\partial \lambda}\right)_T = \frac{\partial}{\partial \lambda}\left(\frac{NkT(\lambda^2 + 2\lambda^{-1} - 3)}{2}\right) = NkT(\lambda - \lambda^{-2}) \tag{26}$$

Finally, if the strain is defined by $\varepsilon = \lambda - 1$, within the limit where $\varepsilon \rightarrow 0$

$$\sigma = NkT\left(1 + \varepsilon - \frac{1}{(1+\varepsilon)^2}\right) = NkT\frac{(1+\varepsilon)^3 - 1}{(1+\varepsilon)^2} = NkT\frac{\varepsilon^3 + 3\varepsilon^2 + 3\varepsilon}{(1+\varepsilon)^2}$$
$$\approx 3NkT\varepsilon \tag{27}$$

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And Young's modulus is

$$E = \frac{\varepsilon}{\sigma} = 3NkT \quad (28).$$

This result is quite astonishing! The elasticity of a network of flexible chains in the rubbery state depends only on the crosslinking density, *N*, and the temperature! (Note that this result does not depend on C_∞ because all terms in na^2 cancel out). We also notice that Equations 26 and 28 are consistent with Equation 12: The stiffness of an elastomer increases with temperature.

Finally, **the shear modulus G for an incompressible material is simply $G = E/3 = 3NkT$.**

Obviously, our approach is a bit simplistic. For example:

a) We consider that each sub-chain constituting the network changes conformation independently from other chains, implying that it can intersect its neighbors as if they weren't there (we speak of a "phantom network").

b) The distribution of Equation 13 suggests that $P(r)$ remains finite for $r > na$, which does not make sense. This expression remains a good approximation at small strains, but Equation 28 is no longer valid when

$$\lambda \rightarrow \frac{na}{\sqrt{n}a} = n^{-\frac{1}{2}} \quad (29).$$

c) The crystallization, which can take place at large deformations in natural rubber, is ignored.

d) For excessively high crosslinking densities, *N*, the number of bonds per subchains becomes small and the freely jointed chain model is no longer valid.

Nevertheless, this approach works well enough for small strains and low degrees of crosslinking, and the difficulty b) can be solved by using more realistic distributions such as "Langevin" distribution, which tends towards zero for $r = na$. In this case, ***E* suddenly increases towards large deformations, because one begins to draw directly on the C-C connections once all chains are extended** (Slide 218).

3.3 Empirical Approaches

While Equations 26 and 28 are remarkably realistic, **an engineer often needs even more precise expressions, like the empirical Mooney-Rivlin expression**. Here we assume that the strain energy is a scalar quantity and therefore independent of the choice of a reference (a coordinate system) that we used to express a deformation. It is therefore a function of the "invariants" of the deformation:

$$\begin{aligned} I_1 &= \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \\ I_2 &= \lambda_1^2\lambda_2^2 + \lambda_2^2\lambda_3^2 + \lambda_3^2\lambda_1^2 \\ I_3 &= \lambda_1^2\lambda_2^2\lambda_3^2 \end{aligned} \quad (30).$$

If we admit that an elastomer is incompressible, $\lambda_1\lambda_2\lambda_3 = 1$, and

$$\begin{gathered} I_1 = \lambda_1^2 + \lambda_2^2 + \lambda_3^2 \\ I_2 = \lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2} \\ I_3 = 1 \end{gathered} \tag{31}$$

Thus, assuming that ΔA = 0 in the absence of deformation, or if $\lambda_1 = \lambda_2 = \lambda_3 = 1$:

$$\Delta A = \sum_{m,n=0}^{\infty} C_{mn}(I_1 - 3)^m (I_2 - 3)^n = C_{10}(I_3 - 3) + C_{01}(I_2 - 3) + \cdots \tag{32}$$

$$\sigma = \frac{d\Delta A}{d\lambda} = \frac{d}{d\lambda}\left(C_{10}(\lambda_1^2 + \lambda_2^2 + \lambda_3^2 - 3) + C_{01}(\lambda_1^{-2} + \lambda_2^{-2} + \lambda_3^{-2} - 3) + \cdots\right) \tag{33}$$

Thus, for a uniaxial tension, $\lambda_1 = \lambda$, and

$$\sigma = 2C_{10}(\lambda - \lambda^{-2}) + 2C_{01}(1 - \lambda^{-3}) + \cdots \tag{34}$$

We thus find Equation 26 (assuming that C_{10} = 0.5 NkT) plus other terms with arbitrary constants, which can be adjusted as desired, to better simulate the real behavior.

4. Summary

• Elastomers are materials capable of undergoing very large reversible deformations: this phenomenon is at present limited to lightly cross-linked flexible polymers above T_g.

• Thermodynamic analysis reveals a dominant entropic contribution to the stress-strain behavior of elastomers.

• The forces opposing deformation arise from the reduced number of conformational states available to a stretched chain (equivalent to a decrease in entropy and hence an increase in free energy).

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