

Lab Week 4 – Module α_1

Polymer chains as entropy springs: Rubber stretching experiment and XRD study

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Objectives

- Review thermodynamic principles of deformed elastomers as entropy springs
- Review statistical theory of deformed elastomers relating stress-strain behavior to changes in molecular structure
- Study the structural development of uniaxially stretched rubber using X-ray diffraction (XRD)
- Study the thermo-mechanical behavior of rubber under uniaxial stress

Summary of tasks

- Prepare rubber samples of various extension ratios for X-ray Diffraction (XRD) analysis.
- Obtain X-ray patterns for all samples.
- Compare diffraction patterns and comment on similarities/differences.
- Identify the crystalline phase occurring at high strain level and calculate unit cell parameters.
- Perform peak profile fitting to determine percent crystallinity.
- Verify the theoretical equation relating extension and temperature for a rubber under uniaxial stress. Comment on any deviations from theory.
- Calculate cross-link density of a stretched rubber.

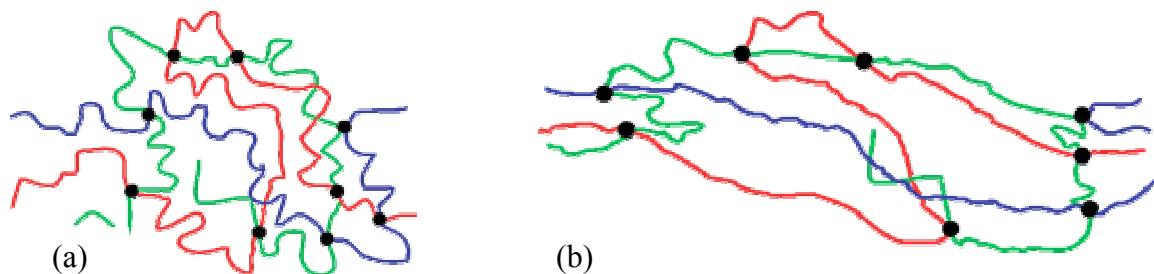
Introduction

Most materials, such as crystalline solids and amorphous glasses, when subjected to an external stress, behave elastically only until about 1% strain, after which they undergo plastic deformation. Rubbers or **elastomers** are polymeric materials that can sustain large elastic strains without deforming plastically or breaking. In this lab, we will study the structure and mechanical stress-strain response of rubber, and explain our results through a consideration of the thermodynamic properties of rubbers. In particular, we will see that the molecular structure of rubber causes entropic effects, rather than energetic effects, to control its mechanical properties.

Elastomer Structure

Undeformed Elastomers¹

Elastomers are polymeric materials that are composed of randomly oriented polymer chains. The chains are typically coiled rather than aligned, and typically are able to slide past each other and to sustain rotations about the bonds along the chain backbone. Elastomers deform by these mechanisms: chains can slide or uncoil to adopt different conformations in response to an applied stress.



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Figure 1 (a) Elastomers consist of random networks of coiled polymer chains joined at points by crosslinks (represented by black dots). (b) Upon deformation, the chains uncoil and align along the direction of the applied stress, but the bonds along the chain backbones are not stretched. From reference 2.

Crosslinked elastomers consist of a three-dimensional network of polymer chains that are linked together at random points in the chains (Figure 1a). These links restrict the flow of chains under an applied stress; however, the chain segments between crosslinks are still free to move, rotate, coil, and uncoil (provided the temperature is above the glass transition temperature, T_g). Cross-linked rubbers are able to deform elastically under stress up to several hundred percent strain because of this structure: the crosslinks are sufficient to keep the chains in place and prevent plastic flow, but the chains are free to uncoil and generate elastic (reversible) strain (Figure 1b). Only after the chain segments have been uncoiled as far as possible do the bonds of the chain backbone begin to be stretched. This ability to adopt various chain configurations in response to an applied stress makes the stiffness of elastomers much less than that of crystalline solids.

At low temperatures, below the glass transition temperature T_g , elastomers are in a glassy state in which the polymer chains do not have much freedom of motion (Figure 2). The high modulus ($\sim 10^9 \text{ N m}^{-2}$) indicates that in this temperature regime, the elastic properties of the elastomer are determined by bond stretching along the chain backbones more than by configurational changes of the chains.

As temperature increases above T_g the polymer becomes rubbery. If the polymer is crosslinked, its modulus will remain approximately constant in this region ($\sim 10^6 \text{ N m}^{-2}$), indicating that deformation is occurring via changes in chain conformation. At very high temperatures, the modulus will decrease and eventually the elastomer will behave as a liquid.

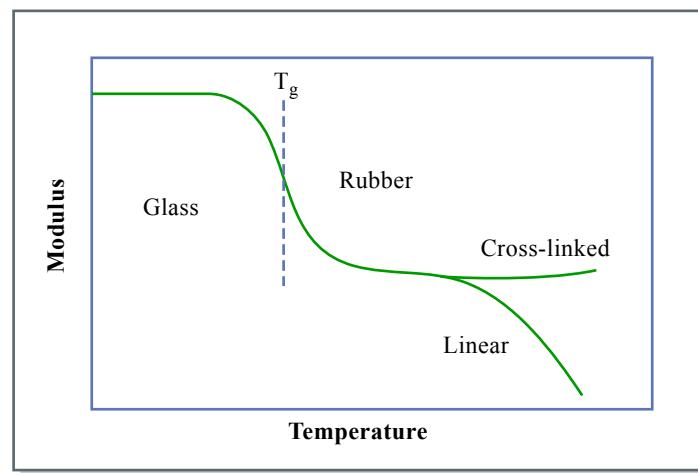


Figure by MIT OCW.

Figure 2 Variation of the modulus of a typical elastomer with temperature. See reference 1.

Stress-Induced Crystallization

In response to an applied stress, polymer chains in an elastomer will tend to align along the direction of the stress, forming small crystalline regions. The complexity of the polymer chains prevents the entire sample from crystallizing, so crystalline sections are

generally confined to regions that can be as small as 10 nm, and are surrounded by amorphous, randomly oriented chains. The degree of crystallization depends on the extension of the sample and the length of time the extension is maintained. A schematic of the elongation process is shown in Figure 3.

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Figure 3 Stress-induced crystallization of an elastomer. (a) An initially randomly oriented crosslinked elastomer is subject to uniaxial tension. (b) The polymer chains uncoil and begin to align along the direction of the applied stress. The shortest chains become fully elongated. (c) The fully elongated short chains act as nuclei for localized crystallization. From reference 4.

The structural evolution of a stretched rubber can be studied using X-ray diffraction by measuring the positions and intensities of the diffraction peaks.^{3,4,5} Unstretched rubber shows a broad peak that is indicative of amorphous material that possesses only short-range order. Upon stretching, small crystalline regions develop, and the diffraction pattern shows sharper peaks superimposed onto the broad amorphous peak. (Note that most commercial rubbers are doped with other materials to enhance certain properties; thus, even in the unstretched state we will see some sharp peaks due to these dopants.)

The degree of crystallinity can be determined from the relative areas under the crystalline peaks and the broad amorphous peak. The mass fraction X_c of the crystalline phase is given by

$$X_c = \frac{A_c}{A_a + A_c} \quad (1)$$

where A_c is the area under the crystalline peaks and A_a is the area under the amorphous peak.

Thermodynamics of Elastomers^{1,2}

To treat this system thermodynamically, let us first consider the Helmholtz free energy

$$A = U - TS \quad (2)$$

If we apply a force F , the rubber will stretch from an initial length l_0 to a final length l . Differentiating the Helmholtz free energy with respect to l at constant T gives

$$\frac{\partial A}{\partial l} = \left(\frac{\partial U}{\partial l} \right)_T - T \left(\frac{\partial S}{\partial l} \right)_T. \quad (3)$$

At constant temperature, we also know that the work done by the system during a reversible extension of the sample by an amount dl against the restoring force is given by

$$dA = F dl. \quad (4)$$

Combining equations (3) and (4), we get

$$F = \left(\frac{\partial U}{\partial l} \right)_T - T \left(\frac{\partial S}{\partial l} \right)_T = F_u + F_s \quad (5)$$

There are two components to the restoring force: F_u , due to the change in internal energy upon extension, and F_s , due to the change in entropy. The internal energy of a material is related to the stretching of primary bonds. In most solids, it is this contribution that most strongly affects the restoring force. However, for elastomers, deformation happens through the uncoiling and eventual alignment of polymer chains. There is minimal stretching of primary bonds along the backbone of the chains, but there is a significant decrease in entropy as the chains uncoil and align. Thus, the restoring force for elastomers is dominated by entropic effects that attempt to return a stretched elastomer to a configuration of higher entropy. Neglecting the internal energy contribution, we can then write the restoring force in terms of only the entropic contribution:

$$F = -T \left(\frac{\partial S}{\partial l} \right)_T \quad (6)$$

This is the expression for an **entropy spring**.

Statistical Approach to Elastomer Deformation^{1,2}

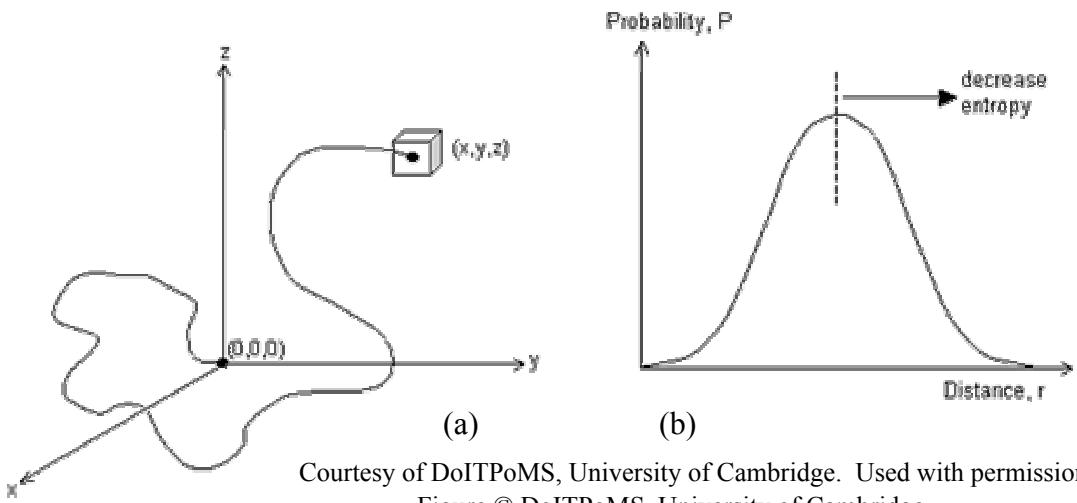
The above thermodynamic treatment is general, and we could have applied the same formalism to determine the thermodynamics of any material. To consider in detail how the composition and structure of rubber affect its properties, we must approach the problem from a molecular level. We have stated that elastomers are composed of randomly oriented polymer chains that uncoil and align upon application of an external stress. Here, we will develop a statistical theory that describes the behavior of an elastomer under an applied stress in terms of the entropy change that occurs.

Entropy of deformed rubber

Let us first consider one individual polymer chain with one end located at the point (0,0,0). The chain is randomly oriented, and the probability that the other end of the chain will be found at the point (x,y,z) is given by $p(r)$, where $r^2 = x^2 + y^2 + z^2$ (Figure 4c). This probability takes the form of a Gaussian distribution (Figure 4b):

$$p(r) = \left(\frac{\beta}{\sqrt{\pi}} \right)^3 \exp(-\beta^2 r^2) \quad (7)$$

where $\beta = \sqrt{3/(2na^2)}$, n is the number of links in the chain, and a is the length of each link. Note that the maximum in $p(r)$ corresponds to the most likely distance between the ends of one individual chain in an elastomer.



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Figure 4 (a) Schematic of a polymer chain with one end at the origin and the other end at the point (x,y,z) . (b) The probability of finding the chain in the configuration shown in (a) is a Gaussian with respect to distance from the origin. From reference 2.

From this description of chain conformation, we can understand the entropy of the elastomer. Remember that entropy, S , is a description of the number of microstates, Ω , available to a system:

$$S = k \ln \Omega. \quad (8)$$

The number of microstates is proportional to the probability the chain has of adopting each conformation: $\Omega \propto p(x,y,z)$.

Now, consider that we apply a stress to the rubber such that the chains stretch to a new endpoint, (x',y',z') where $(r')^2 > r^2$. According to the distribution given in Eq. (7), the probability $p(x',y',z')$ is lower than the unstressed probability $p(x,y,z)$ and thus the entropy of this stressed configuration is reduced. We can develop an expression for change in entropy of the rubber upon stretching:

$$\Delta S = k \ln \Omega' - k \ln \Omega = k \ln \frac{\Omega'}{\Omega} = k \ln \frac{p'}{p}. \quad (9)$$

Substituting for the probabilities and defining $x' = \lambda_x x$, $y' = \lambda_y y$, and $z' = \lambda_z z$, we get

$$\Delta S = -k \beta^2 \left[(\lambda_x^2 - 1)x^2 + (\lambda_y^2 - 1)y^2 + (\lambda_z^2 - 1)z^2 \right]. \quad (10)$$

In the unstressed state the conformations of the polymer chains should exhibit no preferential orientation, such that $\langle x^2 \rangle = \langle y^2 \rangle = \langle z^2 \rangle = \frac{\langle r^2 \rangle}{3}$ (where the triangle brackets indicate an average value). Furthermore, the conformation of the chain can be modeled as a random walk, in which $\langle r^2 \rangle = na^2$. Making these substitutions into Eq. (10), we find the entropy change upon stretching a single polymer chain:

$$\Delta S = -k\beta^2 \frac{na^2}{3} (\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3). \quad (11)$$

Finally, to determine the entropy change for a sample of elastomer consisting of N polymer chains, we simply multiply the entropy change of each individual chain by N :

$$\Delta S_{tot} = -\frac{1}{2} Nk(\lambda_x^2 + \lambda_y^2 + \lambda_z^2 - 3). \quad (12)$$

Stress-strain behavior of rubber

Let us consider the entropic effects of subjecting the rubber to uniaxial tension in the z direction. Thus, $\lambda_x = \lambda_y$. Elastomers tend to deform at constant volume, so $\lambda_x \lambda_y \lambda_z = 1$.

We can thus rewrite Eq. (12) as

$$\Delta S = -\frac{1}{2} Nk \left(\frac{2}{\lambda_z} + \lambda_z^2 - 3 \right). \quad (13)$$

We stated in the classical thermodynamics section that elastomers behave as entropy springs. Thus, an applied force F that induces a length change ∂l affects the entropy as:

$$F = -T \left(\frac{\partial S}{\partial l} \right)_T. \quad (14)$$

Differentiating Eq. (13) and recognizing that $F = \sigma A_0$, we can obtain a relationship for the stress-strain behavior of the rubber:

$$\sigma = \frac{F}{A_0} = \frac{kTN}{V_0} \left(\lambda_z - \frac{1}{\lambda_z^2} \right) \quad (15)$$

where $V_0 = A_0 l_0$ is the volume of the rubber and A_0 is the initial cross-sectional area of the sample.

Note the implication of this equation: a rubber will **contract** when heated.

We can test this behavior experimentally by measuring the temperature-dependent strain of an elastomer placed under constant tension. Eq. (15) states that the stress will increase as temperature is raised, and that the elastomer will respond by contracting. Note that although we have considered elastomers to be solely entropy springs, in reality there are also small changes in internal energy in response to stress. The elastomer will also undergo ordinary thermal expansion that is not accounted for in this theory. Thus, as we verify Eq. (15), it is important to keep in mind the limitations of this approach.

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