Rubber Elasticity

Introduction

Rubber is a three-dimensional network of randomly coiled chains. Each primary chain is linked to other chains at 10 to 20 points, called crosslinks. As the rubber swells with liquid, these chains expand, straightening out. The equilibrium swelling theory of Flory and Rehner gives the following equation

$$-[\ln(1 - \nu_2) + \nu_2 + \chi_1 \nu_2^2] = V_1 n [\nu_2^{1/3} - \nu_2/2]$$

with ν_2 the volume fraction of polymer in the swollen mass, V_1 the molar volume of the solvent, n is the number of network chain segments bounded on both ends by crosslinks, and χ_1 is the Flory solvent-polymer interaction term. For poly(butadiene-co-styrene) rubber χ_1 is 0.39. V_1 for toluene is 106.3 cm^3/mole. This equation allows the calculation of the number of crosslinks, n (mole/cm^3), from swelling data.

Another way to approach n is through the theory of rubber elasticity. In the relaxed state the polymer chains of an elastomer form random coils. On extension, the chains are stretched out, and their conformational entropy is reduced. It is this reduced entropy that makes rubber bands "snap back" when released. The phenomenon is identical to the entropy increase obtained when releasing a gas from under pressure. The equation of state for an elastomer may be written as

$$\sigma = nRT (\alpha - 1/ \alpha^2)$$

where σ is the stress in Pa, n is the number of active chain segments per unit of volume in mol/m^3, R is the gas constant (8.314 J/ mole K), T is the temperature in K, and α is the extension ratio L/L_0. The strain is $(L - L_0)/L_0$ or α - 1. If stress is plotted versus strain a comparison can be made with Hookian behavior (stress is directly proportional to strain).

Procedure

I. Swelling and the number of crosslinks

Cut a rubber band in one place to make a long rubber strip. Measure and record its length in the relaxed state as well as the thickness and width. Measure the thickness and width with a micrometer or vernier caliper. Place the strip in a 600. ml beaker with toluene, making sure the rubber band is completely covered. Remove after 5-10 min. Blot dry. Again measure and record the length. Repeat for about 1 hour until the rubber band reaches its maximum length. Measure the length as well as the thickness and width when it reaches the maximum length. The before and after volume data gives the volume fraction in the swollen mass and allows the use of the Flory-Rehner equation.

II. Extension

1. Measure and record the length of the rubber band in the relaxed state. Use a vernier caliper or micrometer to measure the width and thickness. Weigh a basket and hanger to be placed at the bottom of the rubber band so that the total force on the rubber band can be calculated. Suspend the rubber band from a high place. Begin by placing a weight on the hanger and measure the length of the rubber band. Record the total weights and measure the corresponding rubber band length until the rubber band breaks.

2. Whereas rubber is classified as an elastomer, other synthetic polymer materials can be classified as fibers and plastics. Repeat the extension experiment with a plastic and a fiber, such as the polyethylene plastic used in sandwich bags grocery bags and a fiber such as a piece of thread. (See Gilmer and Williams in the November 1996 *J. Chem. Ed.* for a good discussion.)

Calculations

I. Use the Flory-Rehner equation to obtain the value for n, the number of moles of cross-links per cm^3 for the rubber band. Use the solvent parameters given in the introduction. No propagated error analysis is required.

II. a. Calculate the cross-sectional area for the band. We will assume that this is fairly constant until breakage. Calculate the stress (Force per unit area) for each point. (Remember that force = mg with m in units of kg and g = 9.80 m/s^2. This gives force in units of Newtons) Plot stress (N/m^2) on the dependent axis and strain , $(L-L_0)/L_0$, on the independent axis.

b. Determine: tensile strength (peak stress), elongation-to-break (strain at the break point times 100), and toughness (energy-to-break, the area under the stress/strain curve). Also comment in your report on the shape of the stress/strain curve. Compare to Hooke’s Law stress/strain curves. No propagated error analysis is required.

Determining the area under the curve used to be an interesting exercise. In the old days a rather elegant way went like this. Graph the data and photocopy it twice. Take one of the copies and cut out the desired area (yes, with scissors). Weigh this piece of paper on a balance to plus or minus 0.0001 g. Then take the other copy and cut a good size rectangular or square block from the paper. Choose your block so that you know the length and width (on the graph scale) easily. Weigh this piece of paper and then compute (length x width) what this mass corresponds to in area units. A simple ratio and proportion using the unknown mass gives the desired area for the unknown mass. Now other options are available such as curve fitting the equation and integrating using calculus. Our curve may not curve fit very well and if you don’t have a good background in calculus this may not be an option anyway. Our easiest option now is to use the integrate function on the "Graphical Analysis" program.

c. Plot σ versus (α - 1/ α^2) for the rubber band and determine the number of crosslinks from the slope. (Force the curve to be linear using the linear regression curvefit.) Compare your value to the value obtained from the Flory/Rehner equation. Remember that your answer using the equation of state will be in units of mol/m^3 and your answer using the Flory/Rehner equation is in units of mol/cm^3.

d. Calculate the cross-sectional area for the other materials. We will assume that this remains fairly constant until breakage. Calculate the stress (Force per unit area) for each point. (Remember that force = mg with m in units of kg and g = 9.80 m/s^2. This gives force in units of Newtons) Plot stress (N/m^2) on the dependent axis and strain , $(L-L_0)/L_0$, on the independent axis. Compare to the rubber band and discuss the significance. (See Gilmer and Williams, *J. Chem. Ed*. 1996, 73(11), 1062.)

References:

Gilmer, T.; Williams, M. *J. Chem. Ed.* 1996, 73(11), 1062.
Etzel, A.J. et. al. *J. Chem. Ed.* **1986**, 63(8), 731.
Sperling, L.H. et. al. *J. Chem. Ed.* **1982**, 59(8), 651.
Mark, J.E. *J. Chem. Ed.* **1981**, 58(11), 898.