

Experiment 7: Characterization of uncrosslinked natural rubber from rubber tree latex and of crosslinked natural rubber.

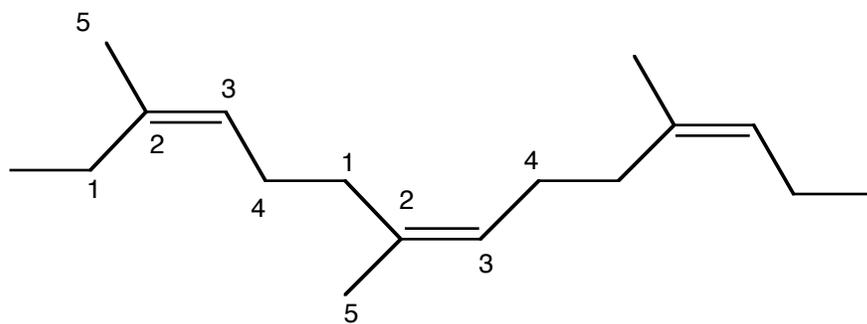
Aim: To study the stress-strain properties (and effects of time and temperature) of uncross-linked natural rubber synthesized in the lab from latex and commercial cross-linked rubber.

Materials and Apparatus:

Latex uncross-linked rubber
Commercial vulcanized rubber pads
Ice
Ring stand
Clamps
Thermometer
Dial micrometer (0.001")
Force gauge
Stop watch

Brief Background:

Natural rubber: It has been established especially by nuclear magnetic resonance spectroscopy that "natural rubber" from the tree *Hevea Braziliensis* is more than 98% poly(1,4 cis isoprene). This configuration is shown below:

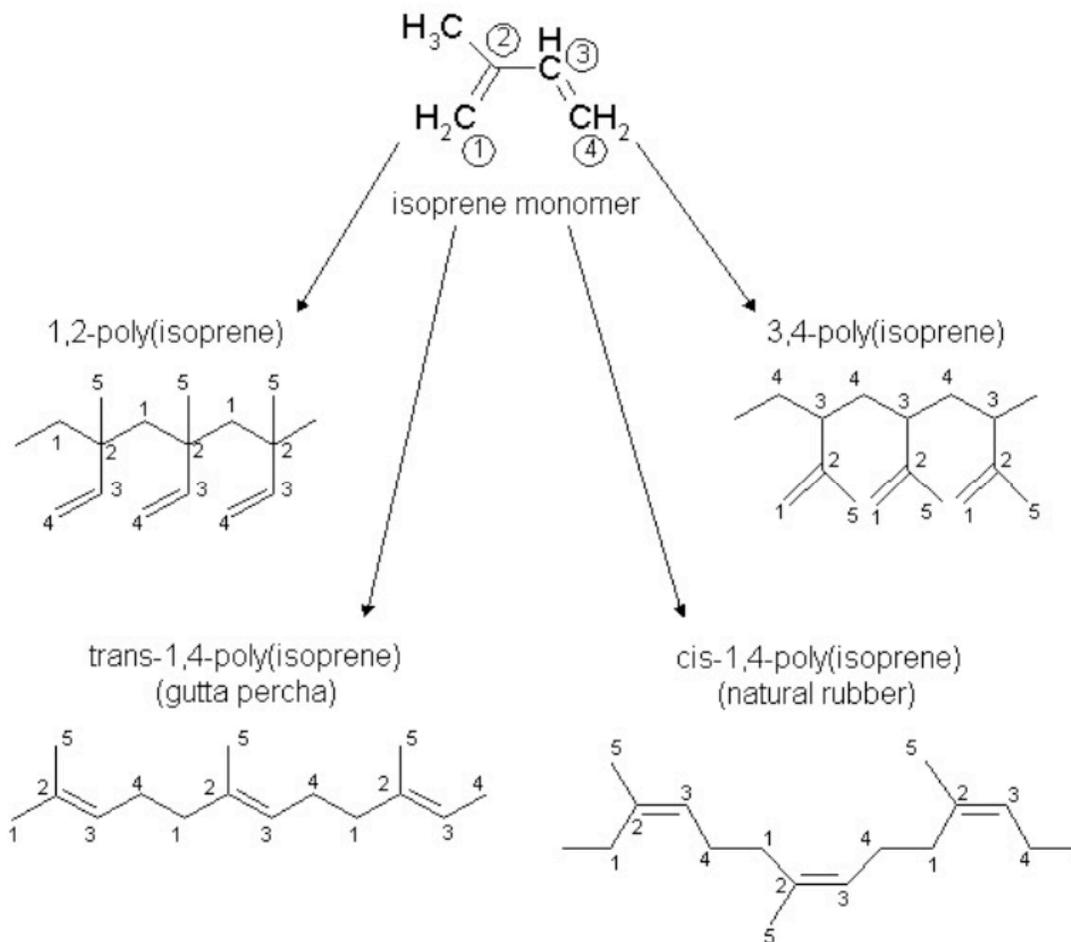


(1)

Rubber is drawn from the rubber tree in the form of an emulsion, called "latex". Latex from the tree *Havea Braziliensis* consists of ~ 60 % poly (1,4 cis isoprene), 40% water, soap and

NH₃. Upon evaporation of water, the sub-micron globules of rubber coalesce, yielding a material that is strong mechanically, yet tacky (sticky). GPC has established that the molecular weight distribution is very broad: some fractions run into few million g/mol in molecular weight (this fraction is the origin of strength) and others are only a few thousand g/mol (this fraction is the origin of "tackiness").

Other configurations of polyisoprene: In the case of polydienes, several possibilities of addition of the monomer onto the growing chain are possible. In the case of isoprene, for instance, the polymerization can involve only one double bond (1,2 -addition, or 3,4-addition), or it can involve both together (1,4-addition). In the former cases, the stereo placement of the substituent in 1,2- or 3,4- units can be controlled in some instances. In the latter case, the double bonds in the chain also involve stereoisomerism: They can be 1,4-cis or 1,4-trans, the properties of the corresponding polymers being widely different, ranging from a soft, amorphous gum to a hard, crystalline, non-elastomeric solid.



Condition for exhibiting rubber-like properties: Any material with rubber-like properties is characterized by chains which exhibit significant flexibility and mobility at the temperature under consideration. Hence, for polybutadiene and polyisoprene to exhibit rubber-like properties, the molecules must be preferably cis-1,4 or at least a random copolymer of cis and trans units. The all 1,4-trans arrangement results in a very regularly packed organization of the molecules into crystals with high melting points (well above room temperature). The second requirement is the presence of crosslinks (permanent covalent crosslinks and chain entanglements), which hold the material together at specific points during deformation.

Mechanical properties vs. time and temperature for rubbers: A rubber sample (of initial length, L_0 and cross sectional area, A_0) under tensile stress (f/A_0) stretches to a length, L and exhibits a resistance against further deformation. One unique aspect of this resistance in rubbers is that it originates from the tendency of the chains to increase their entropy again following the reduction of entropy of the chains on stretching. This is very different from what happens in other materials where the tendency to reduce total energy (not entropy) is the source of resistance.

The following relationship is found to hold for small elongation ratios ($\lambda \sim 1$) between stress and elongation ratio ($\lambda = L/L_0$) in rubber:

$$\lambda = \frac{f}{A_0} = E_0 \left(\lambda - \frac{1}{\lambda^2} \right) \quad (4)$$

where,

$$E_0 = RT \left(\frac{\lambda_e}{V_0} \right) \quad (5)$$

where,

E_0 = Tensile modulus of rubber.

R = Universal gas constant.

T = Absolute temperature.

(λ_e/V_0) = moles of elastically effective chains per unit initial volume

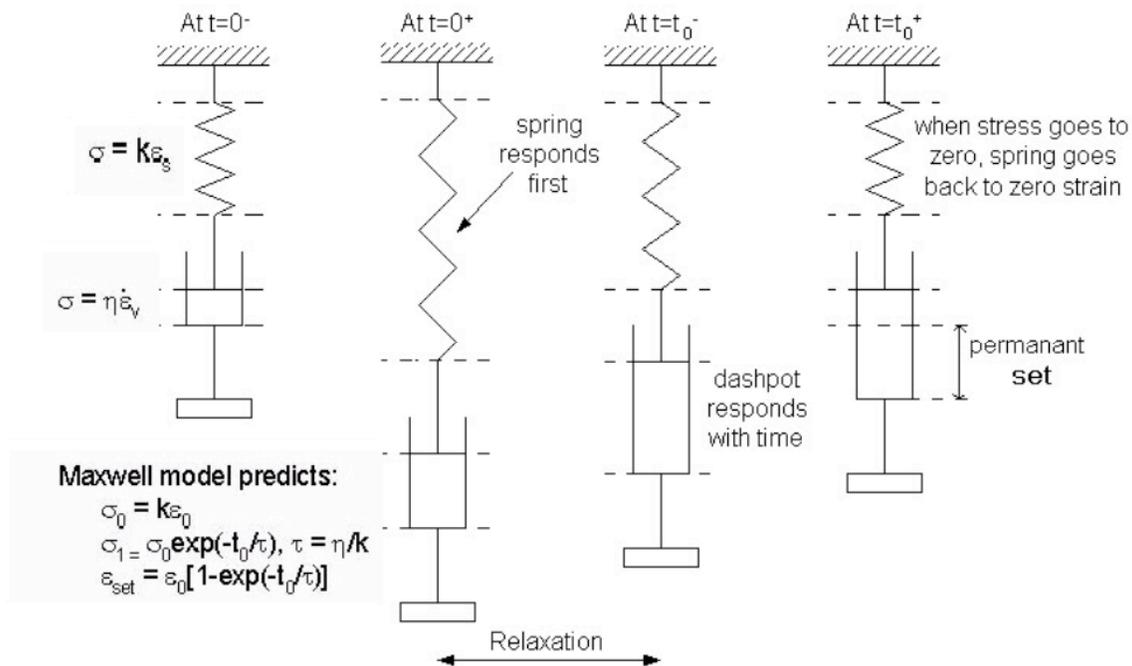
= network chain density

Using this equation, what happens to stress when the elongation ratio is kept constant and the temperature is increased? What happens to the elongation ratio if the temperature is increased while keeping the stress constant? (Rubber shrinks on increasing the temperature). Contrast this with what happens when you heat a piece of metal.

The non-crosslinked material is viscoelastic – not an ideal rubber – and hence "flows" (or "creeps") with time. The chain entanglements can act as effective crosslinks over short time frames (like the time it takes to “snap” a rubber band) but not over the long time frames of a stress relaxation or creep experiment (minutes to hours). Under the applied stress, the entanglements slowly “unwind” and/or polymer chains slip and flow past each other.

Viscoelasticity: It may be easier to understand the viscoelastic effect – which is akin to a combination of traditional viscous and rubber elastic deformation behavior - using a spring and dashpot model (called the Maxwell model). The spring is elastic; stress is directly proportional to strain. The dashpot is plastic; it behaves like a liquid and flows in response to a stress.

Stress Relaxation experiment and creep experiment: In a relaxation experiment, the strain is kept constant and the variation of stress with time is monitored (i.e., the stress relaxation is observed). In a creep experiment, the stress is kept constant and the variation of strain with time is monitored (i.e., the creep of the material is observed).



Precautions:

No special precautions.

Procedure:

The session before this lab

At the end of the preceding lab session, you will have made (at least) two latex rubber bands for Experiments 7 and 8 (optional). You will need at least one of the rubber bands for this experiment. Rubber band preparation will be done by carefully syringing the unvulcanized (uncrosslinked) latex into O-shaped molds. Syringing of the polymer must be done slowly to maintain a continuous stream out of the needle, and you must avoid introducing holes or bubbles that may serve as mechanical defects. The mold should be filled as close to the top as possible. The bands will be allowed to “dry” under the hood. You will also be working with cross-linked rubber bands that are available commercially. These bands will be provided in lab (they are the traditional rubber bands used in offices).

Note: Calculate stresses and elongation ratios as you move along in these experiments. Also note that experiments A.2-3 and B.2-3 may be done simultaneously in the same ice bath.

A. Experiments with non-crosslinked rubber:

1. You have already prepared non-crosslinked rubber bands (prepared in the lab from latex by evaporation of water) which look like O-rings, are somewhat tacky, and are cast from D inch diameter circles. The circumference is $\pi(D \times 2.54)$ cm. When this ring is stretched, it effectively behaves as two equal length specimens, each of initial length $L_0 = \pi(D \times 2.54)/2 = (\text{half of the circumference})$. If the ring had an initial cross sectional area of A_0 , then the cross sectional area bearing the stress is $2 A_0$.
2. Strain at low temperature: Set up the ice-water mix and measure the temperature. Holding the "O-ring" under the ice-water mix, pull it as far as you can. Measure the length to which it gets stretched. Release the rubber band, and measure the length (if different) upon release.
3. Strain at high temperature: Now remove the ice cubes, while keeping a thermometer immersed along with the rubber. Slowly add tepid water with stirring. Observe a) the temperature at which the rubber band starts to shrink from its stretched state and b) the temperature at which it has regained its initial circular state (D inch diameter) or the temperature at which no further shrinking occurs.
4. Stress relaxation experiment: Using the force gauge, a ring stand, and suitable clamps so as to pull the band to an elongation ratio of L/L_0 of about 3 at room temperature (you may need to use lower strain ratios depending on the thickness of the band you made). Whatever the elongation ratio is, record it, and keep it fixed. Record ambient temperature. Record force as a function of time at 5 minute intervals for 30 minutes. After 30 minutes, remove the load, let the band relax, and measure its new diameter D' . The original diameter being D inches, $(D'-D)/D$ is the fractional permanent "set" or fractional creep.
(conversion factor: 1 lb = 0.454 kg)

B. Experiments with commercial vulcanized rubber bands:

1. You are given commercial rubber bands that are thinner in cross section than the non-crosslinked rubber bands, are non-tacky and usually race track shaped (two straight runs connected to semicircles).
2. Strain at low temperature: Set up an ice-water bath and measure the temperature. Holding the commercial rubber band under the ice-water mix, pull it as far as you can. Measure the length to which it gets stretched. Release the rubber band, and measure the length (if different) upon release.
3. Strain at high temperature: Now remove the ice cubes, while keeping a thermometer immersed along with the rubber. Slowly add tepid water with stirring. Observe the

temperature at which the rubber band starts to shrink from its stretched state and the temperature at which no further shrinking occurs.

4. Using a hand held force gauge, determine the tensile stress-strain at room temperature. Record the temperature. Recall that two strands of rubber support the load equally, so that the cross-sectional area = $2 A_0$. A_0 is the cross-sectional area of the rubber band.

5. Thermoelastic Property Experiment: Arrange a set-up like that discussed in section A.4 of the procedure, so that you can impose an elongation ratio L/L_0 of 3. Record the tensile force and the temperature.

6. Keeping the elongation ratio at 3.0, pour ice water (near 0 C) over the band until you get a constant force reading. Record it.

7. Remove the ice water and substituting hot water of known temperature (say 60-70 C). Again try to obtain a constant force reading. Record the temperature.

8. Stress relaxation experiment: This experiment is the same as in section A.4. Using the force gauge, a ring -stand, and suitable clamps, pull the band to an elongation ratio of L/L_0 of about 3 at room temperature (you may need to use lower strain ratios depending on the thickness of the band you made). Whatever the elongation ratio is, record it, and keep it fixed. Record ambient temperature. Record force as a function of time at 5 minute intervals for 30 minutes. After 30 minutes, remove the load, let the band relax, and measure its new length L' . The original diameter being L inches, $(L'-L)/L$ is the fractional permanent "set" or fractional creep.

Your report:

Observations and Calculations:

1. Record required observations in the procedure/brief background in the lab notebook. Be sure to record all relevant dimensions of the samples.
2. Report all relevant stresses and elongation ratios.

Discussion:

1. Non-crosslinked rubber:
 - a) Plot the circumference of the band as a function of temperature for the ice bath experiment.
 - b) After reporting exact elongation ratio and other relevant conditions, plot the tensile stress vs. time for the relaxation experiment. Choose appropriate units. Compare your results with what the Maxwell model predicts.
 - c) Report fractional creep. Explain why you observe creep in these samples.

2. Crosslinked rubber:

a) Plot tensile stress vs. elongation ratio, λ .

b) Plot the reduced modulus, σ^* , vs $1/\lambda$ where,

$$\sigma^* = \frac{\sigma}{(\lambda - \lambda^{-2})} \quad (6)$$

c) Use plot in part b) to calculate the tensile modulus using equation 5. (The tensile modulus is the reduced modulus as elongation ratio approaches 1.) Use the tensile modulus to calculate the network chain density.

d) Plot tensile stress vs. temperature (in Kelvin) and discuss the results with respect to the background given in this handout and the lecture.

3. Discuss experimental difficulties or inaccuracies, sources of error etc. (For example, were there air bubbles or did the rings cast from latex have uniform thickness? What will be the effect of such errors on your result? Or was temperature control a problem?)