Polymer Properties*

A. Dilatancy (shear thickening) of a corn starch suspension[1]

The flow properties of many liquids are described as Newtonian. That is, the applied stress is equal to the constant viscosity times the rate of strain.[2] In simple terms, if you apply twice as much force to a paddle in water, the paddle moves twice as fast.

Definitions:
Stress is the force per unit area.
Strain is the deformation of matter when force is applied, and the rate of strain is a measure of how fast the matter deforms when force is applied.
Shear is the internal force tangential to the section on which it acts. Remember how shears cut.
A **colloidal suspension**, or simply **suspension**, consists of solid particles (that have at least one dimension in the range 3 to 1000 nm) suspended (or dispersed or mixed) in a liquid.

Polymers and polymeric solutions and suspensions of polymers frequently show deviations from the simple Newtonian behavior. Paints, for example, are formulated to be pseudoplastic; that is, they exhibit shear thinning -- a decrease in viscosity as the rate of shear increases. As you apply paint with a brush or roller, you quickly apply much force or stress, and the paint flows easily. Then you look at the paint on the ceiling or walls and hope that it does not flow to the floor. Acted upon only by the weak constant force of gravity, the viscosity is now too high to allow flow.

In this experiment you will observe dilatancy -- an increase in viscosity as the rate of shear increases. After you do this experiment you should understand why dilatancy would be a terrible property for a paint.

Procedure: Add 21.5 ml of water to 25.0 grams of powdered corn starch and stir together until a uniform suspension is obtained which shows no indication of settling.

1. Stir the suspension slowly and then quickly, noting the difference in viscosity.

2. Pour the suspension into a petri dish. Throw a small solid rubber ball onto the suspension at an angle and observe. Contrast this behavior to that which you observe when you gently set the rubber ball on the suspension.

***Suggestion for efficient use of lab time: Do steps 1 & 2 of Part B.2 first. Then do Part B.1 and Part A.**

B. The Glass-Rubber Transition[3]

Below its glass-rubber transition temperature, T_g, a thermoplastic polymer will be hard and rigid and glassy. Above this temperature the same polymer will be flexible and rubbery. In this experiment we will take a polymer which is a rubber at room temperature and cool it in liquid nitrogen to 77K, or -196^oC, which is well below its glass-rubber transition temperature.

B.1a Demonstration. Obtain a hollow rubber ball such as a racquetball and bounce it on the floor. Describe its behavior.

Cool the ball in liquid nitrogen for 10-20 minutes. Remove it carefully with tongs and throw it hard against the floor or wall. Record your observations.

What happens to the polymer as it warms up?

B.1b Using tongs, dip adhesive tape into liquid nitrogen until you think the tape has cooled to 77 K. Test its stickiness by placing it on paper immediately after removal from the liquid nitrogen.

Test its stickiness after 30 seconds and compare to uncooled tape.

B.1c Note the flexibility of a latex lab glove at room temperature. Cool it in liquid nitrogen for about a minute. Describe the physical properties of the glove now.

B.2 Behavior at the glass-rubber transition.

1. One partner should hold a meter stick vertically on the floor and drop a solid rubber ball (such as a small Superball) from a height of 100 cm. The other partner closely observes the return bounce height and records it.

2. Cool the ball in liquid nitrogen for about 30 minutes.

3. Immediately upon removing the ball with tongs from the nitrogen, one partner drops the ball from a height of 100 cm.
The other partner observes and records the bounce height. This is the bounce height at time = 0.
Measure the bounce height once a minute or more often for the first 10 minutes and then less frequently as the bounce height approaches the pre-cooled value.
Record your measurements in a table with columns for "Elapsed time after removal from liquid nitrogen," "Bounce height in cm," and "Sound of bounce."

As time passes, the cold rubber ball warms, and the bounce height versus time will go through a minimum at T_g. "Below T_g the ball is glassy and bounces much like a marble. At T_g, the bounce is at a minimum owing to conversion of kinetic energy to heat. (The ball actually warms up slightly.) Above T_g, normal rubber elasticity and bounce characteristics are observed."[3]

4. Plot "bounce height" vs "elapsed time" starting with time = 0.
(See http://chemlab.truman.edu/DataAnalysis/PreparingGraphs_files/PreparingGraphs.htm)
You may wish to compare to the curve in reference 3.

5. Should T_g for an automobile tire be below or at or above room temperature? Why?

Additional Background Information

Part A deals with one type of colloid, a suspension. In freshman chemistry we normally deal with either solutions (homogeneous mixtures) or with mixtures of substances that clearly are insoluble, such as oil and water, or a precipitate and a supernatant. On occasion, we use a centrifuge because a precipitate fails to settle rapidly, and some such precipitates are in fact large agglomerations of ions, or suspensions. For further information on colloids, see a General Chemistry or Physical Chemistry textbook or a monograph on colloids.

Part B illustrates a fundamental property of amorphous solids. Solids may either have long-range order (and be called crystalline) or they may lack long-range order and only have short-range order (and be called amorphous). A bowl of cooked spaghetti exhibits short range order; short portions of spaghetti noodles often lie parallel to one another, but there is much random criss-crossing of noodles and there is no long-range order. Hence the cooked spaghetti is a model for amorphous materials. As an aside, it should be noted that crystalline and amorphous materials are two extreme models for solid materials; real crystals have defects, and polymers may have crystalline and amorphous regions involving the same polymer molecule; such polymers would be characterized as semi-crystalline or micro-crystalline.

Typical amorphous solids for which the glass-rubber transition is important include polymers, or very large molecules. The location of T_g determines if and when a solid may be used as a rubber tire or an O-ring seal on a space shuttle or as a paint. Thus we are looking for responses of materials to a force exerted over a specified period of time. As chemists we ask ourselves how the atoms or molecules respond to these forces.

Even without applied external forces, atoms, molecules, and ions are in constant motion. (We never attain absolute zero at which classical motion would cease. Due to the Heisenberg Uncertainty Principle molecules would still have residual vibrational motion at absolute zero.) These motions may be of several types. Gases and plasmas have huge **translational** motions. For gases, the atoms and molecules are in continual random motion, bouncing off one another like colliding marbles or billiard balls. This is an assumption of the Kinetic Molecular Theory of Gases. Actually we should qualify this viewpoint by taking into account the weak attractions and repulsions between the atoms and molecules. In the case of a plasma, there are strong electrostatic attractions and repulsions between ions.

Polyatomic molecules and ions also have **vibrational** and **rotational** motions. Consider a gaseous HCl molecule. The H and Cl nuclei may be visualized as being connected by a spring and the two nuclei oscillate or vibrate about some average bond distance. In polymers one has thousands of atoms and there are many possible vibrational motions. Parts of the polymer molecule may be twisting relative to other portions, and the whole molecule may translate. Two possible analogies are a pit full of moving snakes or a can filled with wriggling earthworms. (This dynamic picture of an amorphous material overcompensates for the static "cooked spaghetti" picture in cases where the material takes eons to flow.)

Whether the mass of snakes or earthworms appears to be solid (definite shape) or liquid (assume shape of container) depends on the time scale of our experiment. If we watch for a very short period of time, then the mass appears to be solid. If we watch for a very long period of time, then the mass assumes the shape of the container. Likewise, an amorphous polymer or a suspension (as in part A) show different responses depending on our experiment.

Not only the time allocated to the experiment but also the temperature determines what properties we see. When we go through a phase transition the properties of a material change; compare water at -50^{o}C and at +50^{o}C, or remember Part B.

Below T_g no more than 4 chain or backbone atoms of a polymer are involved in coordinated molecular motion. When the glassy material is subjected to an external force, the molecules are limited in their ability to respond without breaking bonds and hence the glass often fractures. The glass-rubber transition region is characterized by the onset of the coordinated molecular motion of 10 to 50 chain or backbone atoms. Above T_g linear and lightly cross-linked polymers act like rubbers since the large coordinated molecular motions allow the material to dissipate impacts harmlessly rather than rupturing bonds.

References:

1. F. Rodriguez, Polymer Preprints 27 (April 1986), #1, 402-3.
2. R.B. Seymour and C.E. Carraher, Jr., *Polymer Chemistry: An Introduction*, New York: Marcel Dekker, ©1981, or 2nd ed., ©1988, ch. 3.
3. L.H. Sperling, *Introduction to Physical Polymer Science*, New York: Wiley-Interscience, ©1986, pp. 299-300, or 2nd ed., ©1992, pp. 380-1.

Polymer Properties

Equipment and Supplies:

25 mL or 50 mL graduated cylinder (per group)
balance
powdered corn starch (25 g per group)
spatula to remove corn starch
stirring rod or spatula to mix water and starch, and test suspension
beaker to mix water and starch
1 petri dish per group
2 solid rubber balls per group
1 hollow rubber ball per lab section
tongs (for removing objects from liquid nitrogen)
watch or clock
meter stick
thick adhesive tape
latex or rubber lab glove
Styrofoam cup per group
Dewar flask to cool hollow rubber ball
liquid nitrogen
work gloves for holding cold objects