Polymers Lab- *Cross-linking*

Objectives Synthesize polymer with different degrees of cross-linking and compare infrared and physical properties.

Background Cross-linking is the formation of covalent bonds between portions of polymer chains, which can result in large, connected networks (Figure 1). Since these bonds are covalent, the cross-linked polymer becomes stronger and more stable mechanically and thermally (although they can burn). Once these bonds are formed, they are difficult to break unlike intermolecular forces (e.g. hydrogen bonding). Cross-linking provides a higher tensile strength, increases fluid resistance, and decreases flexibility. Due to these properties, cross-linked polymers can be found in gels for gel electrophoresis and car tires (vulcanized rubber).

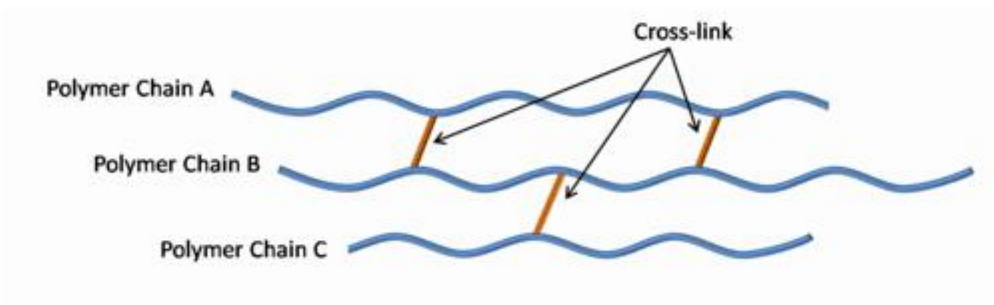

Figure 1. Polymer chains cross-linked to each other.

Cross-linking can occur through two routes: chemical and radiation. We will be studying the chemical cross-linking between polyvinyl alcohol (PVA) and sodium tetrahydroborate (Figure 2) to form didiol (two diol) complex. You may be familiar with this as glue and borax in your earlier years, which produces slime. The degree of cross-linking results in a change in the viscosity and other physical properties of the slime. With an even greater degree of cross-linking, you can form a material that becomes a solid ball that can be bounced on the floor or table.

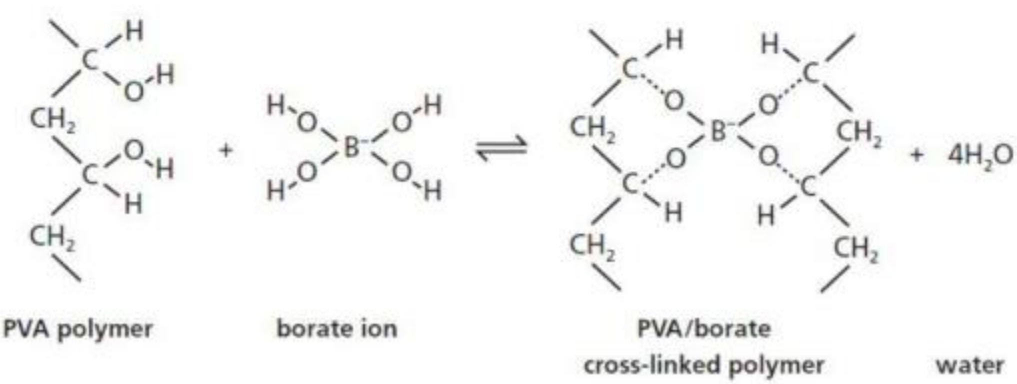

Figure 2. Reaction with PVA and borate forming a cross-linked polymer.

Inclined Plane Test

A very simple way to determine the fluid properties is the inclined plane test whereby a fluid is flowed down an incline plane (Figure 3). We will consider steady-state, viscous flow down a plane at an angle θ wherein the flow has fully developed into a laminar film. Although polymers are non-Newtonian in nature (i.e. viscosity is not independent of stress), we can apply these principles in general and calculate approximate and relative viscosities.

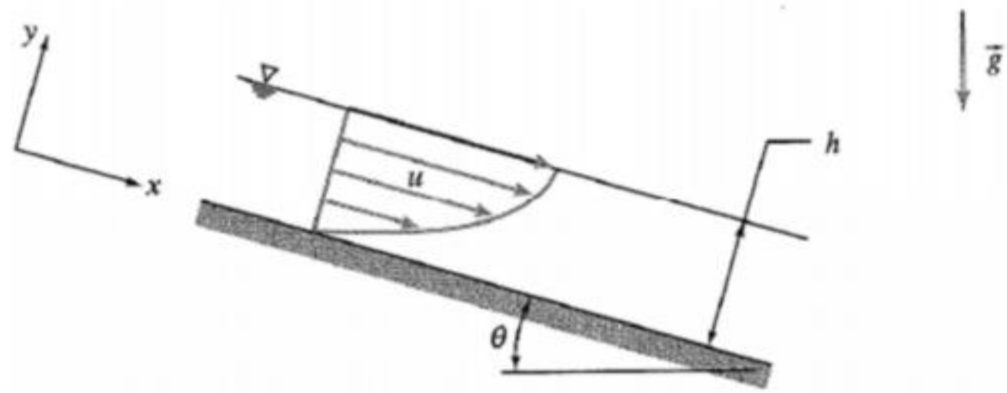

Figure 3. Viscous flow down an inclined plane.

We begin with the Navier-Stokes equation (reduced according to assumptions about flow and the no-slip condition):

$$0 = \rho g_x + \mu \frac{d^2u}{dy^2}$$

where $g_x = g sin\theta$. We can solve for the velocity profile using boundary conditions (no-slip BC and free surface BC) such that

$$u = \frac{\rho g sin\theta}{\mu} y\left(h - \frac{y}{2}\right)$$

Volumetric flow rate per unit width can be solved using the following:

$$Q = \int_0^h u dy = \frac{\rho g h^3}{3\mu} sin\theta$$

Since kinematic viscosity (ν) is $\frac{\mu}{\rho}$ or the dynamic viscosity over density (essentially telling us how fast the fluid is moving when a force is applied) and solving for the height (h), then

$$h = \left(\frac{3\nu Q}{g sin\theta}\right)^{\frac{1}{3}}$$

And solving for the velocity in the x-direction (V) then we have

$$V = \left(\frac{9Q^2 g sin\theta}{\nu}\right)^{\frac{1}{3}}$$

Using these equations, we can set-up an experiment to determine the viscosity of a fluid flowing down an inclined plane by measuring all unknown variables.

Discussion

- Describe how cross-linking works
- How does cross-linking affect the physical properties of the polymer?

- What happens when you apply a force to the polymer? Does it act like a solid or a liquid?
- What does adding cornstarch do to the polymer? What is a filler?
- Why would the swelling of a cross-linked polymer differ from that of a non-cross-linked polymer?

Materials
- Elmer's Glue/Polyvinyl alcohol (PVA)
- Borax/Sodium borate ($Na_2[B_4O_5(OH)_4]\cdot 8H2O$)
- Food dye
- Cornstarch

Equipment
- Inclined Plane
- Fourier Transform Infrared Spectrometer (FTIR)
- Analytical Balance

Experiment
- Use different concentrations of borax solution and mix with the PVA to form different degrees of cross-linking. Add food dye if you want it to be colorful.
- Make observations about the physical properties of the material
- Apply an inclined plane test on the samples to determine viscosity
- Dry a film of each solution on the hot plate for FTIR/ATR measurements
- Perform swelling density tests by measuring the change in weight for a known volume of the material
- If time, you may study the effects of cornstarch on the material

References
1. Shibayama, M. et al. Sol-gel transition of poly(vinyl alcohol)-borate complex. *Polymer* **1998,** *29*, 2066-2071.
2. Wang, H.-H. et al. The Elastic Property of Polyvinyl Alcohol Gel with BoricAcid as a Crosslinking Agent. *J. Appl. Polym. Sci.* **1999,** *74*, 3046-3052.

MSDS
PVA
Sodium borate