Experiment 12: Networks: A)"Epoxy" and "RTV Silicone"; B) Rapid step reaction accompanied by foaming using Hypol.

Aim:

(a1) To study the cross-linking of epoxy/amine using two commercial kits: "5 Minute Epoxy" and "Epoxy Patch".

(i) To determine the range of ratios of epoxy to amine over which networks are formed. To determine the time to gel for the "5 Minute Epoxy" kit.

(ii) To determine the degree of swelling in solvent methyl/ethyl ketone as a function of epoxy/amine ratio, of gels from both kits.

(iii) To determine extractables (via MEK) as a function of epoxy/amine ratio, of gels, from both kits.

(iv) To determine the long term effect of water immersion as a function of epoxy/amine ratio, or gels not treated with MEK, from both kits.

(a2) To study the cross-linking reaction in GE's "RTV Silicone".

(i) To determine the weight loss (%) which accompanies each of the curing reactions.

(ii) To determine the swelling ratio after long term exposure to liquid toluene. To determine extractables, if any.

(iii) To determine the uptake of water after long term exposure to liquid water.

(b) To investigate the reaction of Hypol with pure water as a function of mass ratio, and to qualitatively observe the properties of the foams produced after evaporation of water.

Materials and Apparatus:

Commercial kits: 5 Minute epoxy, Epoxy patch, RTV silicone
Toluene
Hypol
scintillation vials with caps (26)
glass microscope slides
plastic cups --- 12 ounce
Variable speed stirrer with propeller
aluminum weighing dishes
aluminum ring mold
wooden splints

Brief Background:

Summary:

All the polymers you shall study in this experiment have the following features:

a) *Step polymerization mechanism*: All polymerizations in this experiment are step polymerizations. You shall study both polycondensation and polyaddition reactions. For this experiment, you should re-familiarize yourself with the reactions discussed in Ch. 2 of Rempp & Merrill in the Supplemental Reading.

b) *Crosslinking and formation of networks*: All the polymers here result in networks after cross-linking. You shall see glassy networks, rubbery networks and foamed networks.

Exercise: You should be able to say how networks are characterized. What makes a polymer glassy or rubbery (at the molecular level what is happening)? What is the physical property (hint: a temperature) of importance here? How does this difference manifest itself in the mechanical properties? Using simple thinking, what do you think should be required for a network to be made into a foam?

Epoxy-Polyamine:

See supplemental reading from Rempp & Merrill, Polymer Synthesis, pp54-57 for more details.

Exercise: 1) What do you think is the difference between the "5-Minute epoxy" and "Epoxy-patch"? Why is one slower than the other? (Hint: The amine in the "Epoxy patch" is diethylene triamine i.e., three amine groups). 2) Is the epoxy a glassy network? How did you guess? 3) What do you expect will happen as the relative proportions of epoxy and polyamine are changed?

RTV Silicones:

Please read the special handout on Step Reactions Used to Cross-link Poly(dimethyl siloxane) for more details. Appendix 1 consists of excerpts from the GE Silicone data book "Two-Component RTV Silicone Rubber Compounds for Industrial Applications".

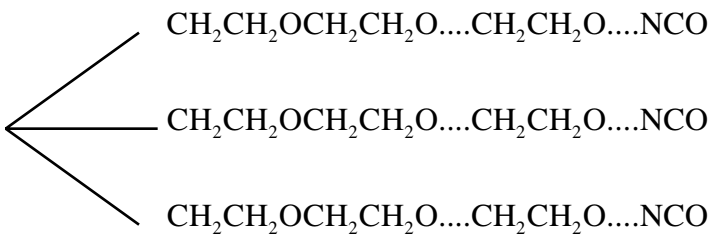
Exercise: 1) Which of the silicones used by you cure by the reaction schemes corresponding to the different reaction schemes (eq. 5.7.2, 5.7.3) in the handout? 2) Why doesn't the RTV Silicone in experiment A2 (part I) not cure within the tube? 3) In the following pages, think about how silicones with different properties can be achieved?

Hypol:

Appendix 2 consists of excerpts from the Hypol instructions sheet produced by Hampshire Chemical Company and other excerpts from the document "Hypol prepolymer: Starter sample kit booklet".

Exercise: 1) What molecular and experimental variables could determine the properties of the foam? 2) Suggest a novel use for the foam considering its properties. The use should be different from those already suggested in Appendix 2.

Hypol, originally manufactured by W.R. Grace Co., is now produced by Hampshire Chemical Co., a spin-off from W.R. Grace. The product (before addition of water) is a trifunctional branched molecule of which the "arms" are poly(ethylene oxide) terminated by toluene isocyanate.



The reactions that lead to the foamed network are given in Appendix 2.

Precautions:

1. Use vinyl gloves while dealing with solvents. Latex gloves are fine for other parts.
2. Use toluene in the hood.
3. Handle Hypol in the hood.

Procedure:

This year, we will make the following changes to the procedure described below:

a) **For the 5-Minute Epoxy, each group is only required to prepare 5 recipes: (a, a1), (c, c1), (e, e1), (g, g1), and (i, i1).**
b) **For the epoxy patch slow crosslinking, Team A should prepare vials j-m for MEK trials, and Team B should prepare vials j1-m1 for water trials. Share data for analysis.**
c) **The material actually used in RTV Silicone: Part I is GE-RTV-108.**
d) **Omit RTV Silicone: Part III**

A1. Crosslinking of epoxy/amine:

1. Preweigh and label 26 scintillation vials which will be coded **a, a^1, b, b^1 ..... m, m^1**. Ultimately the vials a-m will receive methyl ethyl ketone (MEK) and the vials **a^1 - m^1** will receive water. The vials should be weighed without their caps.

2. 5-Minute Epoxy (fast crosslinking):

a) The previously joined syringes have been cut so that each can be used separately. The polyamine syringe has the slightly yellowish liquid. We shall use the vials **a, a^1 - i, i^1**.

b) Introduce the amount shown of epoxy into the middle of the floor of the vial, and then the polyamine on top of the epoxy. You need not dispense exactly the amount shown, but you must record exactly what you dispense. For example, for **a**, you may have taken not 0.50, but 0.45 g epoxy and 4.6 g polyamine.

Table: Recipes

For vial	**a,a^1**	**b,b^1**	**c,c^1**	**d,d^1**	**e,e^1**	**f,f^1**	**g,g^1**	**h,h^1**	**i,i^1**
Add g of epoxy.....	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5
Add g of polyamine..	4.5	4.0	3.5	3.0	2.5	2.0	1.5	1.0	0.5

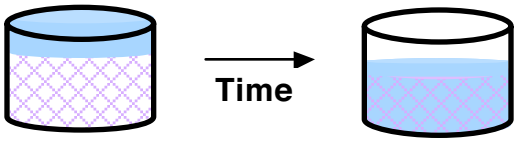
c) Mix thoroughly the **a - i** set of vials with a wooden splint, remove the splint, re-determine the net weight of the mixture in the vial and record it for each vial. (Some will be lost on the splint.)

d) With the **a^1 - i^1** set, use the splint as the gel tester (leave it in). When the splint gets "stuck" (when you can no longer stir), pull the splint out. If it is stuck permanently, break it off at the surface of the gel. For this set **a^1 - i^1** you will be recording the gel time as a function of composition. As above, re-determine the net mass in the vial and record.

e) At the end of the lab period, add about 10 ml of MEK to the vials **a-i**, and 10 ml of water to the vials **a^1 - i^1**. Seal the caps. Let it stand until next week.

f) In the next lab period, pour out the MEK + extractables from the vials **a – i** into pre-weighed and labeled aluminum weighing dishes. Allow the MEK to evaporate in a

hood until the next lab session. Then, weigh the vials to determine the mass of the absorbed MEK and gel in order to calculate the percent uptake of MEK (100 * Absorbed MEK / Original wt. of epoxy). Afterwards, place the vials containing the cross-linked epoxy and absorbed MEK back into the hood and allow the MEK to evaporate until the next lab session.



g) Similarly pour out the water off samples in vials **a^1 – i^1** and determine the percent uptake of water.

h) During the third lab session, record the weight of the residue in the aluminum dishes. Also, record the final amount of material remaining in vials **a – i**. Attempt to close the material balance on the samples exposed to MEK.

3. Epoxy patch kit (slow crosslinking):

a) This consists of a larger tube containing 2.51 ounces epoxy and a smaller tube containing 0.81 ounces polyamine. By reasons of this weight ratio, it is believed that it represents the correct stoichiometric ratio., i.e., about 3.0. Dispense the amounts shown into the scintillation vials **j,j^1 - m,m^1**, the epoxy first, the polyamine next.

Table: Recipes

For vial	**j,j^1**	**k,k^1**	**l,l^1**	**m,m^1**
Add g of epoxy.....	5.0	5.0	5.0	5.0
Add g of polyamine..	0.6	1.1	1.6	2.5

b) Mix thoroughly with wooden splints, discard the splint after mixing, re-determine and record the total mass (some will be lost on the wooden splint). Set these aside for the next lab period.

c) In the next lab period, place the samples in vials **j,j^1 - m,m^1** under 10 ml water, repeatedly, and retrieve these in the following lab session.

d) The objectives are the same as for the 5-minute epoxy.

A2. RTV Silicone (made by GE) experiments:

*Part I: Self condensation from collapsible tube (GE-RTV-105): Acetic acid evolved.*1.

On a glass microscope slide, pre-weighed, place a length of the fluid about 2" long. Determine the gross weight. Set aside in the hood for the next lab period.

2. Also dispense into two pre-weighed scintillation vials about 3 g of the fluid. Accurately record the weight. Set aside for the next lab period.

3. In the next lab period, re-weigh what is on the slide and report the % weight loss (presumably acetic acid). Re-weigh the vials to determine net contents of silicone matter. Then during this lab period add 10 ml of toluene to one of the vials and 10 ml of water to the other.

4. In the lab period following that, pour out the toluene and by weighing the residue determine the % uptake of toluene = (100 X sorbed toluene / original wt. of silicone rubber). Likewise, pour out the water and determine the % water uptake.

Part II: Catalytic condensation (GE RTV 11): Alcohol evolved.

1. Using two tared weighing dishes, weigh out about 10 g of RTV 11 into each (record exact weight), then add 0.050 g of DBTDL (dibutyl tin dilaurate) and mix.

2. First dish: Leave at room temperature. Every 30 minutes probe with a tooth pick, and try to locate the gel time within $\pm$ 15 minutes (gel time is the instant when the tooth pick comes out clean and mass no longer flows). Set aside for next lab period.

3. Second dish: Put into 60 C oven. Probe as above to determine gel time. Set aside for next lab period.

4. Next lab period (beginning of the lab period): Determine the weight loss (due to ethanol evaporation) of each of the two rubber discs. Place each disc, rolled up in a tared scintillation vial. Add toluene to fill vial. Close vial.

5. Toward end of this second lab period, empty toluene from vial into a tared aluminum weighing dish. Determine uptake of toluene by the swollen rubber and report as the mass swell ratio. Here the object is to determine if the cross-linking achieved is the same for the disc vulcanized at room temperature as the disc heated in the oven at 60 C.

Part III: Two component addition crosslinking (GE RTV 615 A and 615 B):

1. Mix the A component (vinyl methyl siloxane) with the B component (SiH + chloroplatinic acid) in the ratio 10 g A to 1 g B in two tared aluminum weighing dishes. Mix.
2. Follow the procedure outlined in part II, with the same objective.
3. In addition, prepare a mixture of 20 g A to 2 g B, and pour this into a ring mold (as used for latex and PVC rings).
4. Next lab period: Remove the ring and determine the reduced modulus at low elongation ratios and from this estimate the concentration of elastically effective chains.

B. Reactions with Hypol:

1. Hypol with water:

   a) Use 12-ounce plastic cups and the variable speed stirrer with propellor. Prepare the following recipes:

Table: Recipes

Composition	P	Q	R
Hypol	20 g	20 g	20 g
Distilled water*	20 g	40 g	10 g

   b) After not more than one minute of stirrer mixing, remove the stirrer, place the propellor and shaft in a second 12-ounce plastic cup filled with water only to wash it off.

   c) Measure the initial depth of liquid (Hypol + water) before mixing, and the final length of foam. Estimate the time required to reach this final height.

2. You will allow your foams to dry out by evaporation in a stream of air, and the following week, you will observe and report (qualitatively) what they look like as compared to the original foam.

Observations and Calculations:

1. Experiment A1, A2: Gel times, mass balances, mass swell ratio and percent solvent uptake.
2. Experiment B: Heights, observations on effect of pH, qualitative observations on the foam.
3. For each system, determine the mechanical nature of the material (hard and glassy, soft, rubbery, etc.). Explain in your own words why you saw such a variation in these

crosslinked materials. (What is the range of Tg for each sample with respect to room temperature? What is the relative cross-link density?)

Discussion:

1. Experiment A: Discuss the effect of compositions and polymer type on gel times, swell ratio, solvent uptake, and mass balance. Be sure to give brief but clear explanations based on the theory, or propose other possibilities.
2. Experiment A2 (all parts): Tabulate swell ratio results for all RTV Silicone experiments such that a comparison can be made. Be sure to include the relevant curing conditions and specific differences between the systems in the table.
3. Experiment A2 (Part III): Compare the mechanical behavior of radiation cross-linked silicone and the room temperature cured silicone in this experiment.
4. Experiment B: Explain what happens and why? Compare the differences between the samples in each group.
5. Other discussion of sources of error, suggestions for improvements etc.