Alkyd Synthesis & Applications

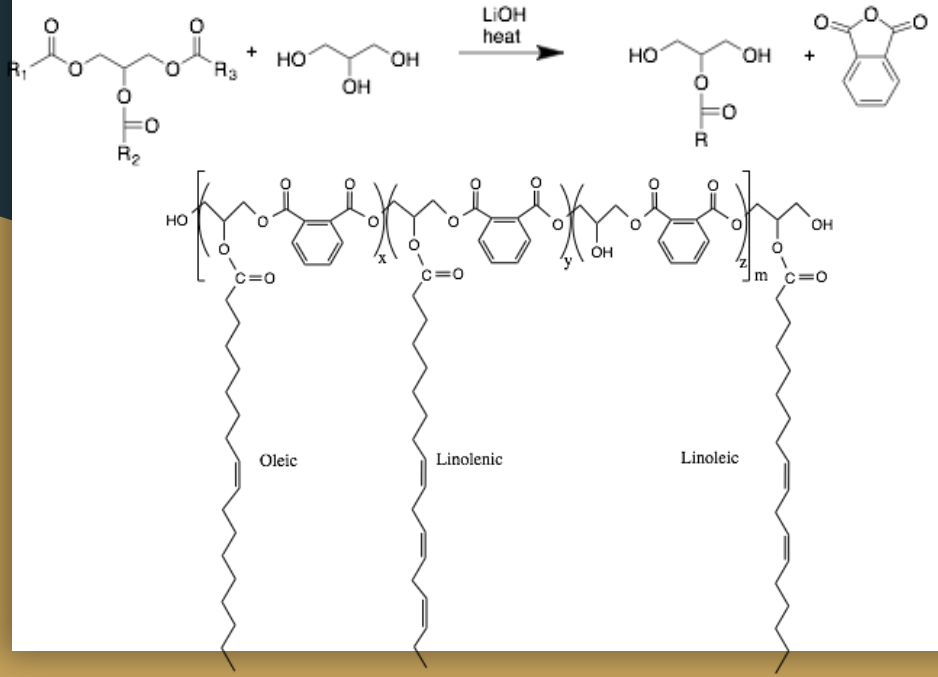
Christopher Kriebel Green High School
Laboratory: Dr. Soucek
Graduate Student Mentor: Brittany Pellegrene
University of Akron
Department Of Polymer Engineering

Topics

Introduction to Alkyds & Polymers
Engineering Design Process
Fluorinated Alkyd Coatings
Encapsulation of Alkyds for Coatings
Principles of Self Healing Polymers
Self Healing Gelatin Laboratory

What is an Alkyd & Why Should You Care About Them?

- Introduced in 1927.
- Derived from alcohol and acid.
- Used as a synthetic coating resin.
- The polymer is considered to be a Polyester Resin.



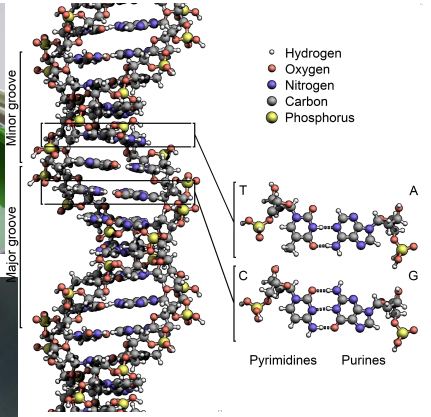
- Inexpensive to produce
- Effective in application:
  - High Gloss
  - Good Color Retention
  - Resistant to Heat and Solvents
  - Ability to undergo Autoxidative Crosslinking
- Few Film Defects
- Require low VOC for High Solids
- Produced from Bio-Renewable FeedStocks

Oil	Fatty Acid (%)				
	Saturated[a]	Oleic	Linoleic	Linolenic	Others
Soybean	15	25	51	9	
Sunflower	9	25	64	trace	
Safflower	11	13	75	1	
Linseed	10	22	16	52	
Castor	3	7	3		87
Palm	49	40	10	trace	

Wait! What is a Polymer?

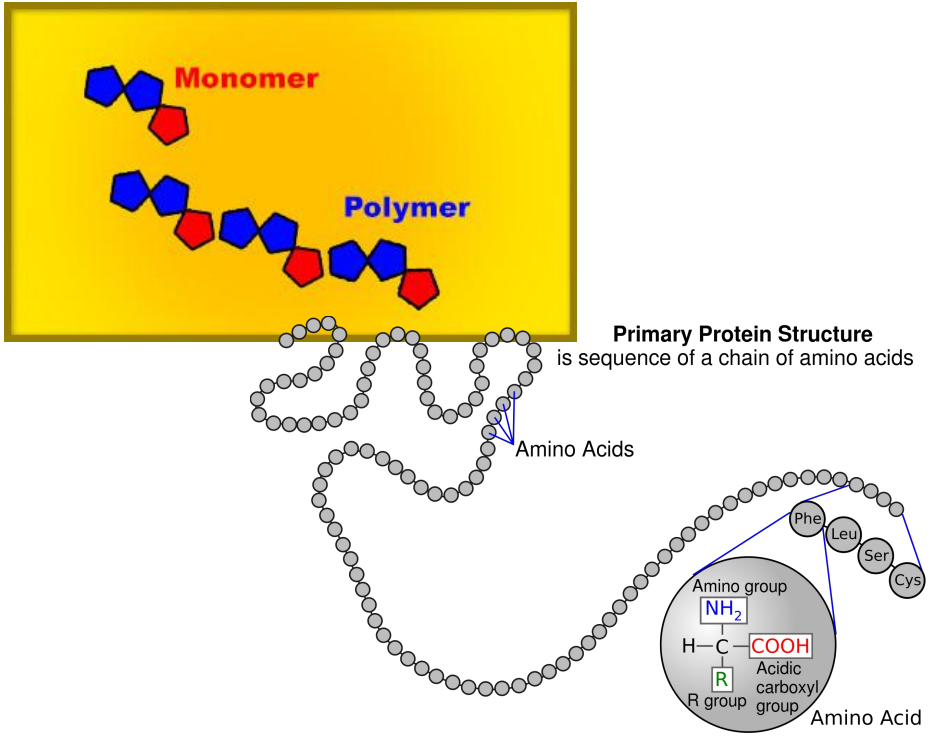
"You act like we should know what these are."

- You see, touch, and use polymers are everyday! In fact you are made up of natural polymers such as proteins and nucleic acids (**Yes our DNA is a polymer!**).
- Polymers are chemical compounds made up many long, repeating chains of molecules (bead demo).



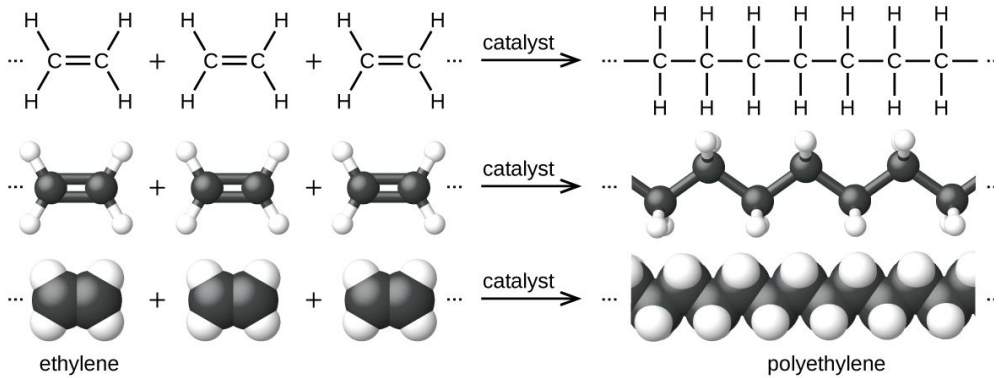
So… What Gives These Polymers Their Specific Characteristics

- We now know polymers are compounds made up of long repeating units of molecules, and it is the type of molecules that make up the polymer along with how they are bonded together that gives the polymer its distinctive properties.
- We call these individual molecules that make up the repeating units of polymers **monomers**.



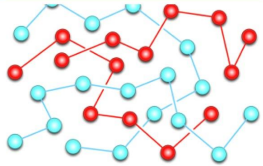
Ok..... So, Now I Know What A Polymer Is How Do We Make Them?

- For this we will use organic chemistry.
- Polymers are created through a process called **Polymerization**, in which monomers are combined into a long chain through a series of chemical reactions performed under specific temperatures and pressures.
- These long chain polymers are held together by *covalent bonds*.
- Polymer chains can be **crosslinked** by forming ionic bonds between the chains.



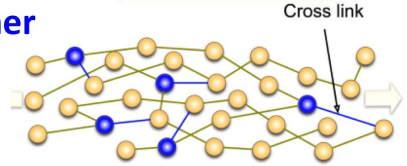
Two types of polymer

Thermosoftening (thermoplastic)



- Tangled polymer chains
- No cross-links between chains
- Weak forces of attraction between chains
- Softens when heated

Thermosetting (thermoset)

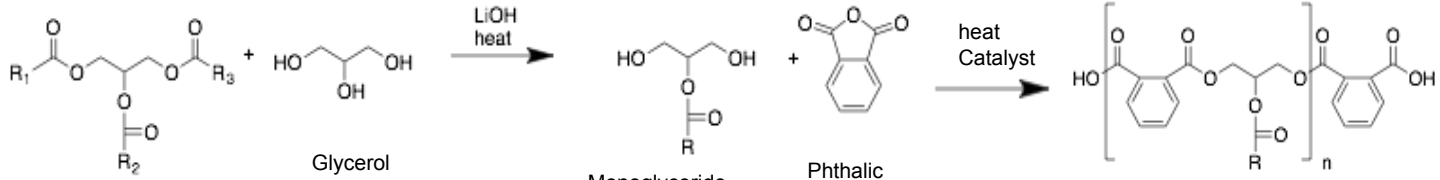


- Polymer chains held together by **strong covalent cross-link bonding** that does not break on heating.
- Remains hard when heated

Types of Alkyd Synthesis Used

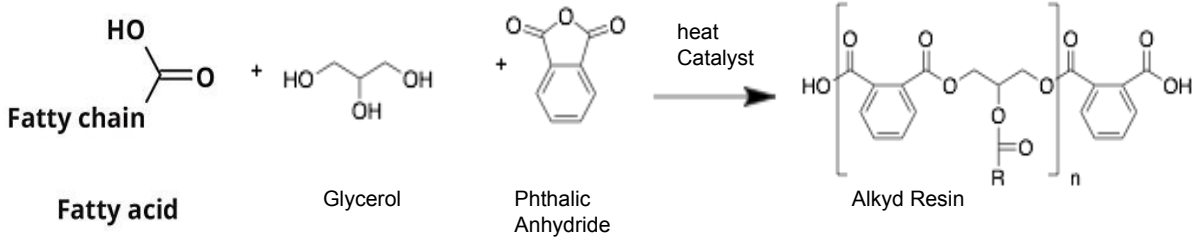
Monoglyceride Process

- Two Stage Process: 1) Transesterification 2) Direct Esterification
- Temperatures between 230°C and 250°C



Fatty Acid Process

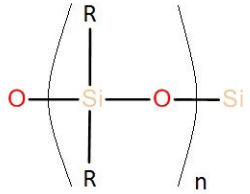
- One Step process that offers better control, but at a higher cost than the Monoglyceride process.
- In this Process the esterification of both aliphatic and aromatic groups occurs at the same time.



Modifying Alkyds

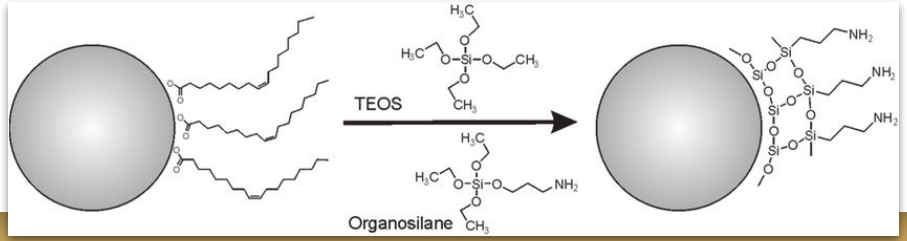
Fluorinated Alkyd Coatings for Graffiti Resistance

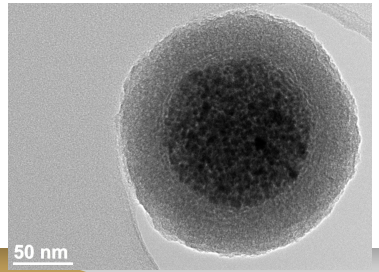
- Adding fluorine (in addition to showing graffiti resistance it increased abrasion resistance, created a more robust surface, increased corrosion resistance).
- Currently working to add siloxane to improve adhesion.



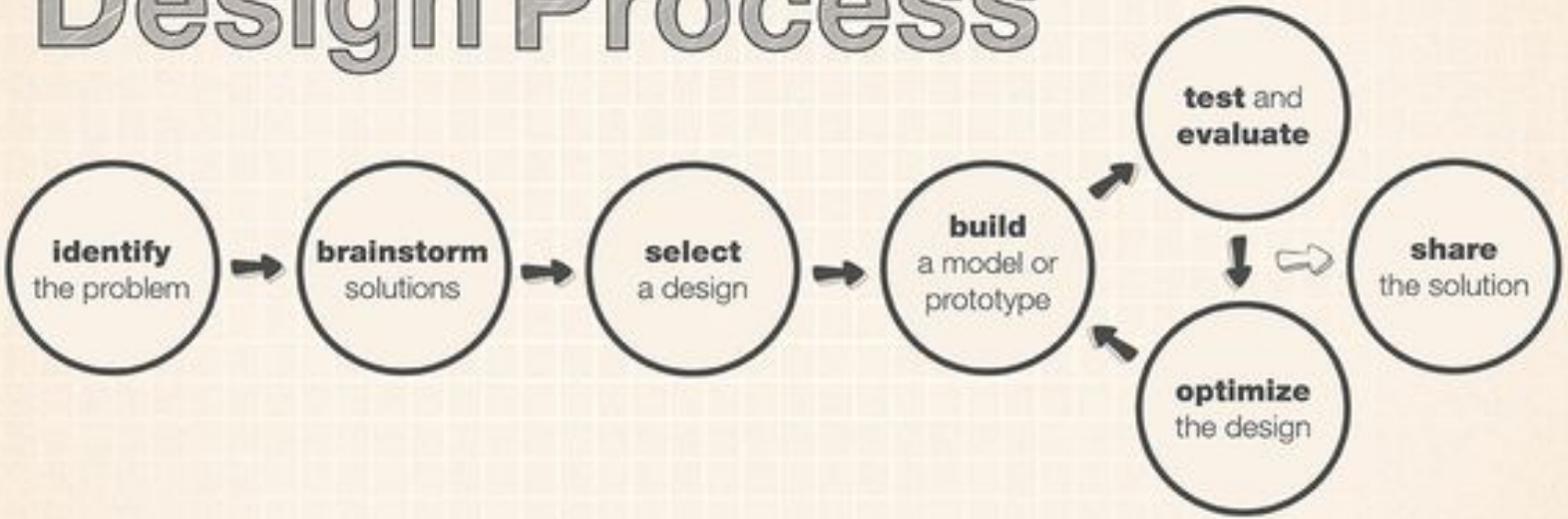
Encapsulation of Alkyds for Corrosion Resistant Self-Healing Coating

- Capsules are created by encapsulating the alkyd in a silica shell and then adding the capsule to a polymer primer.
- Benefits can be synthesized without using harmful ingredients (monomer, catalyst, and solvent).
- Capsule will autoxidate when ruptured.





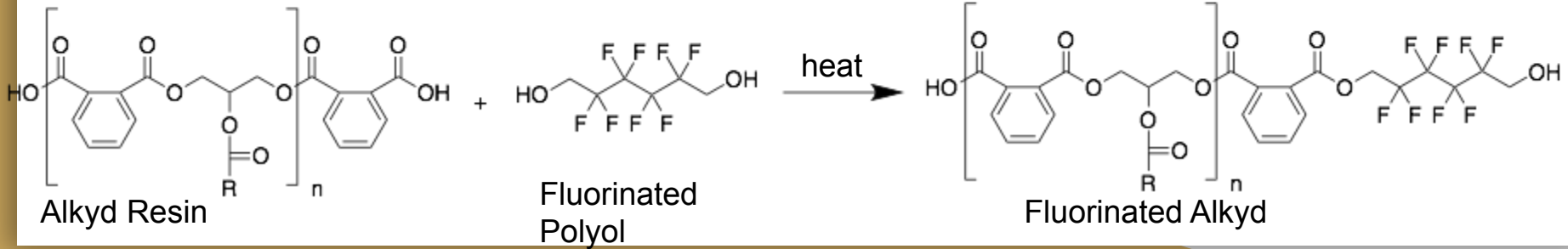
Engineering Design Process



Problem: Graffiti

Engineering Solution: Using Fluorinated Alkyd Coatings for Graffiti Resistance

- Modifying an alkyd using a fluorinated polyol after step growth polymerization has occurred.
- A bio-based resin that has a hydrophobic, graffiti resistant surface.

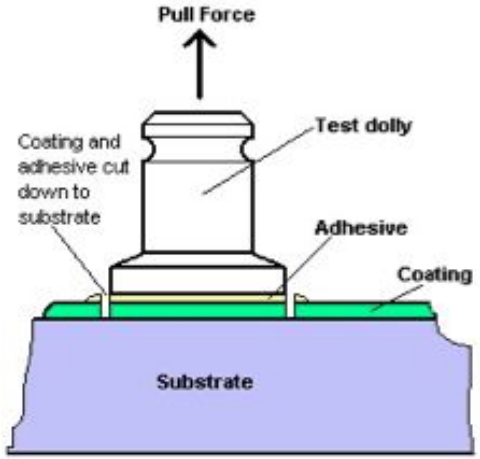


Alkyd Resin

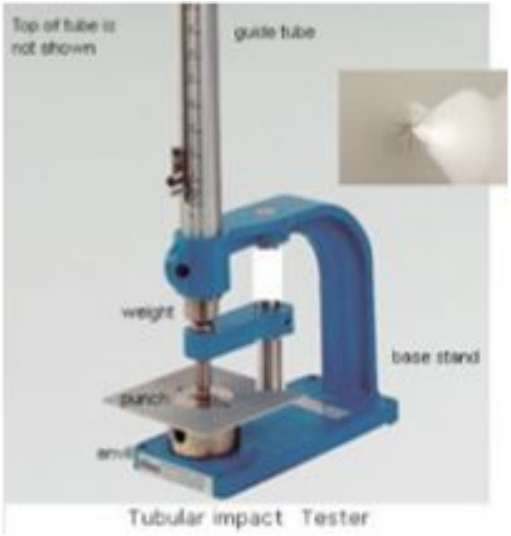
Fluorinated Polyol

Fluorinated Alkyd

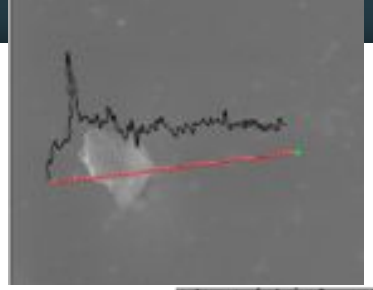
Testing Properties

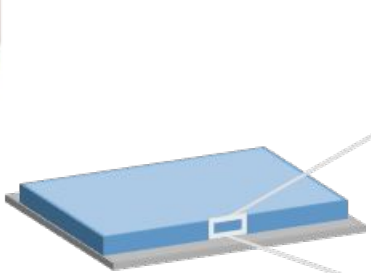


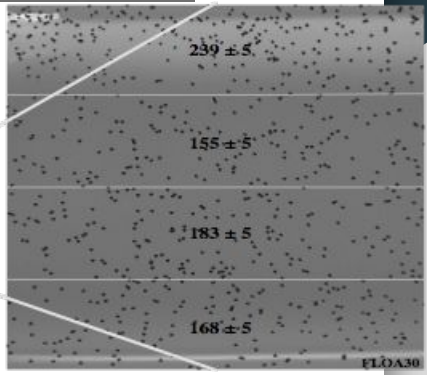
Measures minimum tensile stress



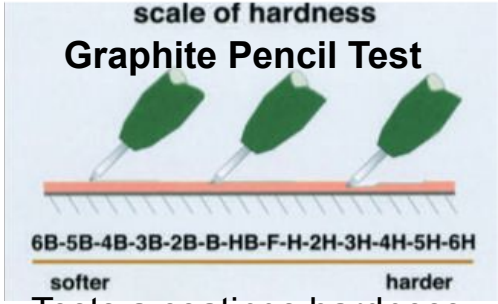
Tests impact resistance



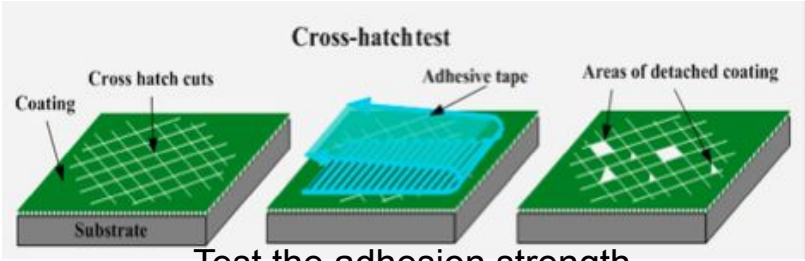




SEM shows stratification & where atoms are



Tests a coatings hardness

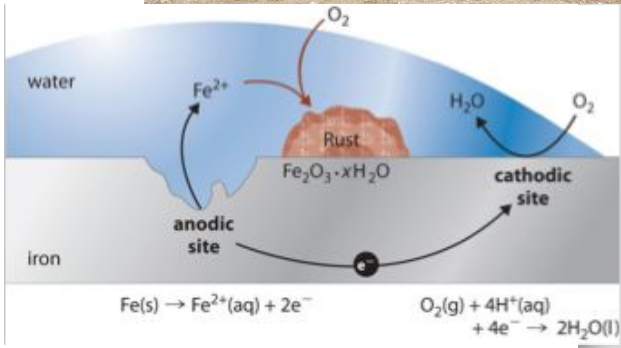


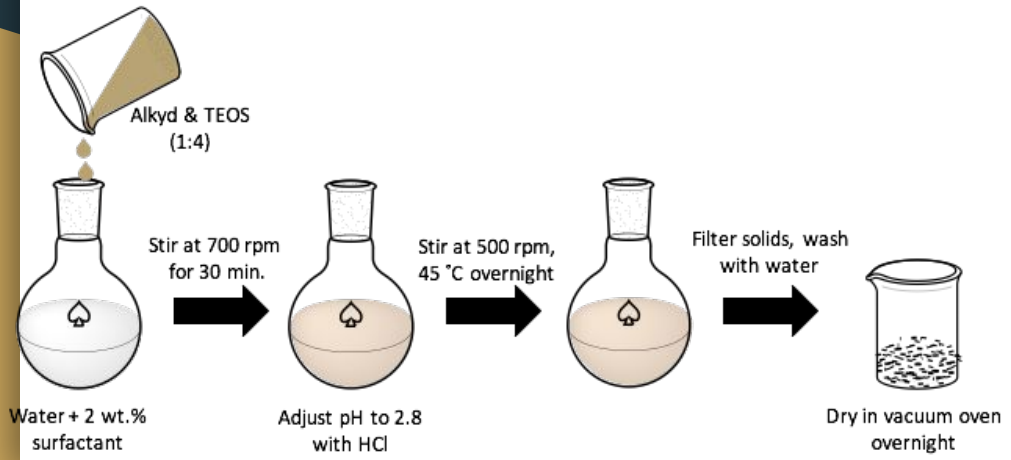
Test the adhesion strength

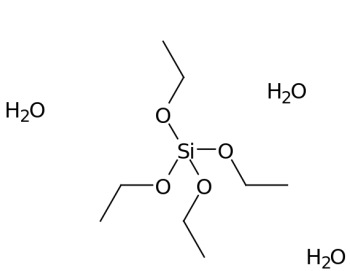
Problem: Corrosion

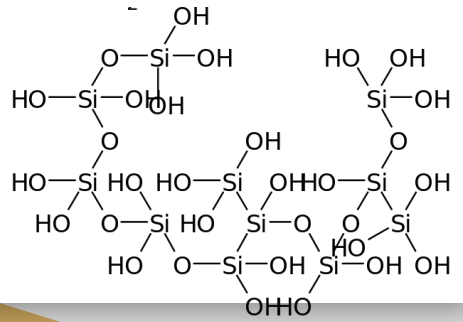
Engineering Solution: Encapsulation of Alkyds for Corrosion Resistant Self-Healing Coating

- Damage surface creates an opportunity for electrochemical reactions to produce rust.
- Coatings can receive an additive that has alkyd encapsulated in a silica shell.
- Capsule gets punctured and alkyd reacts with oxygen to undergo autoxidative curing. .

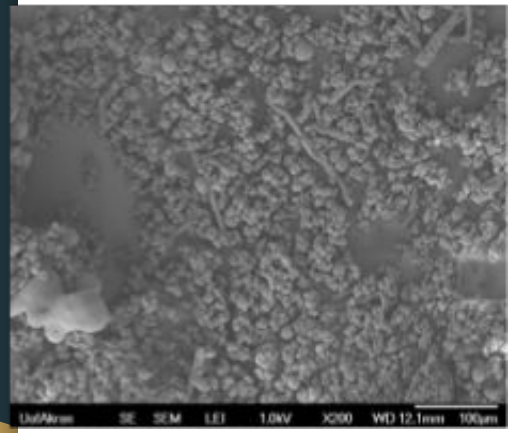


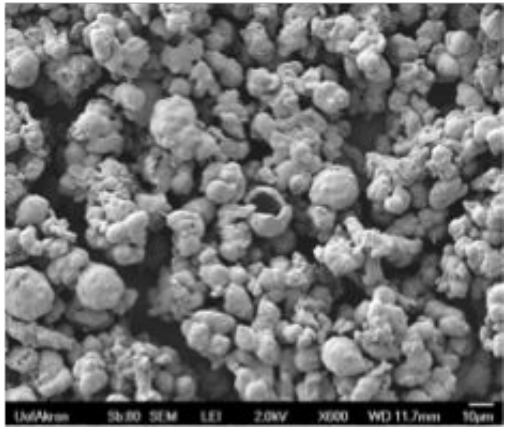


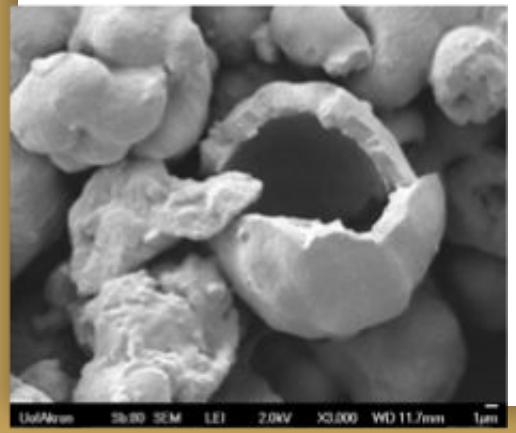


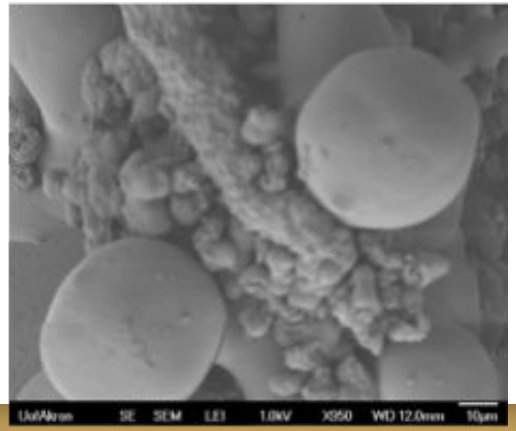


Scanning Electron Microscope- Capsule





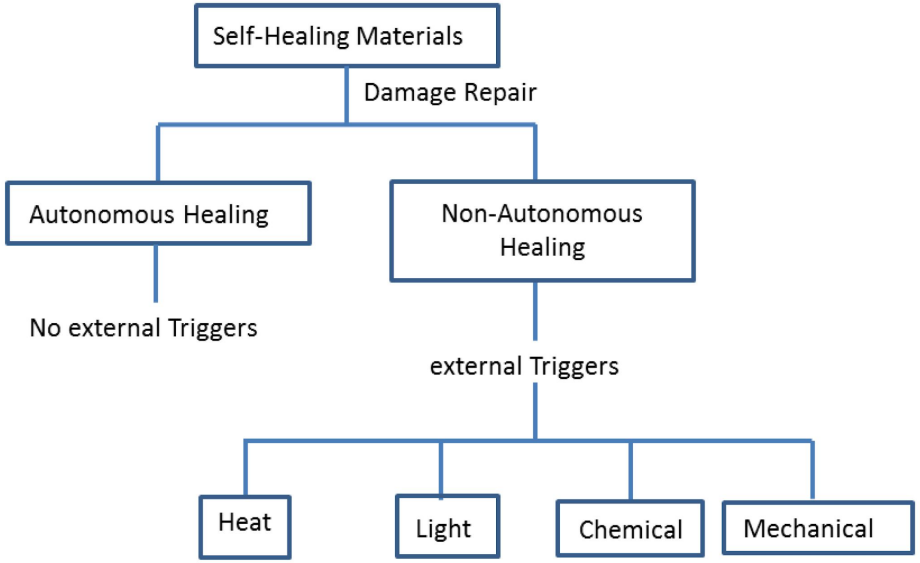


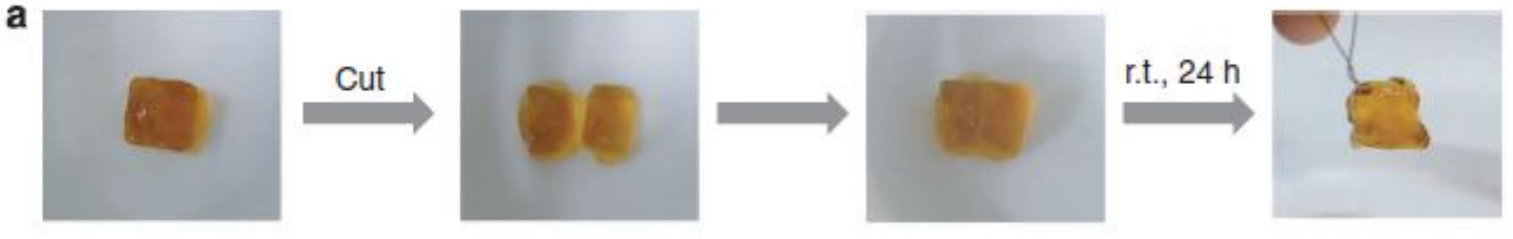


- Alkyd was encapsulated in silica shell.
- Not all silica formed capsules
- Each Capsule consists of about 53%/TEOS (tetraethyl orthosilicate) and 28% Silica Shell
- One problem is that capsules are too large for coating applications.
- Currently trying to make capsules smaller.
- Disperse and test the capsules in a coating resin.

Self Healing Polymers! Wait did you say Self Healing? But How?

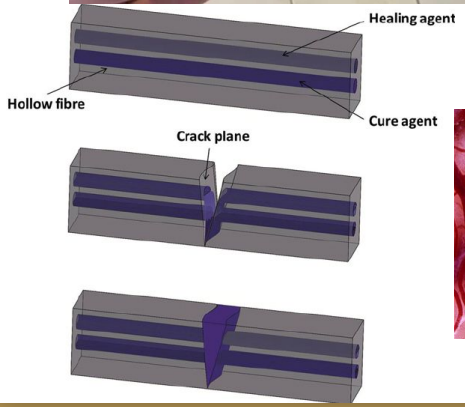
- **Self Healing**- the ability to repair autonomously.
- A **self healing material** has the ability to recover its properties after suffering damage restoring the materials performance.

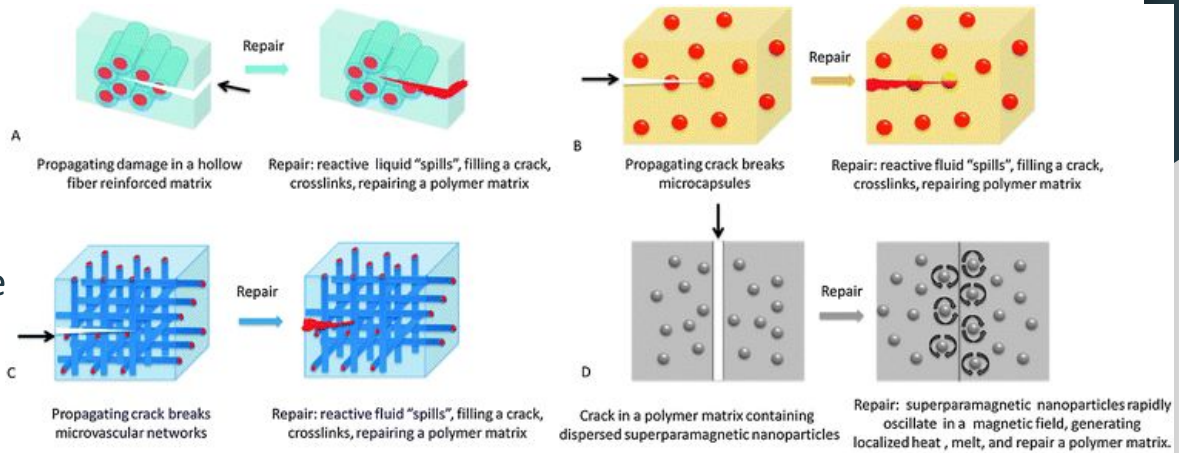


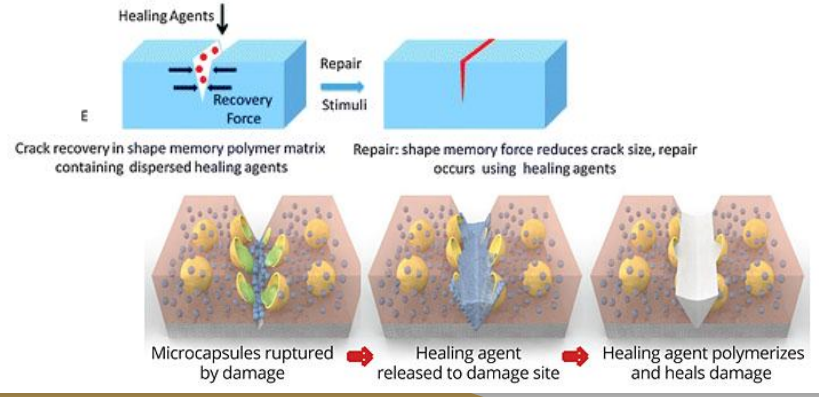


Strategies for self Healing Materials

1. Hollow glass fiber repair
2. **Microencapsulated healing agent**
3. Microvascular network
4. Hollow fiber approach
5. Inclusion of thermoplastic additive







Self Healing Gelatin Laboratory Experience

Concept

- Conduct a polymer engineering laboratory using a direct food spherification reaction.
- Enhance the properties of gelatin to engineer a stronger substance that can self heal using polymer crosslinking.
- Quantify the results using modified engineering equipment.
- Report the data in a scientific manner.

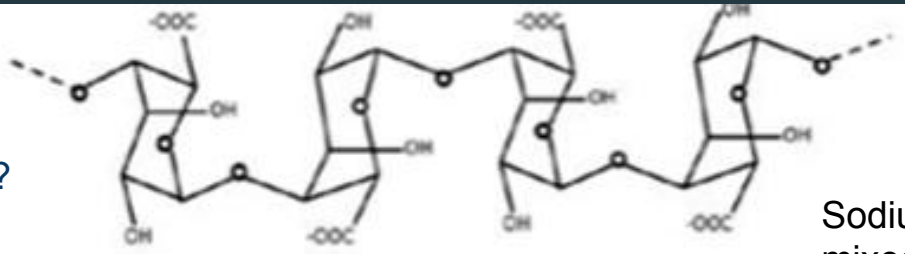
Learning Objectives

- Design and conduct scientific investigations.
- Formulate and revise explanations using logic and evidence.
- Perform and quantify chemical reactions.
- Investigate intramolecular chemical bonding (ionic/covalent).
- Investigate intermolecular chemical bonding (types and strengths).
- Perform stoichiometric calculations (solutions).

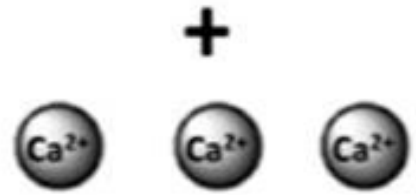
Why does the Calcium displace the sodium if sodium is more reactive?

Entropy Driven-

Entropy is increasing as 1 calcium displaces 2 Sodium ions

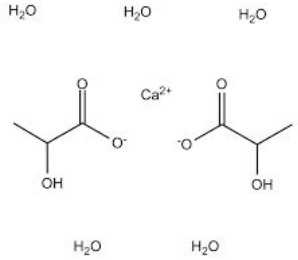


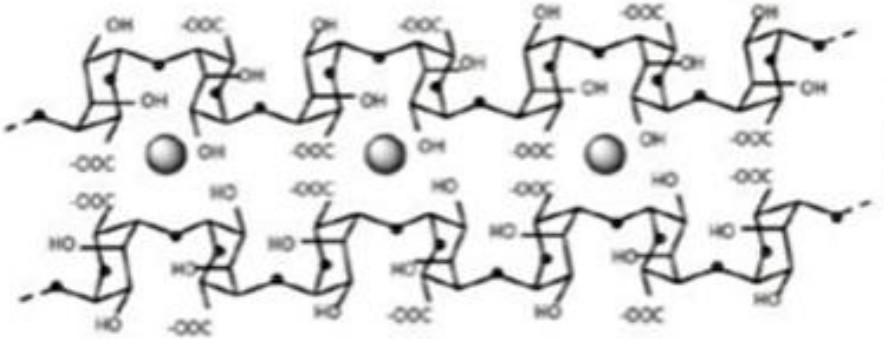
Sodium alginate mixed with Juice



Product added to calcium (Ca^{2+}) bath

From Calcium lactate





Gelation

Spheres

Simplified reaction: Alginate + Calcium ⟶ Calcium alginate

Sodium Polyacrylate & Water Demo

Lesson Design

Engineering problem/goal: Design the strongest gelatin possible that has the ability to self heal when damaged.

Design Method: Students are to meet with their group to evaluate their supplies and design a method to make a self healing gelatin. The variables that can be controlled are the concentration of calcium (calcium lactate solution) in the gelatin, the size of the alginate spheres, the alginate/juice, and the time they leave the spheres in the calcium lactate bath. What cannot controlled is the concentration of alginate juice (pre-prepped to save time), the calcium bath (they will have to make a solution at a specific molarity), and the size of the gelatin mold.

Testing: Gelatin strength will be evaluated by using a durometer to perform a Bloom Test for hardness and self healing will be checked by slicing the gelatin with a knife. Bloom Test will be used to check the hardness of the self healed gelatin. If the gelatin splits during the second Bloom Test the gelatin will be considered to fail and the force should be recorded at which the gelatin failed. The durometer will be used to measure the rupture force of the gelatin and then again once the gelatin has healed.

Reporting: Students will have a lab worksheet to complete that will help them record their data while in the lab and then will be expected to turn in a full laboratory report.

Materials

For Synthesizing Self Healing Gelatin

- Sodium Alginate
- Calcium Lactate
- Gelatin
- Blender
- 12 Cup Pan / Gelatin Shot Cups
- 500 ml beakers
- 10 ml Food Syringes with Attachments
- Mesh Strainer
- 500 ml Measuring Cups
- Plastic Spoons / Knives

For Building the Bloom Testing Durometer

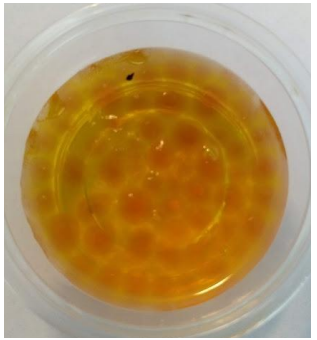
- Pocket kitchen scale 0.01g-500g
- Ruler
- C-Clamp 6”
- Duct Tape
- 8” long 4” x 4” Styrofoam Block

Teacher Set Up

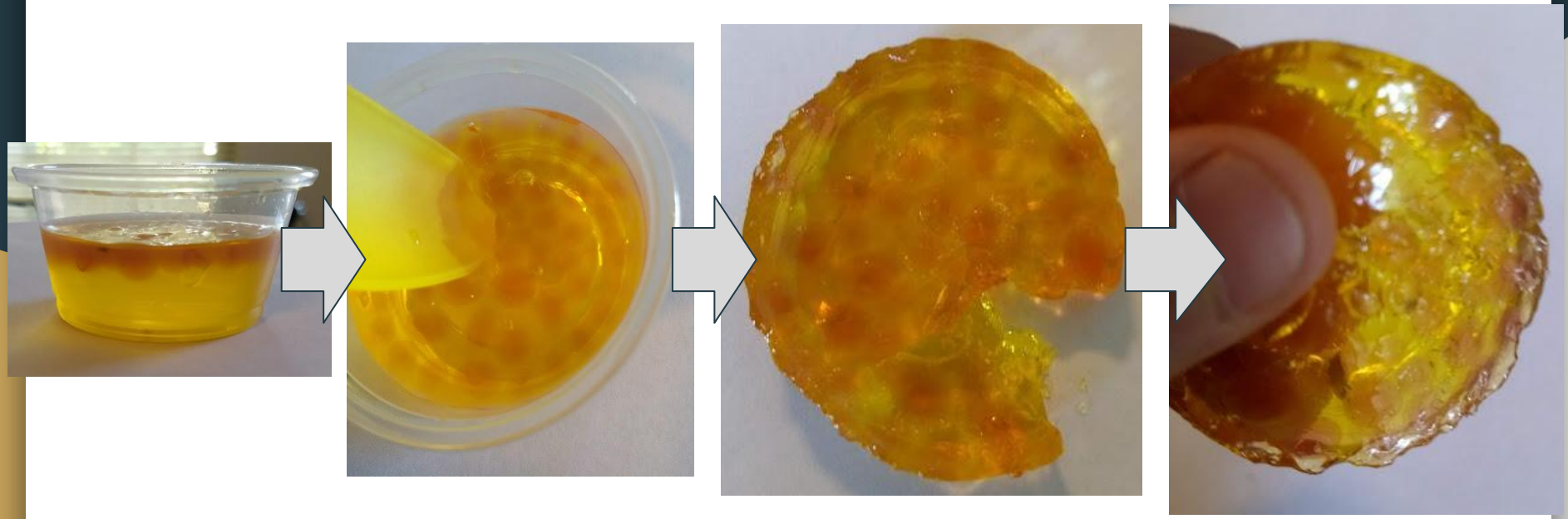
- Teacher will prepare the alginate juice solutions (concentration 0.5% alginate to juice). This is to save time.
- Teacher will set up the durometer.
- Teacher will distribute the supplies to the students laboratory stations.

Student Procedure

- Prepare a 0.046 M solution of calcium lactate and Water.
- Create the alginate juice spheres by using the tools available and dripping the alginate juice solution into a 100 ml calcium lactate bath (students can vary the time they leave the spheres in the bath recommended 2 minutes).
- Recover the spheres from the calcium lactate bath using the mesh strainer. Rinse the spheres in a water bath.
- Make the gelatin mix. Students can experiment with how much gelatin mix and water to use.
- Add calcium lactate solution to the gelation mix. Students can experiment with how much Calcium Lactate solution to add to the gelatin mix.
- Add the solutions and the spheres to the mold (make sure there is one control pure gelatin with no additive).
- Place molds into the refrigerator at 10^{o}C.
- Once the molds are solid test the gelatin on the durometer.



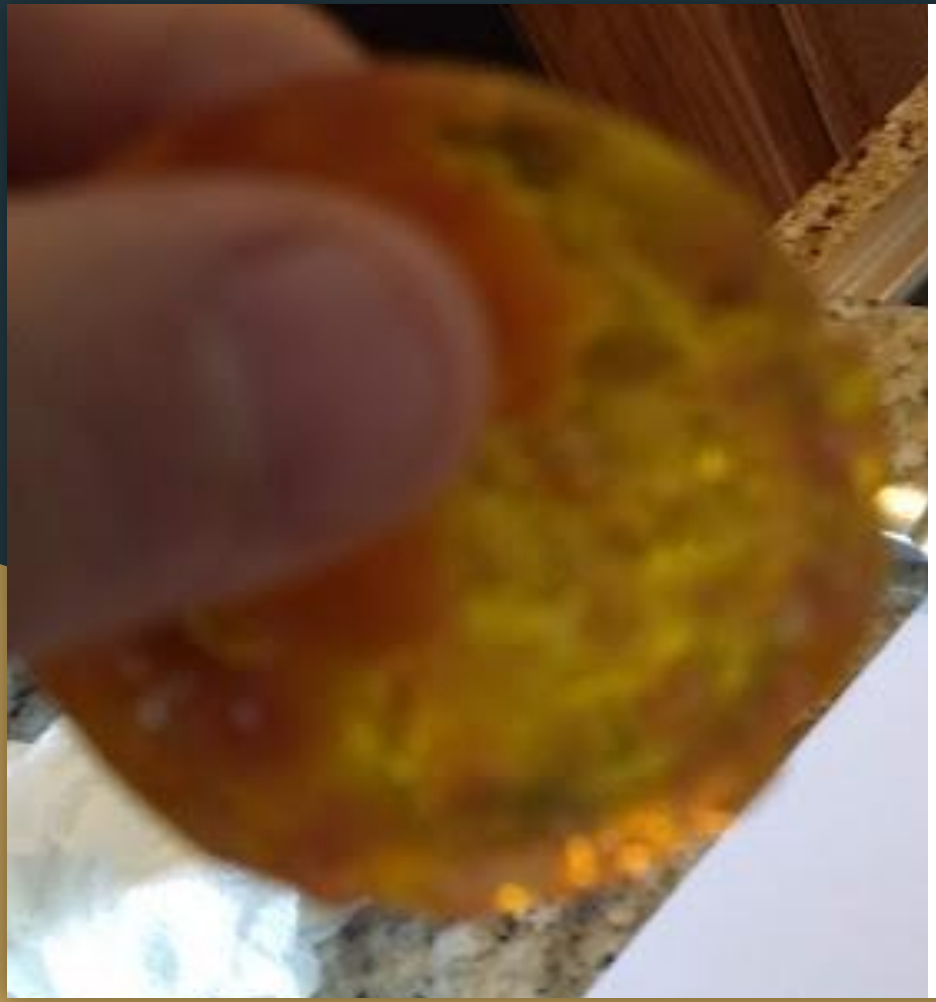
Demonstration of Self Healing in the Gelatin

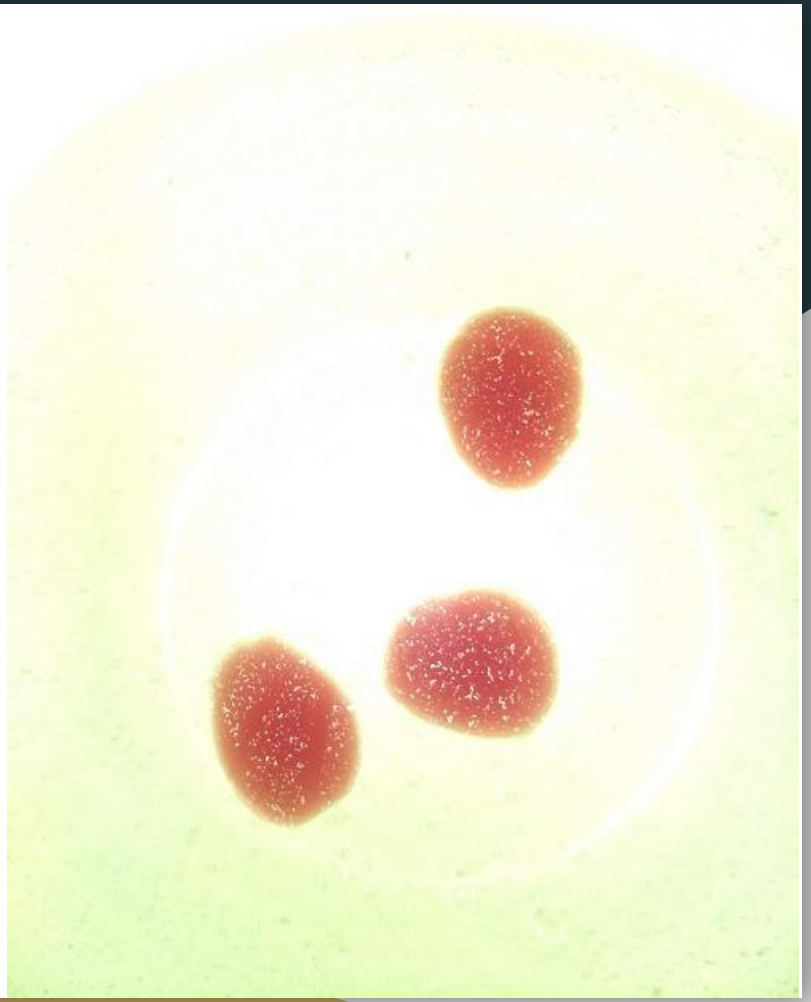


Testing the Hardness of the Gelatin Before and After Using Bloom Test for Hardness & A Durometer

Category	Bloom Number	Average Molecular Mass
Low Bloom	50-125	20,000-25,000
Medium Bloom	175-225	40,000-50,000
High Bloom	225-235	50,000-100,000

1. Students will use the Bloom Test to measure the strength of the gelatin by depressing the gelatin by 4 mm and recording the force needed to due this (Note this is a modified device and the students will have to concert from a mass measurement to a weight measurement to calculate the force and determine their Bloom's number).
2. Students will use the durometer to measure the force needed to rupture the mold and once it has healed the students will then retest the mold to see measure the rupture force of the healed gelatin.





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