Polymer Chemistry in 3D Printing

RPI STEP Program

Lauren Zakrzewski & Lizzie Lepre

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- 3D Printing Materials
- Polymer Putty Synthesis
- Polymer Chemistry
- Liquid Nitrogen Demo

Day 2

- Glass Transition Temperature
- Temperature and Elasticity Analysis Activity
- Polymers in Everyday Life
- Polymers in 3D Printing

Day 3

- SLA 3D Printing
- SLA vs FDM
- Stress and Strain
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- Dynamic Mechanical Analysis (DMA)

Day 4

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- Research Project Goals
- Polymerization Visual
- UV Irradiation
- Phase Separation
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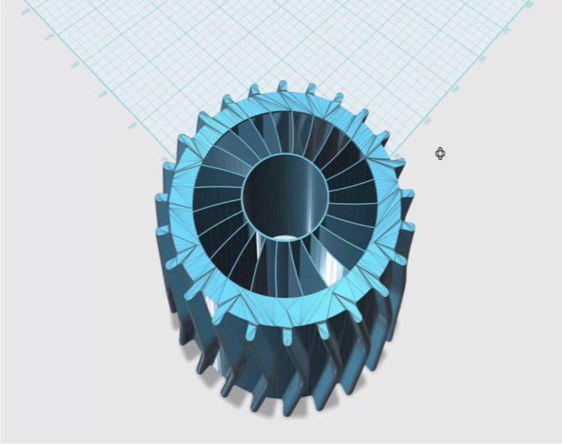
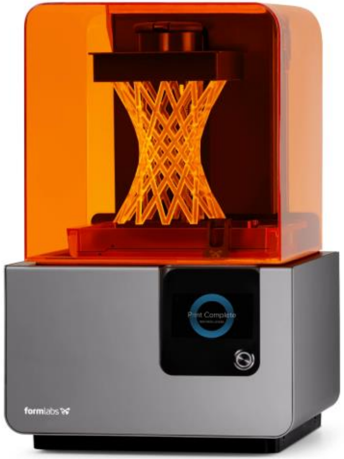
- Phase Separation Lab Demo
- Scanning Electron Microscopy
- Nature and Nano-Structure

3D Printing Review

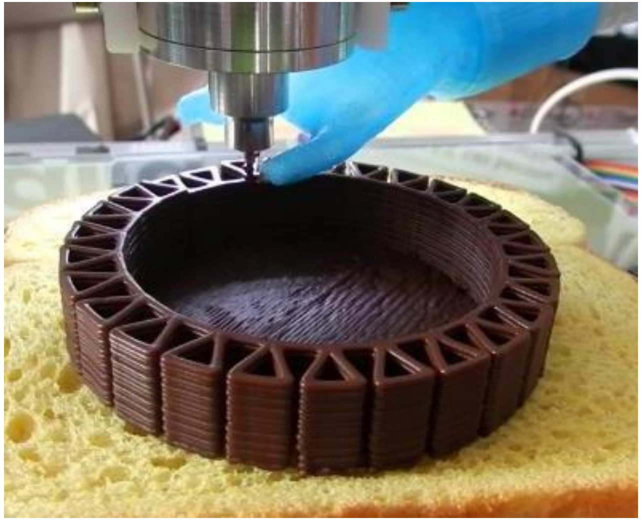


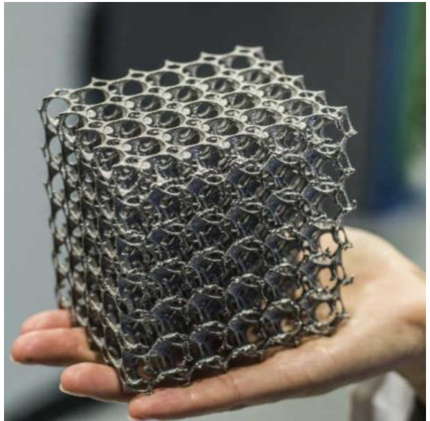
- Additive Manufacturing
- Based off of a CAD drawing (Computer-aided design)
- CAD drawing converted to a digital file that can relay instructions to the 3D printer



3D Printing Materials

- Plastics/ Polymers- Acrylonitrile Butadiene Styrene (ABS), Polylactic Acid (PLA)
- Metals- Stainless Steel, Titanium, Copper…
- Resins
- Carbon Fiber
- Food





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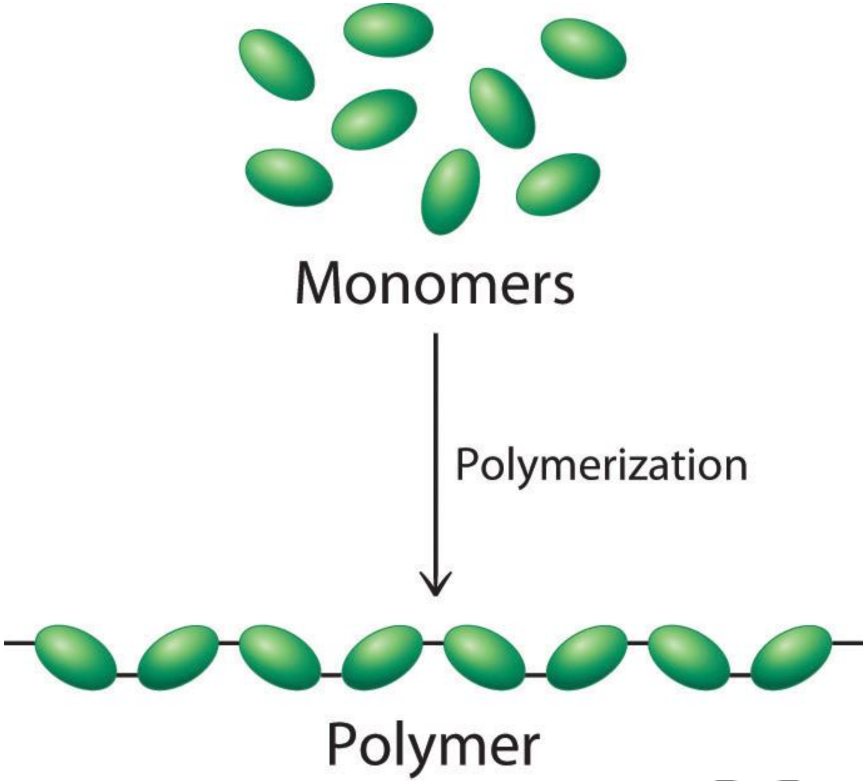
Polymer Chemistry Introduction

- Molecules: the smallest unit of a compound that can chemically react

- Monomers: molecules that can chemically interact with each other, they are known as “Building Blocks”

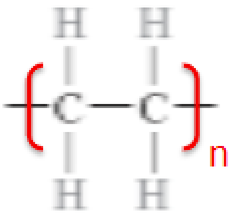
- Polymerization: monomers are chemically combined to make long chains of the same unit, called polymers

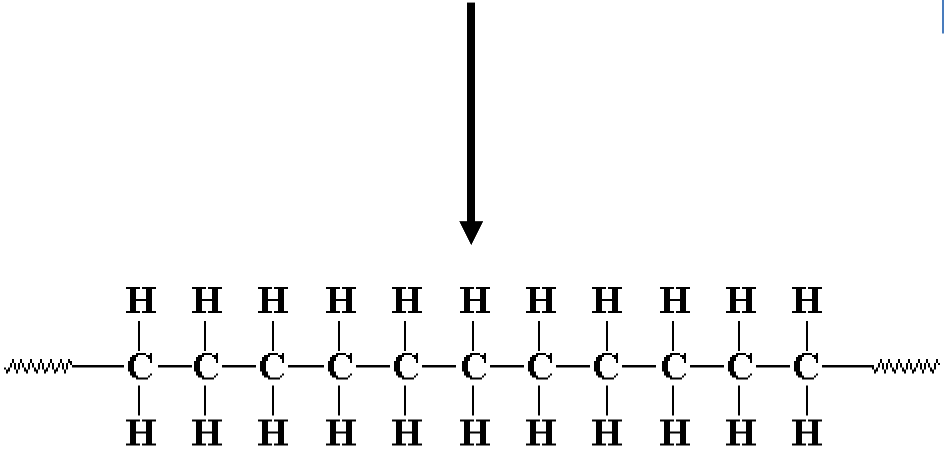


Polymer Notation

This group repeats along the chain **n** times

Poly(ethylene)





Common Polymers

Polyethylene

Polytetrafluoroethylene
(Teflon)

Polyvinyl chloride
(PVC)

Polyepoxides
(Epoxy Resin)

Polynucleotide
(DNA)

Polyisoprene
(Natural Rubber)

Polymer Putty Synthesis Activity

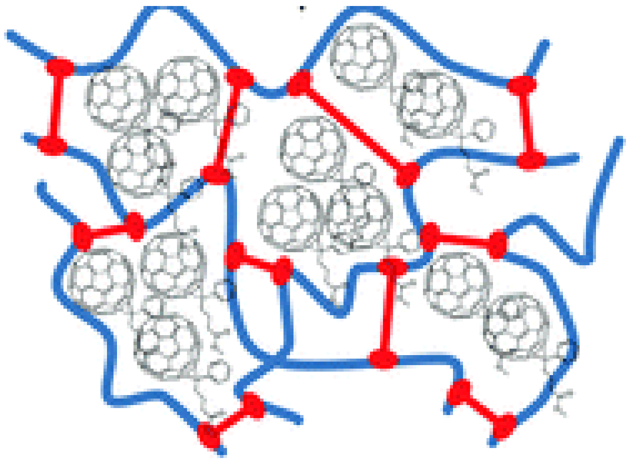
Take out the following items

- Vials of glue (50 ml and 10 ml)
- Vial of contact lens solution (11 ml)
- Vial of baking soda (¼ tsp)

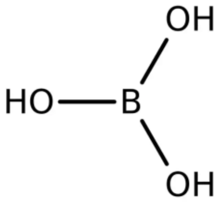
1. In a container, combine the baking soda and the contact lens solution to make an activator.
2. Add the glue to the activator combination, and knead until it has a putty-like consistency.

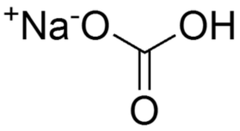
Polymer Putty Background

- Glue [polyvinyl acetate (PVA)]
- Baking Soda [sodium bicarbonate ($NaHCO_3$)]
- Contact Lens Solution
  - Contains Boric Acid [hydrogen borate (H_3BO_3)]



Boric acid combines with baking soda → This combination activates crosslinking between the PVA chains in the glue → The crosslinker makes the glue molecules stick together





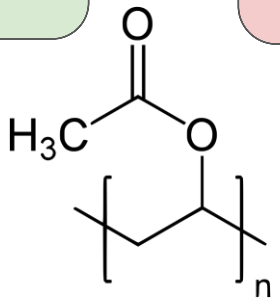
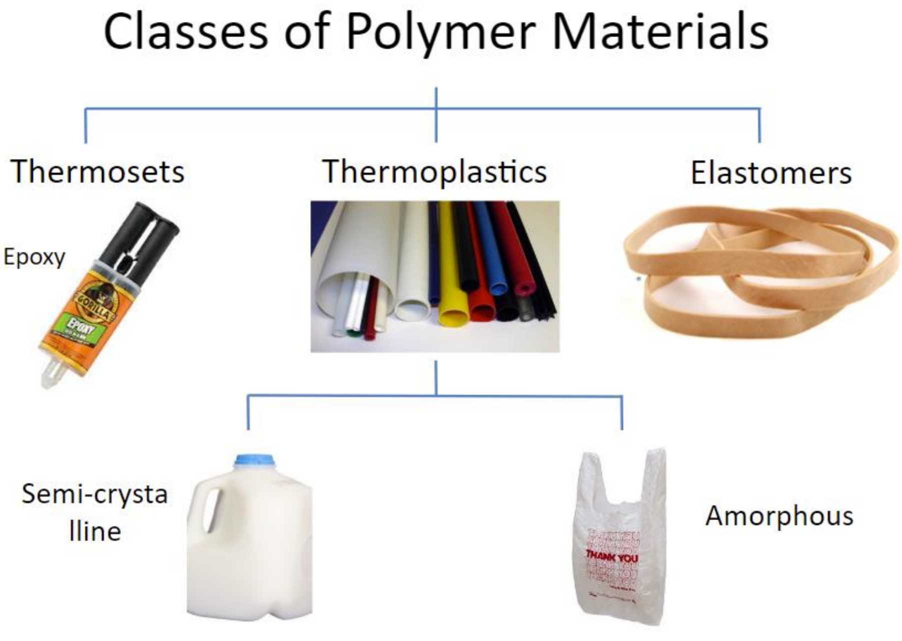
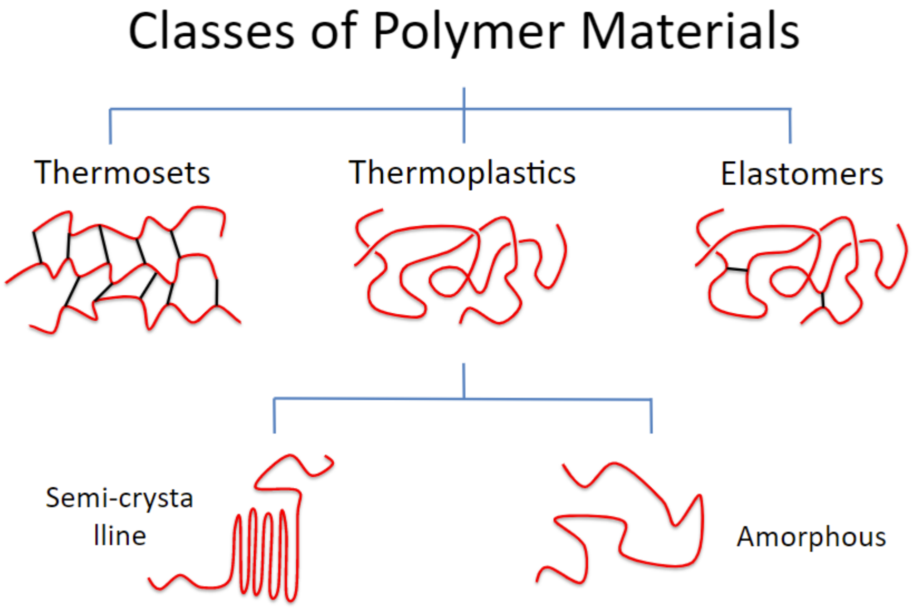


Image Credit to Professor Ed Palermo

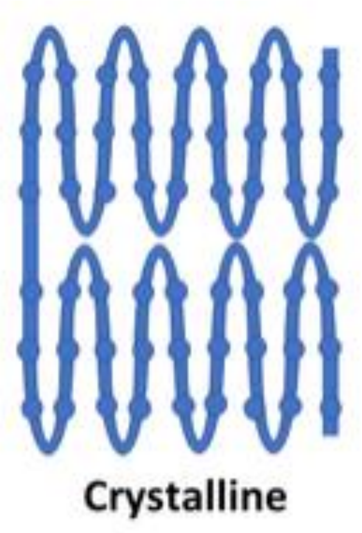




- **Thermoset:** Insoluble, hard material, cannot be melted
- **Thermoplastic:** Can be soluble, malleable, can melt
- **Elastomer:** Flexible, lightly crosslinked, can melt

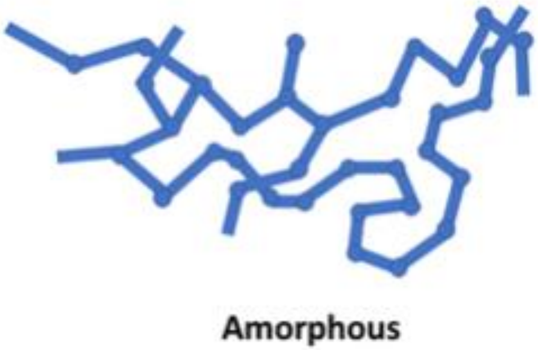
Crystalline

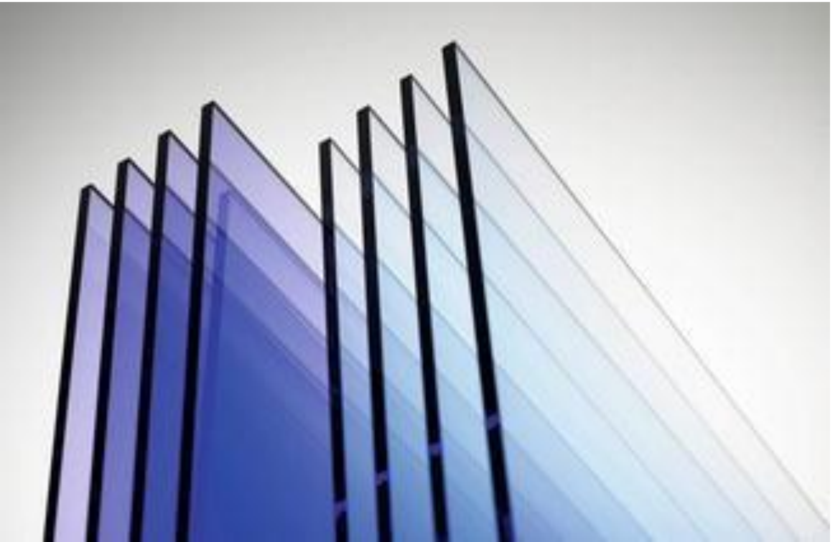
- Molecules are all uniformly packed
- Materials are harder
- Opaque
- Higher density
- Polymers will never be 100% crystalline due to the length of their chains



Amorphous

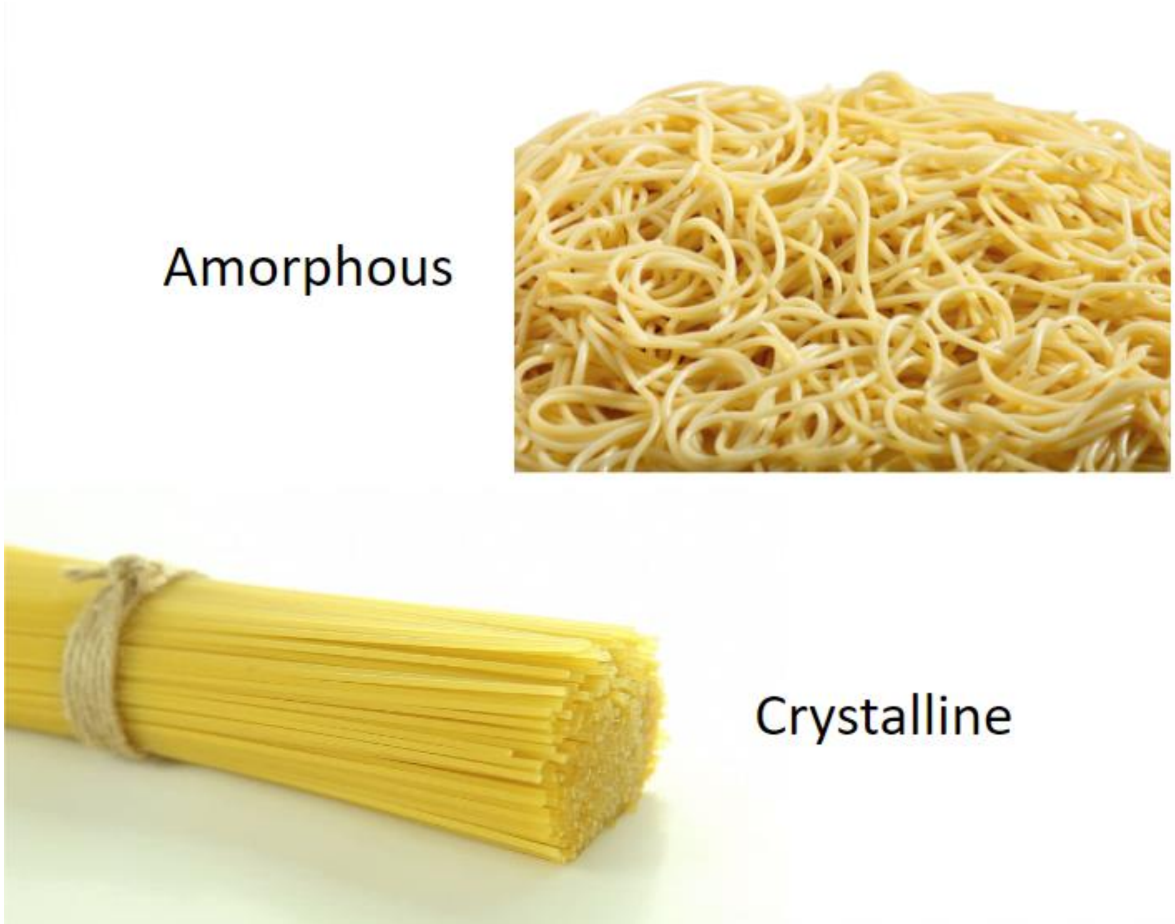
- Molecules are not uniformly packed
- Materials are softer
- Transparent
- Lower Density





Crystalline vs Amorphous

Image Credit to Professor Ed Palermo



Semi-Crystalline

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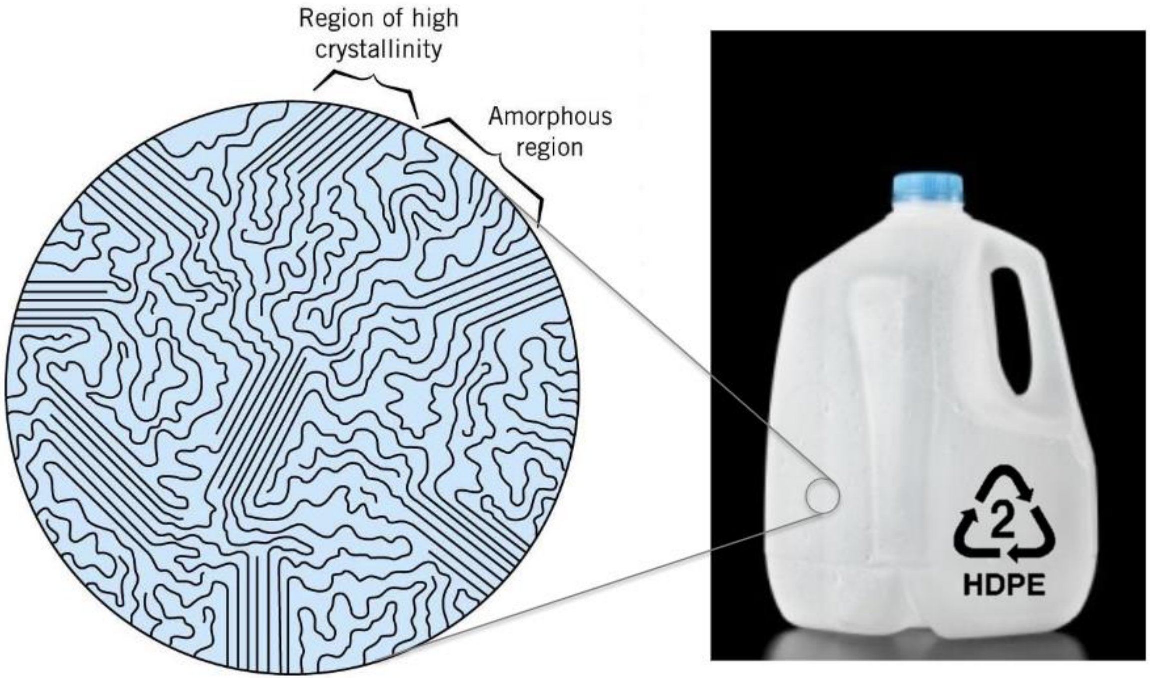
High Density Polyethylene: Milk Cartons



- Contains parts that are crystalline AND amorphous
- More flexible than crystalline, but not as flexible as amorphous

Liquid Nitrogen Demo Results

- The material at room temperature had good elasticity and bent before it broke
- The cold material shattered easily

Temperature a.k.a. Average Kinetic Energy

- At high temperatures, molecules vibrate and move around very fast
- At low temperatures, molecules slow down as there is not enough thermal energy available for movement
  - (Think about how hard it is to move your fingers when outside in the winter with no gloves on)
  - Average kinetic (motion) energy is directly related to temperature

Temp $\uparrow$ $\longrightarrow$ **Average Kinetic Energy** $\uparrow$

The Glass Transition Temperature, T_g

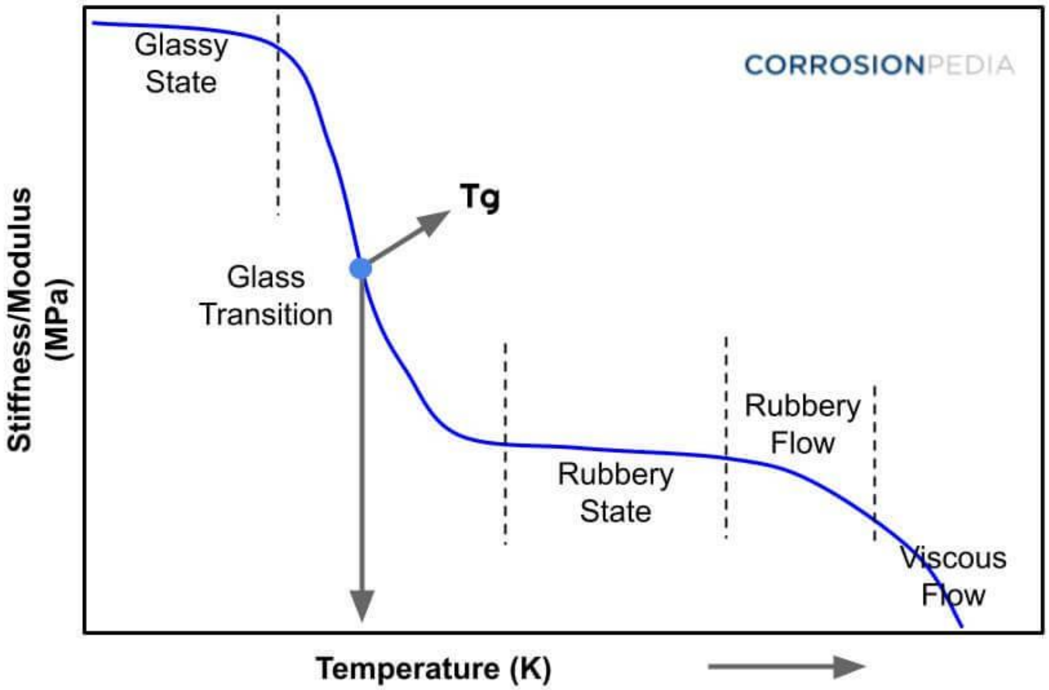
- For polymers, this means chains can wiggle past one another easily at high temps
- At some transition point, the temperature becomes low enough that the polymer chains can NO LONGER wiggle past one another when a stress is applied–they simply break
- This transition is the Glass Transition Temperature, T_g
- This is seen in chewing gum

The Glass Transition Temperature, T_g

- The T_g is the temperature at which amorphous regions within polymers go from rubbery (flexible) to glassy (rigid)
- Occurs in both semi-crystalline and amorphous polymers
  - REMEMBER–semi-crystalline polymers have some percentage of amorphous regions!
- Materials are more brittle at temperature below the T_g

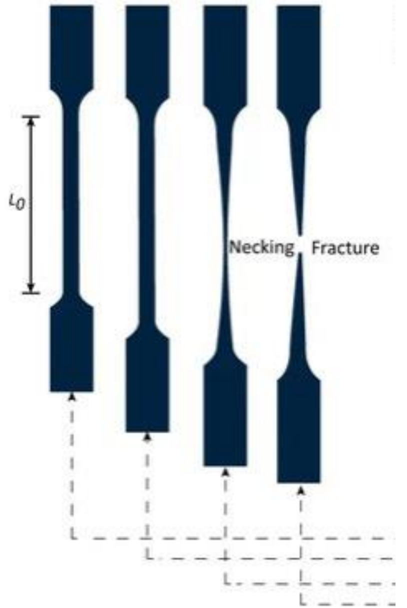
Glass Transition Temperature

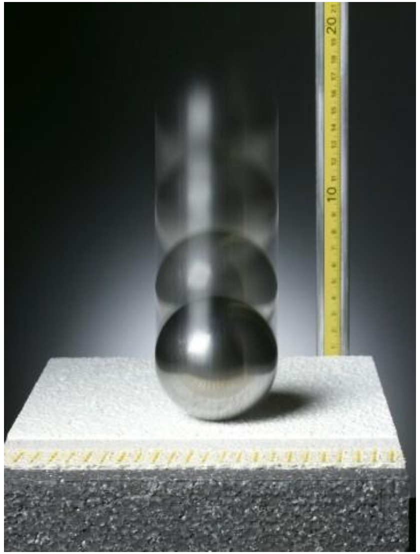
- Transition from glass-state to rubbery-state is reversible
- Elasticity is vastly decreased in the glass-state due to the brittle properties
- Cooling allows amorphous regions to freeze in their previous state



Glass Transition Temperature

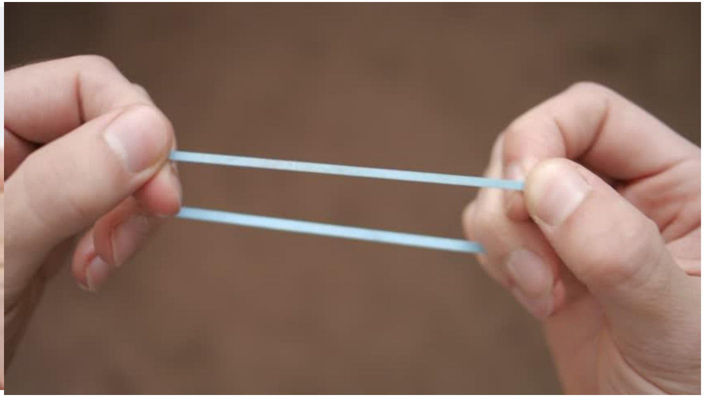
- For polymers, this can vastly range
- Stiffer materials have a higher Tg
- Glass transition temperature effects a materials mechanical properties:
    - Tensile Strength
    - Modulus of Elasticity
    - Operational temperature range
    - Impact resistance





See for yourself!

- Take out your rubber band and putty at room temperature
- Observe its elasticity, how easily does it bend before it breaks?
- Now take out your refrigerated rubber band and putty
- Compare the elasticity, is it more brittle? Does it break easier?

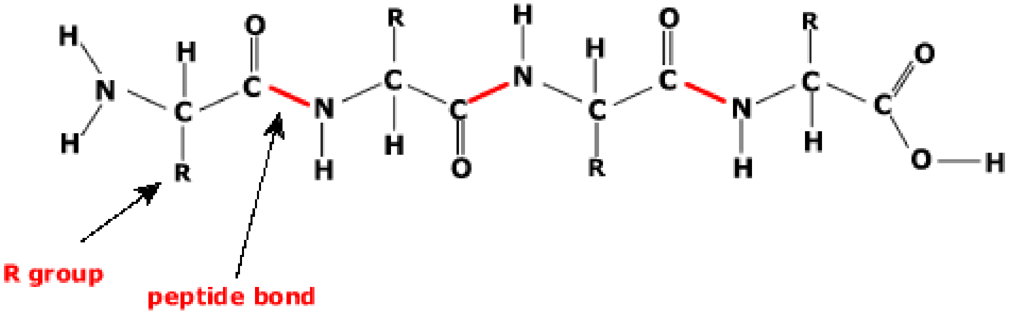


Natural Polymers

- Occur in nature, and are extracted for everyday use
- They can come from animals, plants, and microorganisms
- They have applications in biomedicine, technology, and everyday items

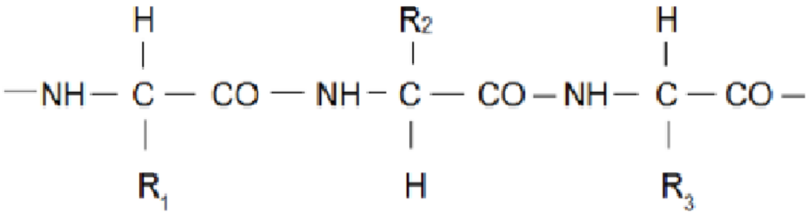
Natural Polymers - Silk

- Silk is a naturally occuring polymer containing sericin and fibroin
- Comes from spiders and other insects
- Silk can be used in cloth, bandaging, gels, tissue engineering



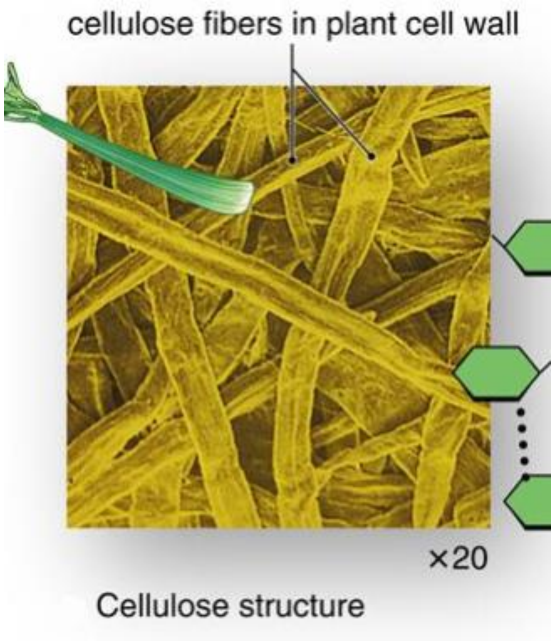
Natural Polymers- Wool

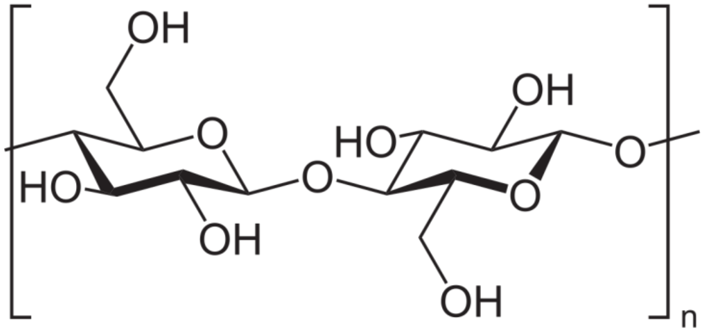
- Wool Fibre contains natural polymers
- Occurs in many mammals
- Contains the protein keratin
- Wool is used in clothing, interior design, blankets, and insulation

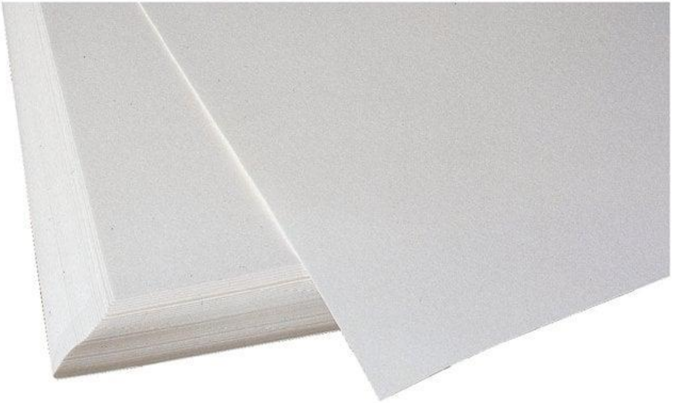


Natural Polymers- Cellulose

- Cellulose is one of the most frequently occurring natural polymers
- Found in the stalks and stems of plants
- Contains glucose molecules
- Can be used to make paper, cardboard, textiles, and renewable fuel





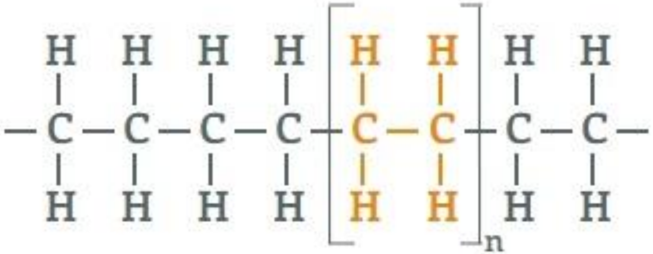


Synthetic Polymers

- Man made polymers for specific uses and containing specific properties
- Often derived from petroleum oils
- They have applications in materials science, technology, and everyday items

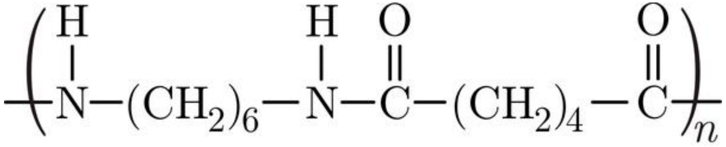
Synthetic Polymers- Polyethylene

- One of the most common plastics used today
- High density or low density can be used to make object with different properties
- Used largely for packaging, which has applications in almost every industry

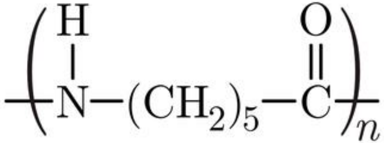


Synthetic Polymers- Nylon

- Nylon can be used in the textile industry, and as a plastic
- Nylon 6 is a type that is used in industrial fabrics and yarns
- Nylon 66 has applications in sportswear, car airbags, parachutes, and tires



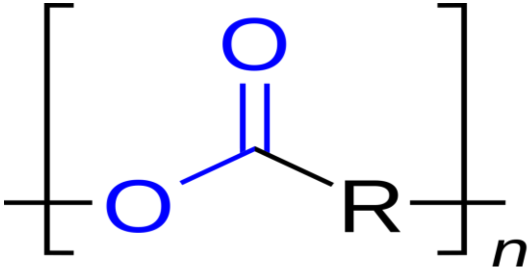
Nylon 66



Nylon 6

Synthetic Polymers- Polyester

- Polyester has textile applications, and is one of the worlds most commonly used fabrics
- Sometimes combines with other naturally occurring or synthetic fibers to make cloth blends
- Seen in clothing, blankets, fabrics, and sheets

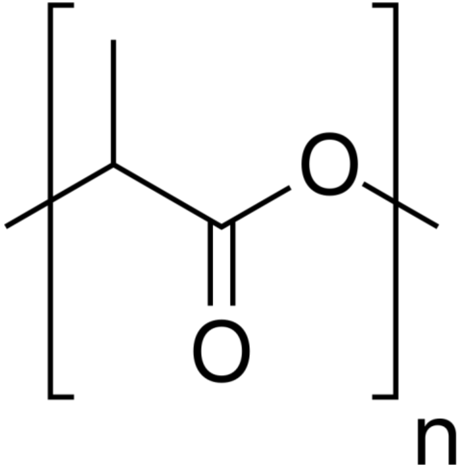


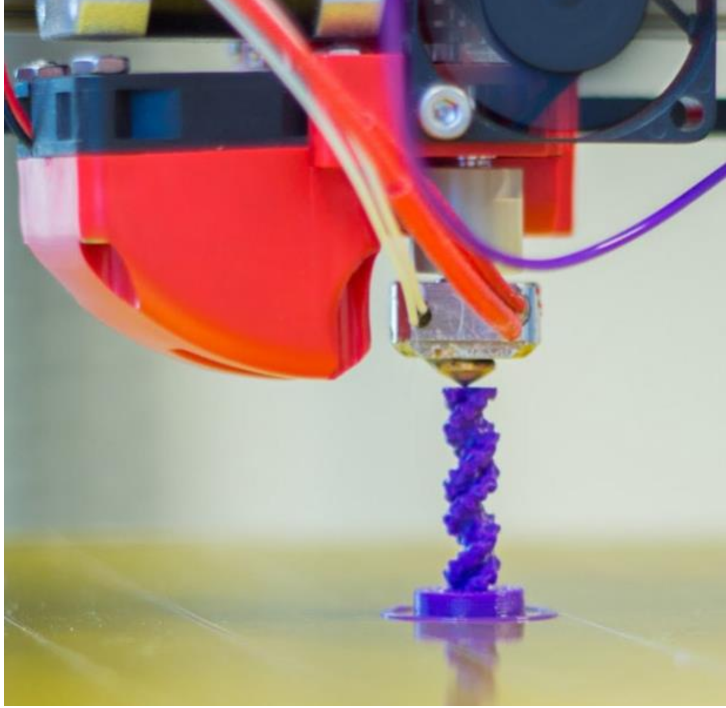
Polymers in 3D Printing

- Many of the plastics, resins, and epoxies that can be applied to 3D printing are polymers
- Different 3D printing methods require materials with specific properties, so polymers are adaptable to meet those needs

PLA

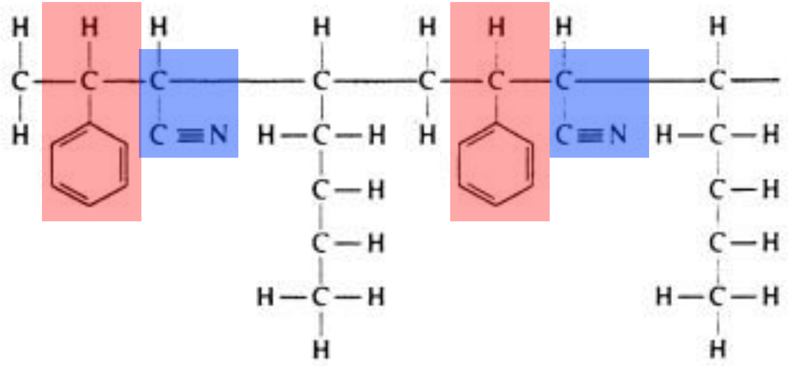
- Poly(lactic Acid), referred to as PLA, is one of the most popular 3D printing plastics
- It is thermoplastic polyester polymer that can be melted down and deposited in layers to synthesize specific objects





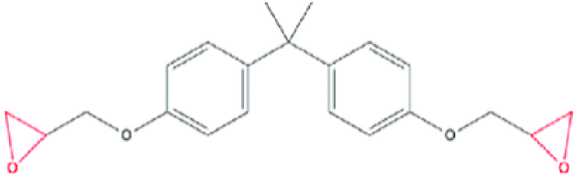
ABS

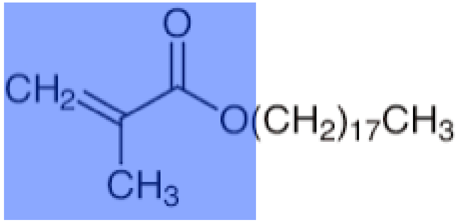
- Acrylonitrile butadiene styrene (ABS) is another very common 3D printing material
- It is also a thermoplastic polymer, containing styrene and acrylonitrile



SLA Polymers

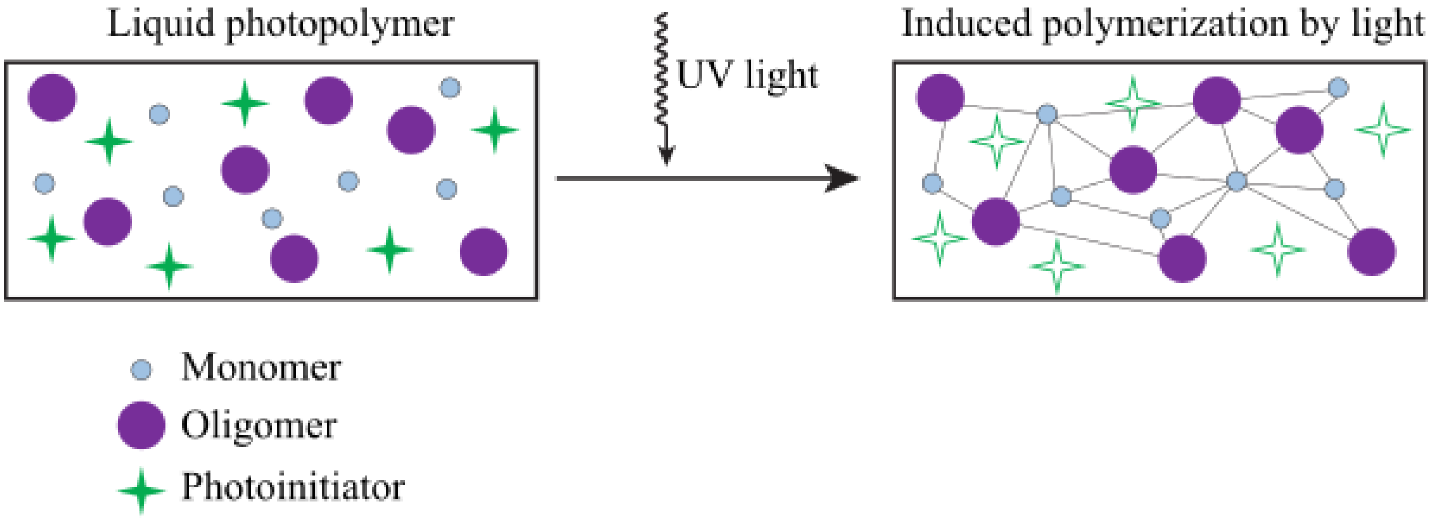
- Liquids used for SLA are known as photopolymer resins
- Photopolymer resins are able to polymerize when exposed to UV light
    - They contain some fraction of photoinitiator which absorbs UV light
- These photopolymers are often comprised of epoxides or (meth)acrylate functional groups
    - Once photoinitiator molecules absorb UV, they activate these functional groups which then react with one another to form polymer chains!





Photopolymerization

- Polymerization which occurs from the absorption of light (typically in the UV range)
- Curing: Another word for polymerization

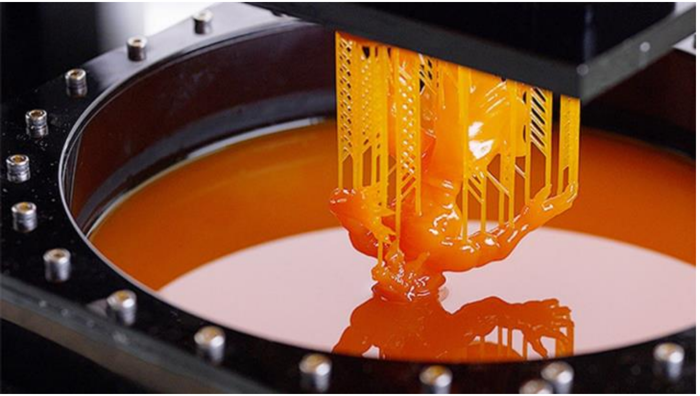


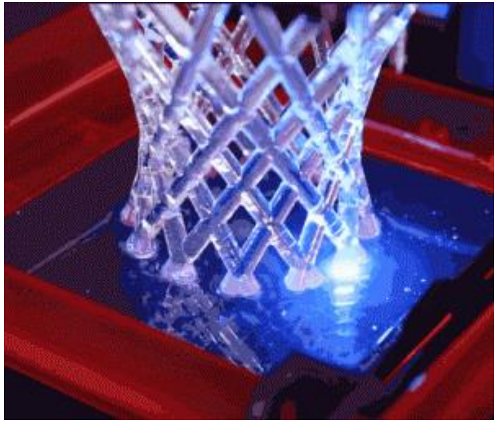
SLA 3D Printing

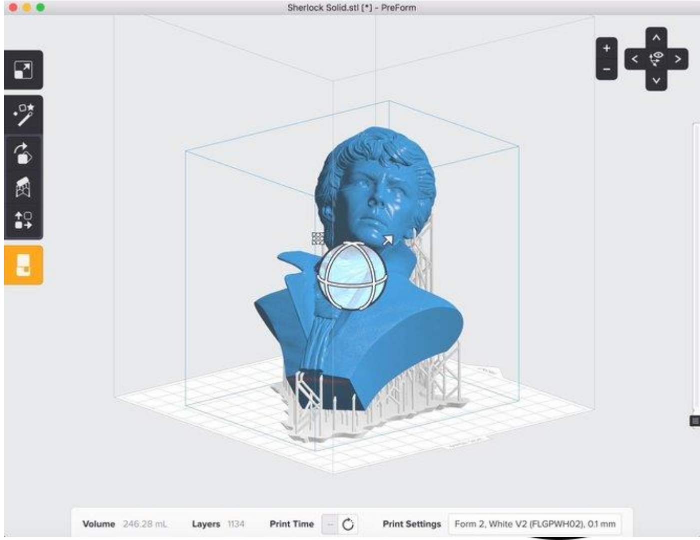
- Stereolithography (SLA) is a process that utilizes a photopolymer and a light source (usually UV) to shape and object
- Creates a smooth and detailed object

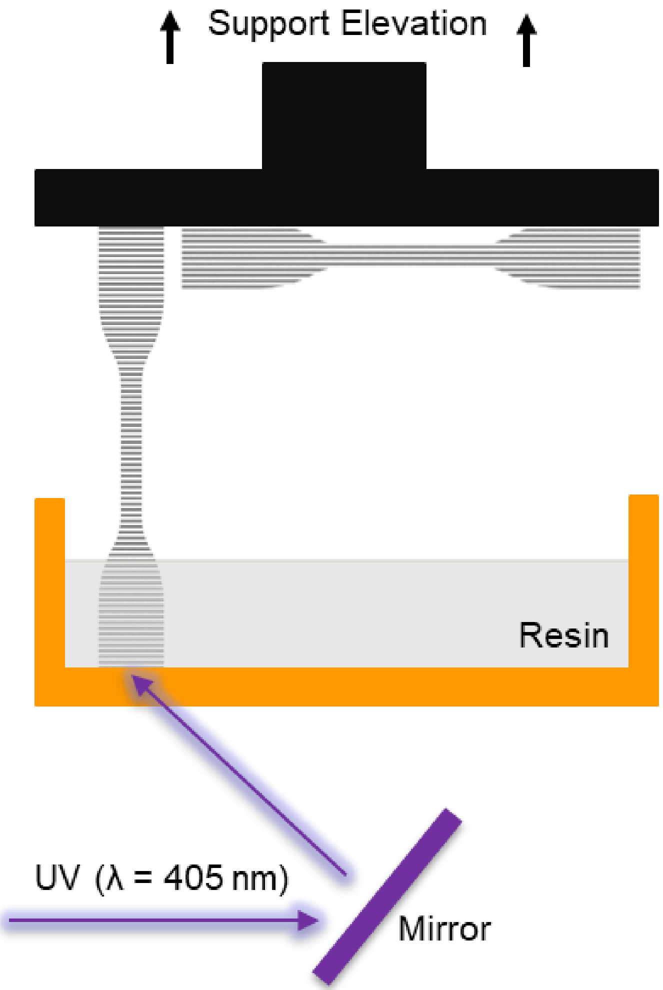
SLA Printing Steps

- The CAD file is converted to code for the printer to utilize
- The object is formed in layers as a UV beam traces out the specific shape of each layer and cures it
- The object is later cured again in a post-printing UV-curing chamber









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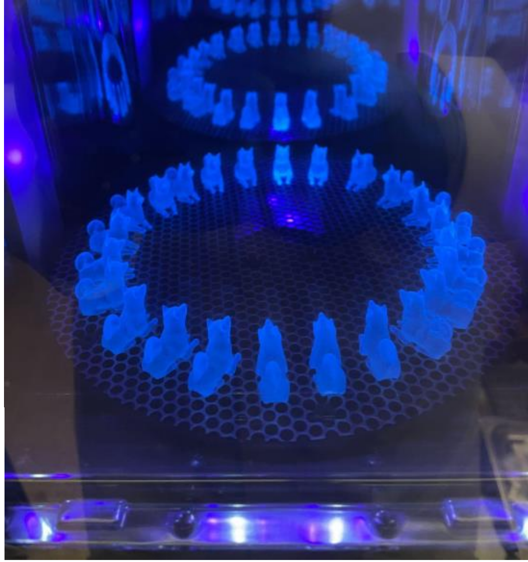
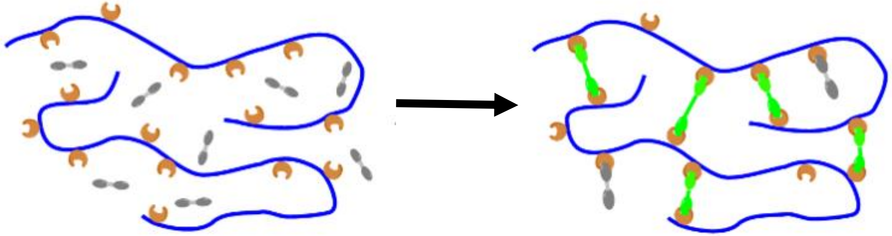
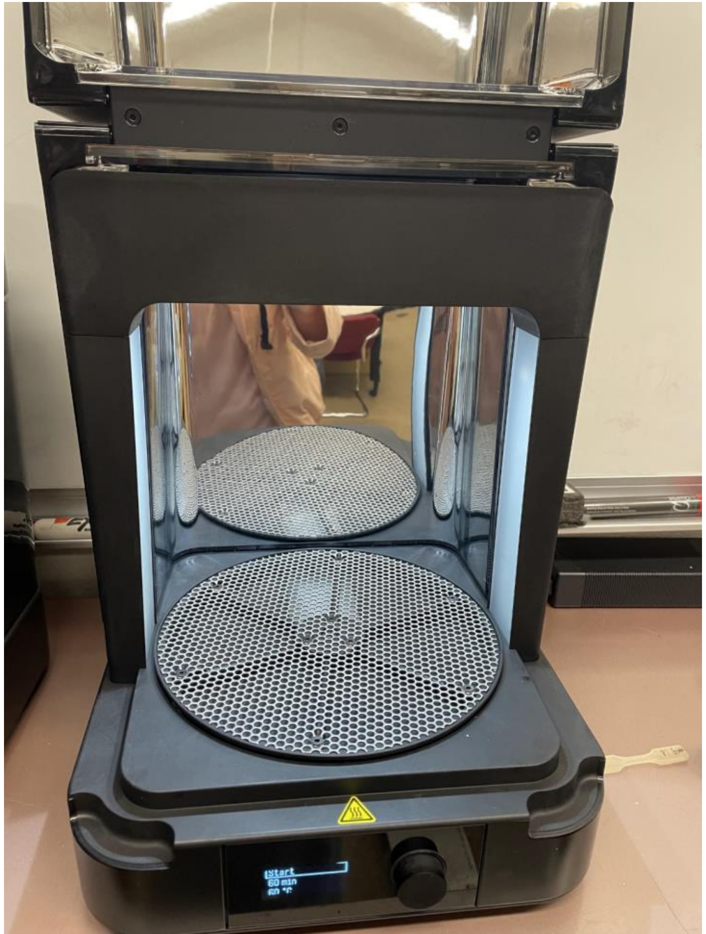
Post-Curing (Crosslinking)

- Crosslinking: The process of further polymerization between polymer chains
  - This happens due to the presence of reactive functional groups within the chains
- Additional UV light (post-curing) after initial photopolymerization causes crosslinking to occur
  - Crosslinking causes the resin to harden because the chemical structure becomes more rigid
- Objects are post-cured in order to improve their physical properties
  - Removes any uncured monomer
  - Improves tensile strength
  - Removes stickiness





In-Lab Post Curing Chamber



SLA vs FDM

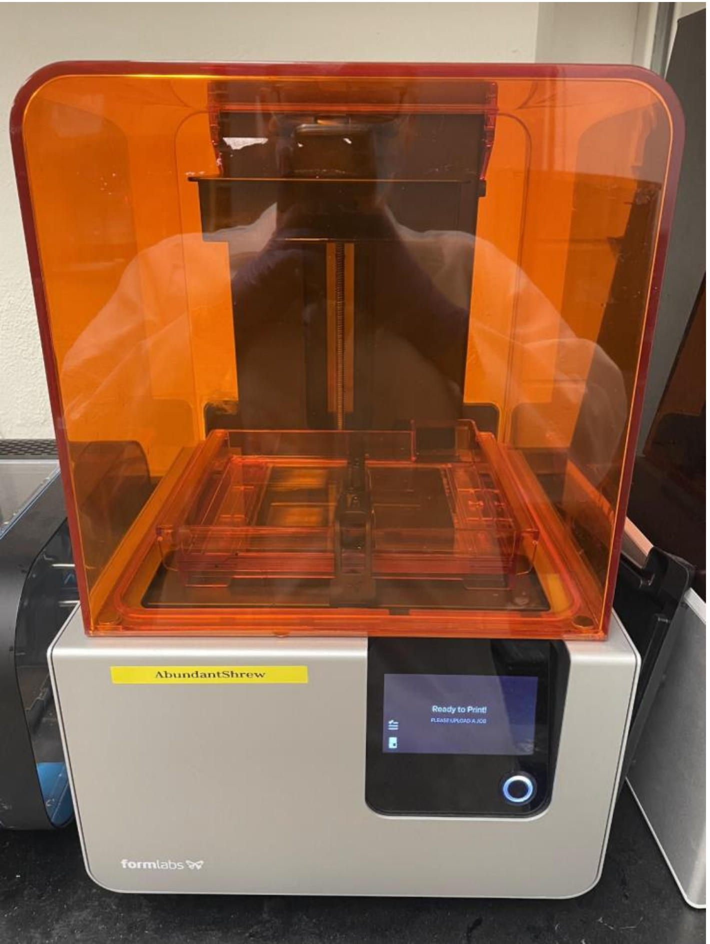
SLA (Stereolithography)

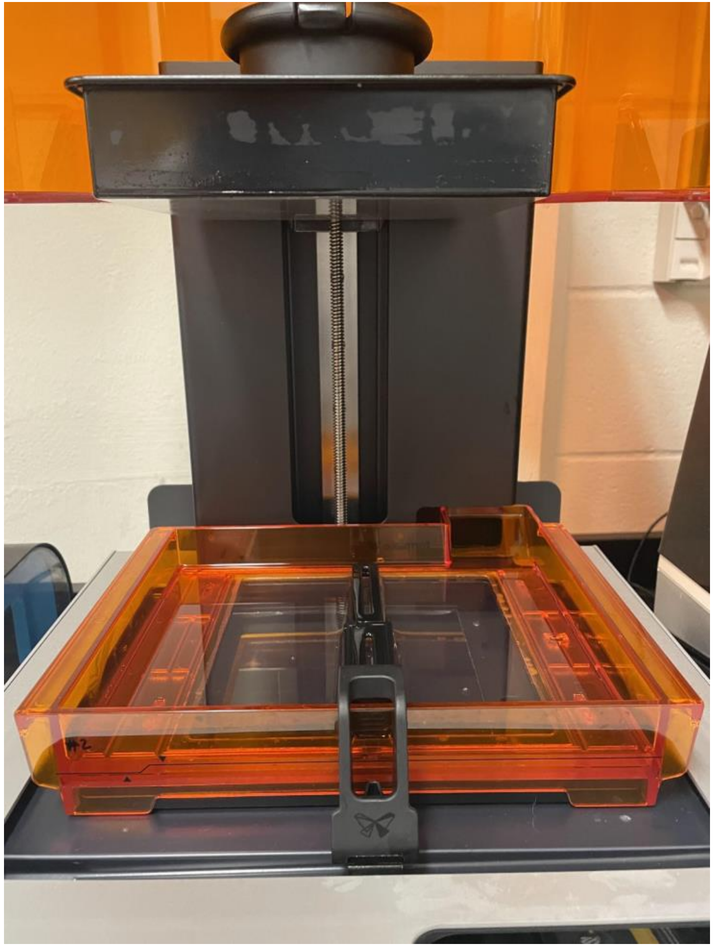
- Uses a **liquid** resin
- Material is typically a photopolymer
- Builds each layer using UV light photopolymerization
- More expensive
- Thin plastic layers, leading to an increase in quality

FDM (Fused Deposition modelling)

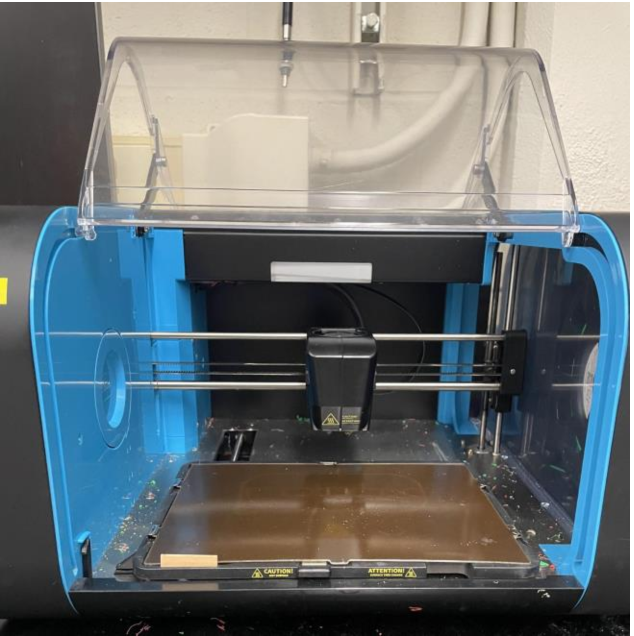
- Uses a **solid** plastic
- Material is commonly a thermoplastic polymer
- Builds each layer by depositing melted plastic
- Less expensive
- Thick plastic layers, leading to decreased quality

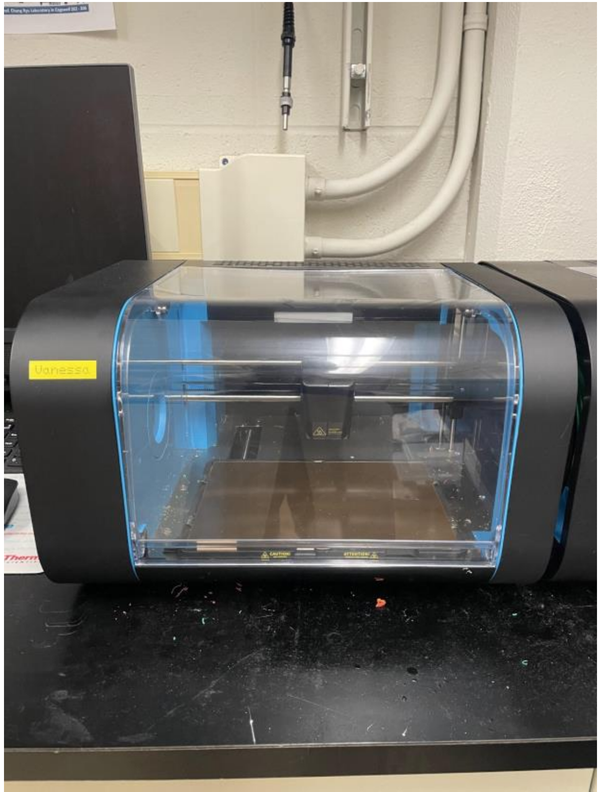
In-Lab SLA Printer

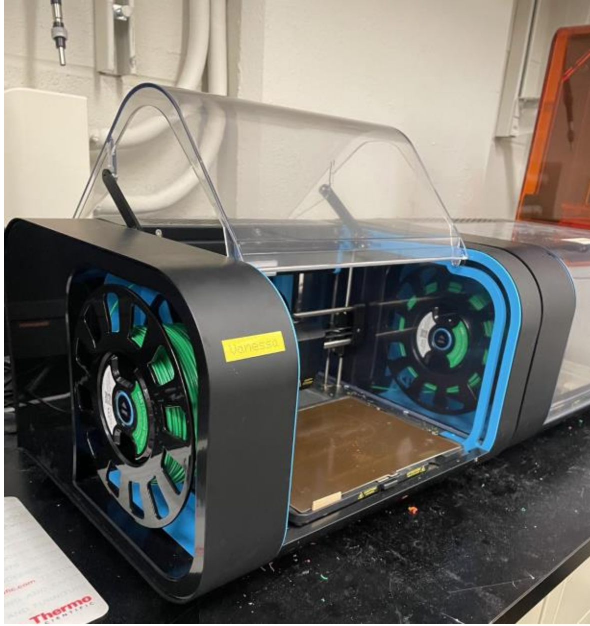




In-Lab FDM Printer

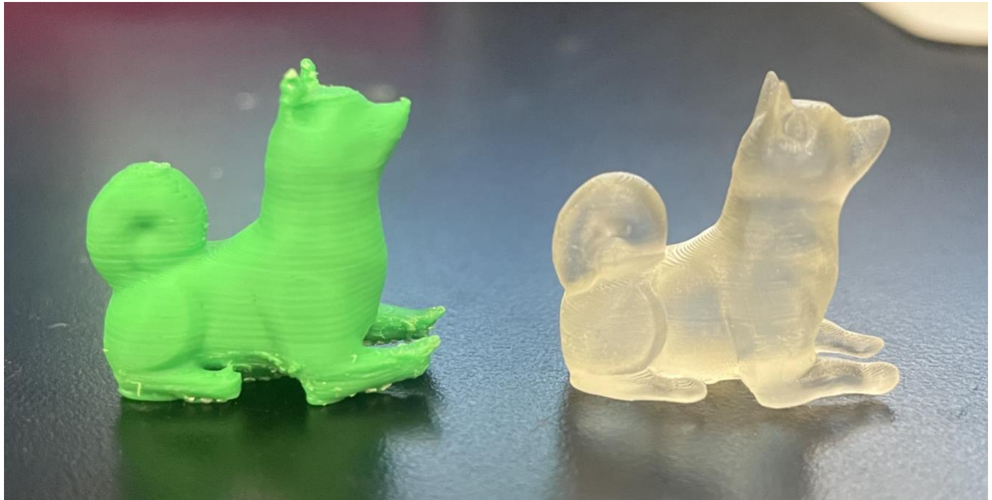






FDM vs SLA

Take a look at your 3D printed dog samples!



Stress and Strain

- Stress and Strain are important mechanical properties
- Stress: The force applied to an object divided by the area
  - Measured in Pascals (Pa) or Pounds Per Square Inch (PSI)
- Strain:The deformation (change in length) of an object in proportion to the original length

$$\sigma = \frac{F}{A}$$

where

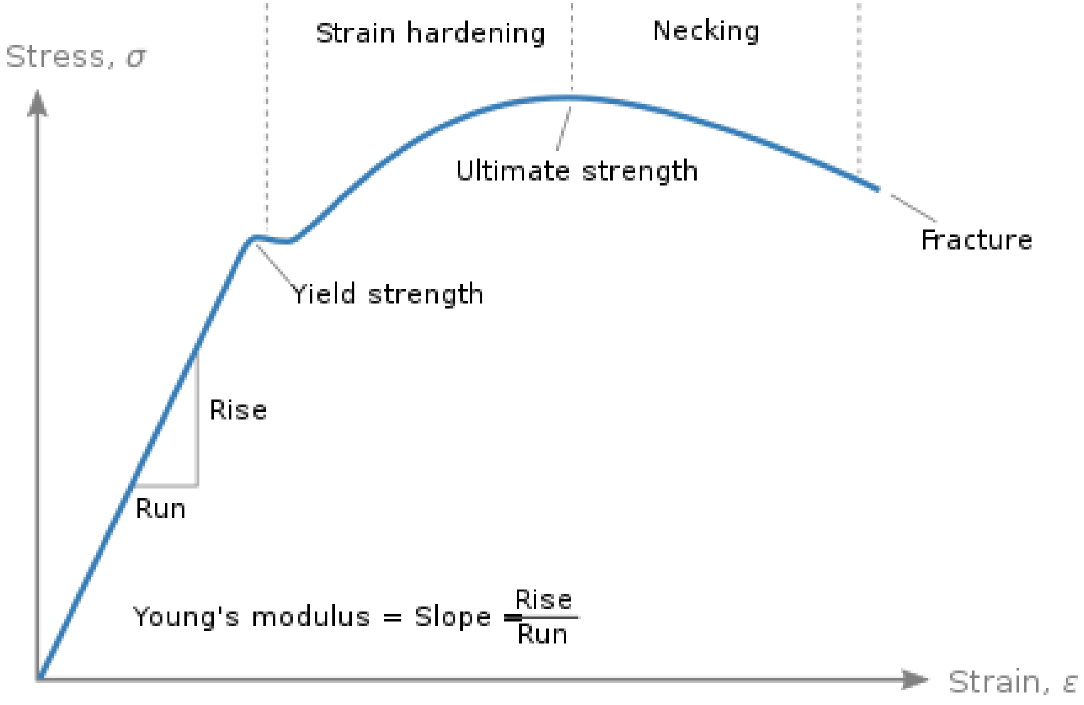
- σ stress [Pa]
- F applied force [N]
- A cross-sectional area [m^2]

$$\varepsilon = \frac{\Delta L}{L_0}$$

where

- ε strain
- ΔL total elongation [m]
- L_0 original length [m]

Stress Strain Curve



- Yield Strength: The maximum stress that can be applied before permanent deformation
- Ultimate Strength: The maximum stress a that can be applied before something breaks
- Necking: A decrease in area when stress applied exceeds ultimate stress

Young’s Modulus

- A measure of elasticity
- The ratio of the stress vs the strain in the elastic region

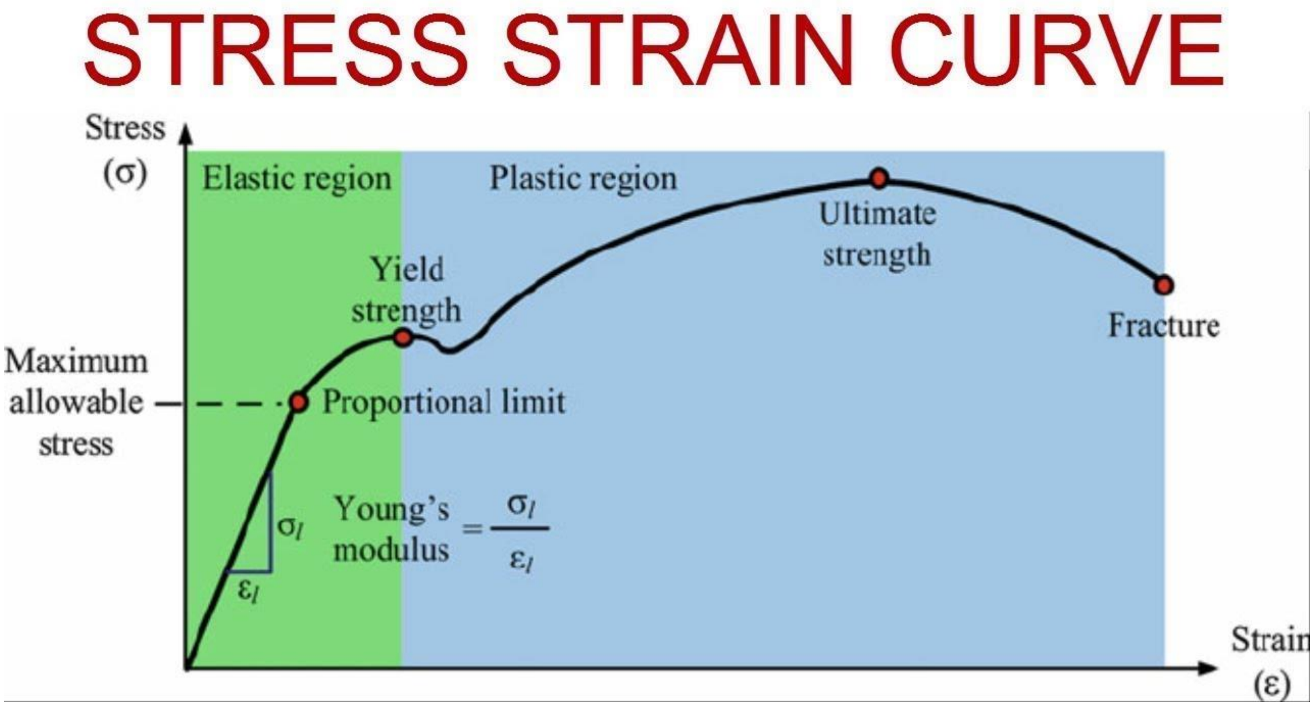
$$E = \frac{\sigma}{\varepsilon} = \frac{\text{stress}}{\text{strain}}$$

E ⟶ Young's Modulus (Elasicity)

σ ⟶ stress

ε ⟶ strain

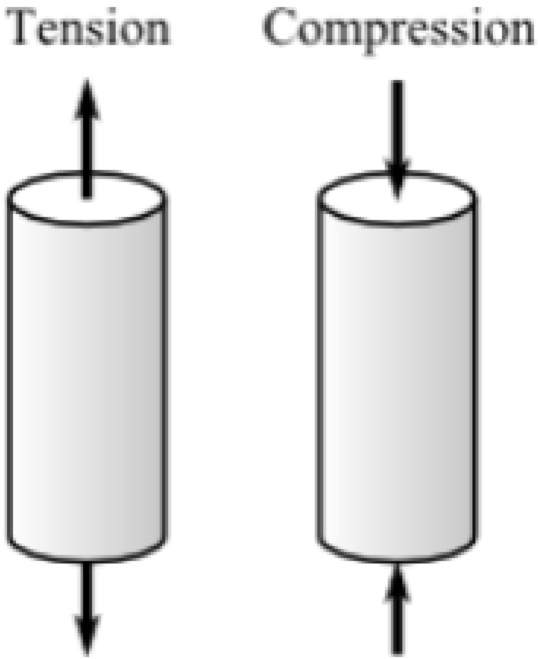
Elastic and Plastic Regions



- Elastic Region: Deformation IS NOT permanent
- Plastic Region: Deformation IS permanent

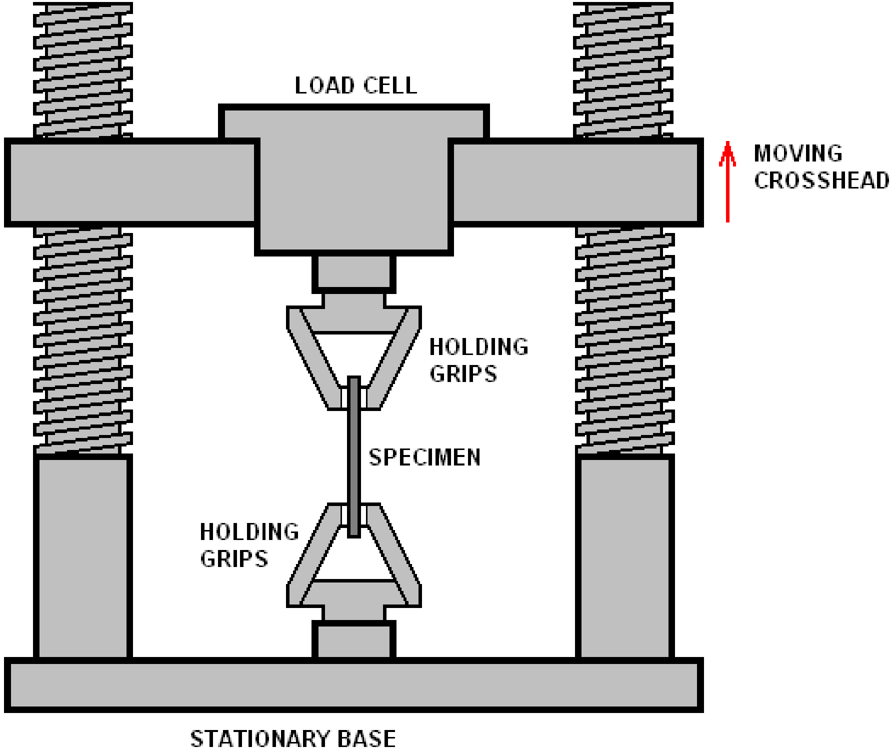
Tension and Compression

- Tension: Force is applied outwards
- Compression: Force is applied inwards



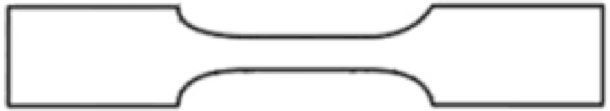
Tensile Test

- Clasps onto each end of a specimen and pulls them, applying tensile force
- The machine can calculate the stress and strain
- Information about strength and elasticity can be gathered

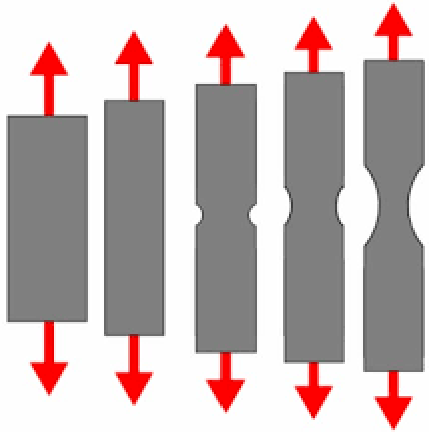


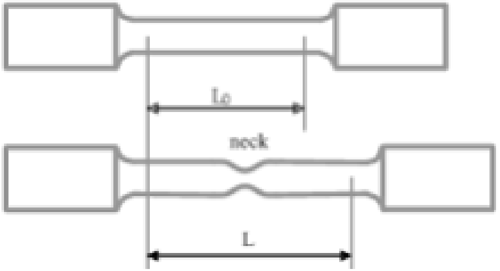
Tensile Test Samples

“Dogbone” Sample



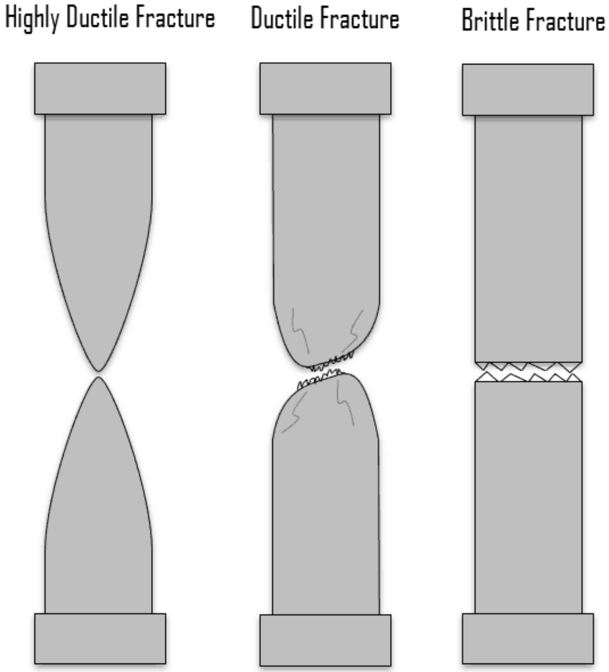
Straight Sample

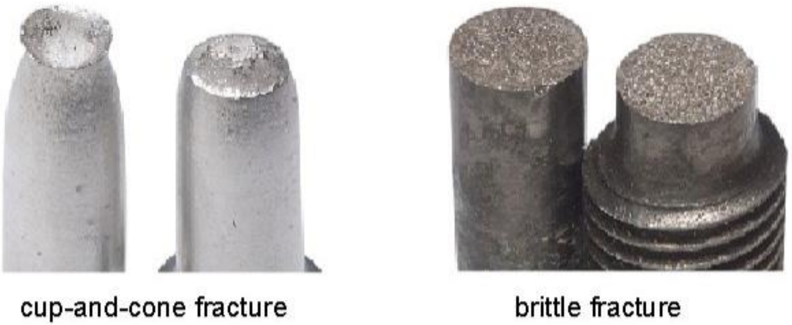




Ductile vs Brittle

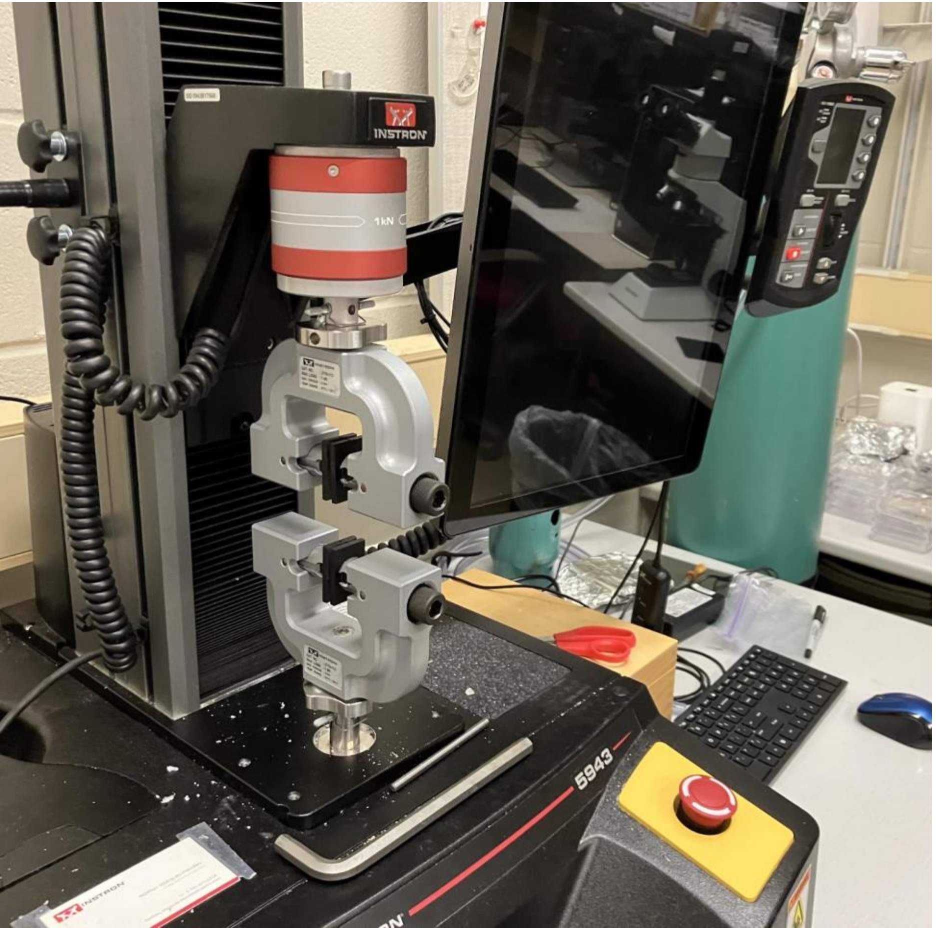
- Ductile: Easily stretched, has high elasticity, slower deformation, lots of necking before fracture
- Brittle: Does not stretch easily, deformation is not visible before fracture occurs, harder to tell when it will break

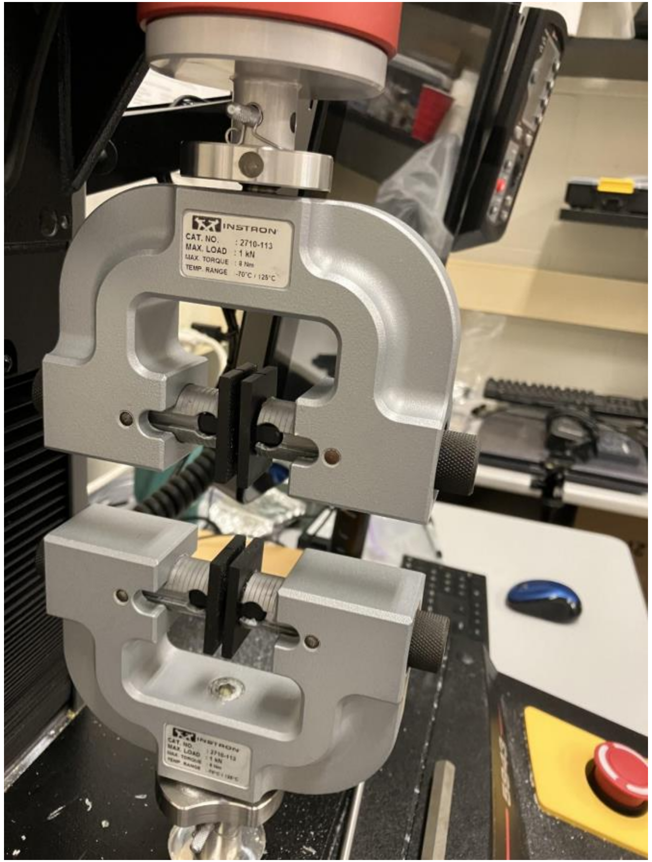




Adapted from Fig. 8.3, *Callister 7e.*

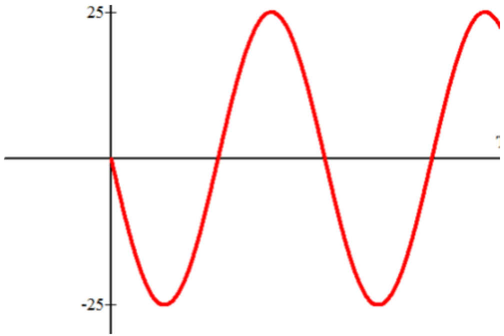
Instron in the Lab

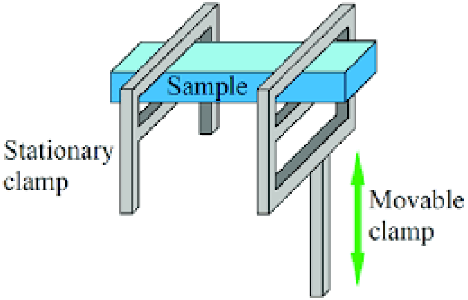




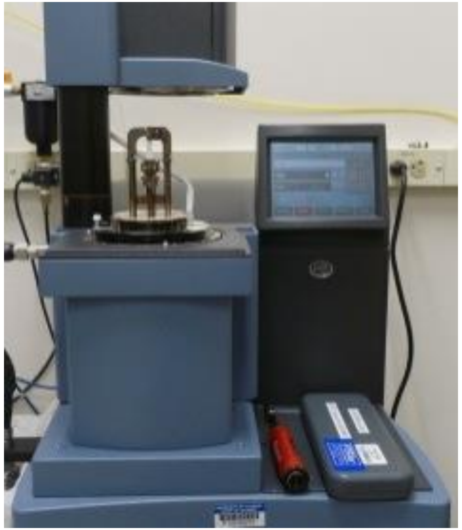
Dynamic Mechanical Analysis (DMA)

- A test that can identify glass transition temperature and other important transitions
- Especially useful for polymers
- The test is usually a few hours long, with the temperature varying from very cold to very hot
- Force is applied in a sinusoidal manner (oscillating from negative to positive) at a given frequency
- Changes within the material are measured





Single-Cantilever



DMA Results Analysis

- Storage modulus
  - Material's ability to store energy elastically
- Loss modulus
  - Material's ability to dissipate stress through heat
- Tan δ
  - Ratio of loss to storage modulus
  - Denotes the glass transition temperature, T_g

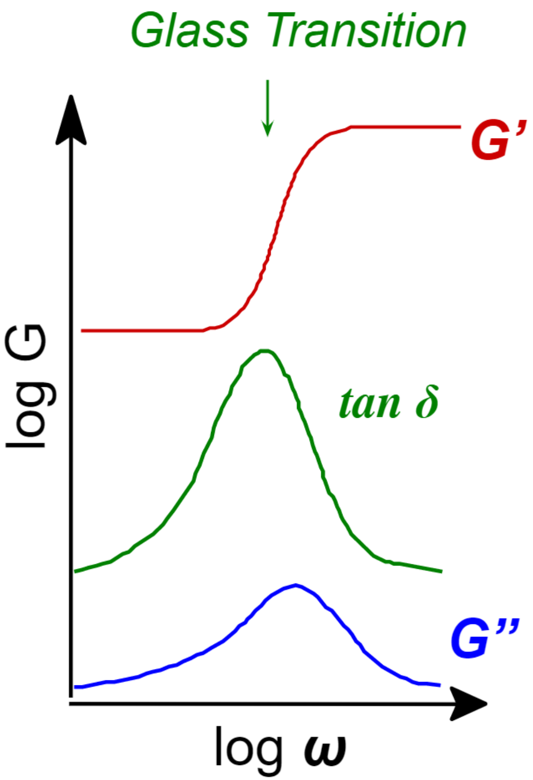
$$G'(\omega) = \frac{\tau_o}{\gamma_o} \cos\delta$$

STORAGE MODULUS

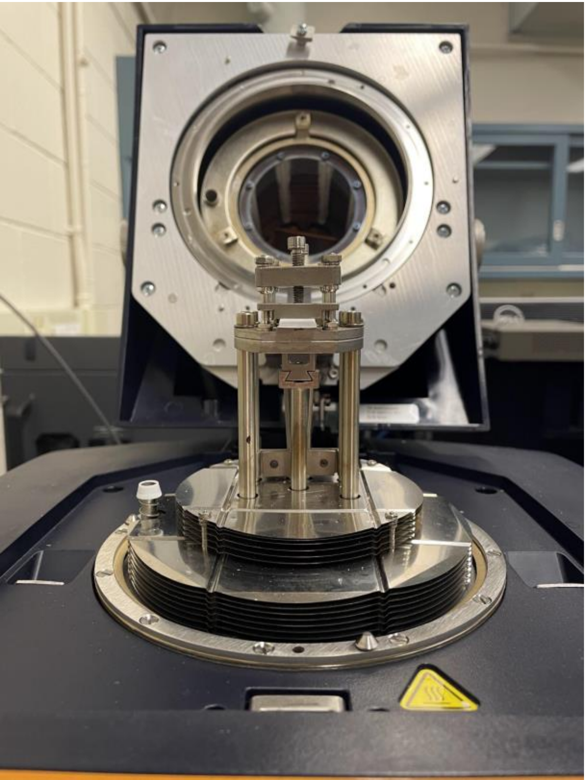
$$G''(\omega) = \frac{\tau_o}{\gamma_o} \sin\delta$$

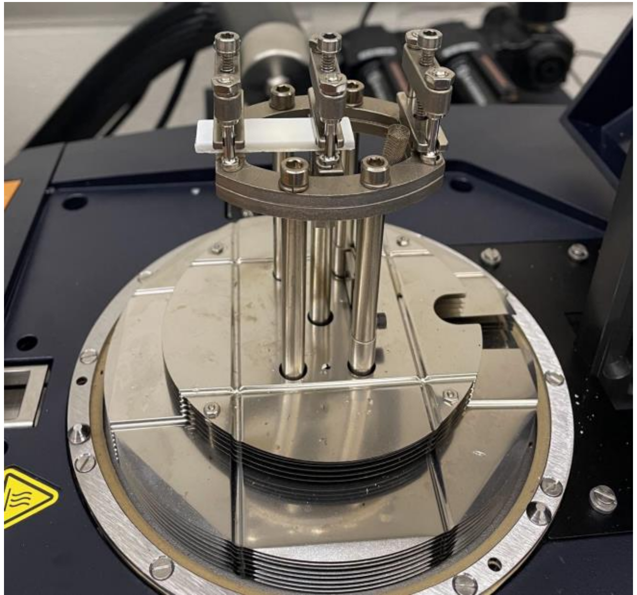
LOSS MODULUS

$$\tan\delta = \frac{G''(\omega)}{G'(\omega)}$$



DMA in the Lab





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Polymer Chemistry in 3D Printing Research Project

NSF

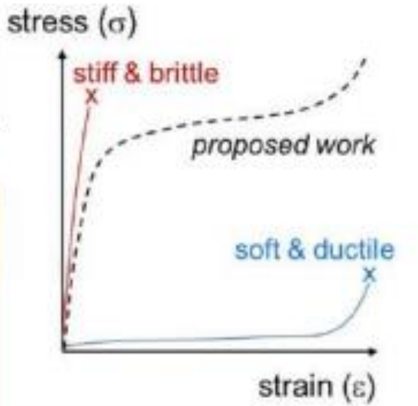
- National Science Foundation: An independent US Governmental agency that supports non-medical related research in fields of science and engineering
- It was established in 1950
- It provides grant funding to research teams

NSF Grant

Background

- Current 3D printed materials have poor physical properties
- Materials in nature possess multiscale (containing multiple regions) structures and good physical properties
- Phase separation has yet to be explored vastly in 3D printing, but it could have broad applications

NSF Proposal Main Goals



nm

100 nm to 100 um

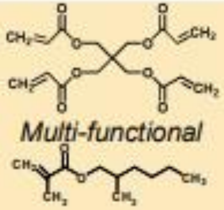
100 um and larger

Relevant Scales

Task 1
Network architecture controllables

Chemistry

- Strand length & flexibility
- Addition of network diluents



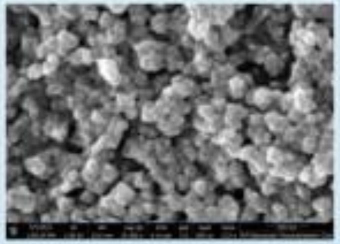
Multi-functional

Mono-functional

Task 2
Control of microstructure

Photo-PIPS

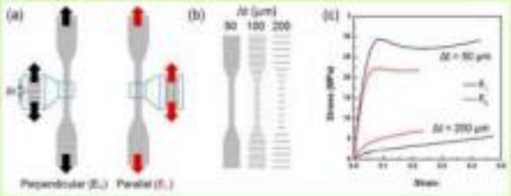
- Network formation by crosslinking
- Phase separation (heterogeneity)
- Formation of soft and hard subdomains



Task 3
Macroscale structure

3D Printing

- Layer-by-layer printing
- 3D structural control

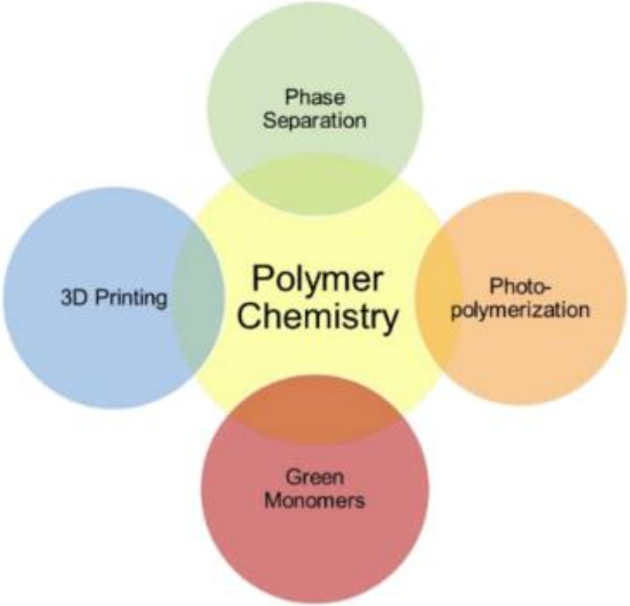


**NSF Proposal*

Rensselaer

NSF Grant Goals

1. Use specific chemistries to alter polymer chain flexibility
    - Molecular level of control
2. Use polymer additive to implement phase separation with neat resin
    - Nano- to microscale level of control
3. 3D print the material and visualize resulting mechanical properties
    - Micro- to macroscale level of control



Research Overview

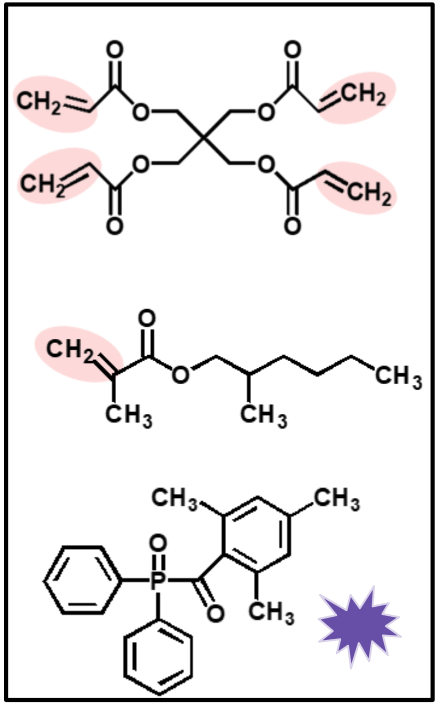
Monomers:

PETA

2-EHMA

Photoinitiator (absorbs UV light):

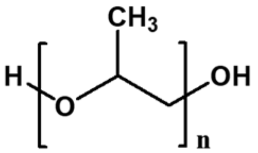
TPO

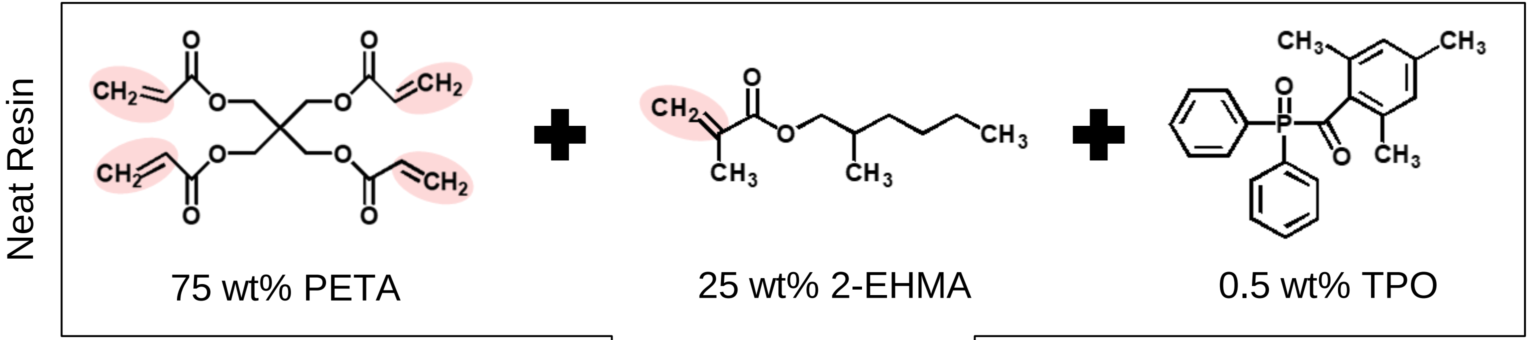


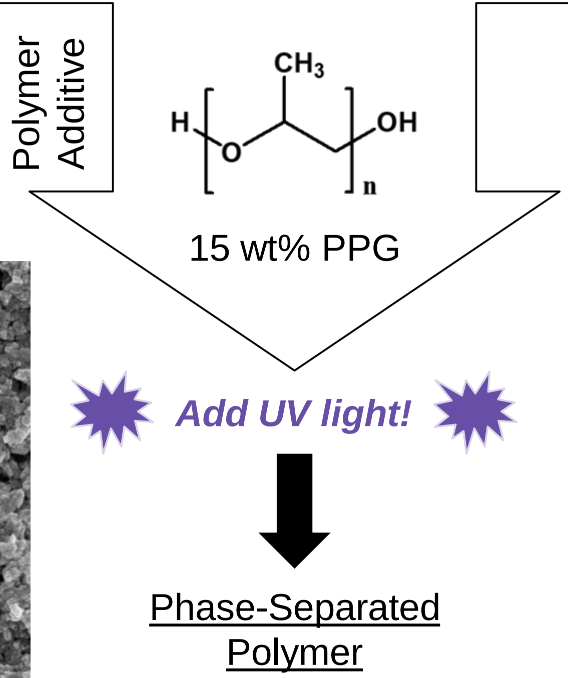
Neat Resin

Polymer Additive (makes phase separation):

Poly(propylene glycol) (PPG)

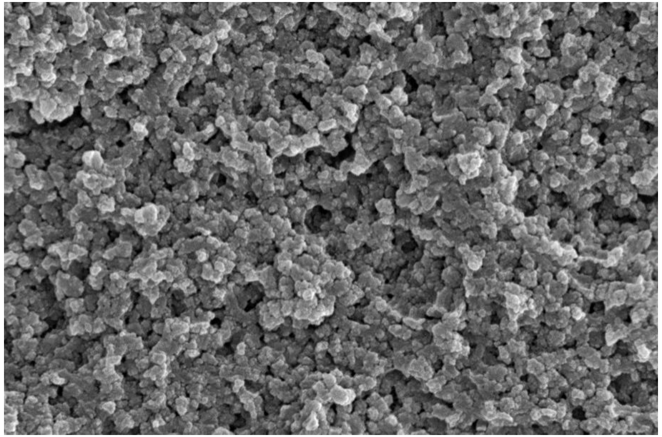






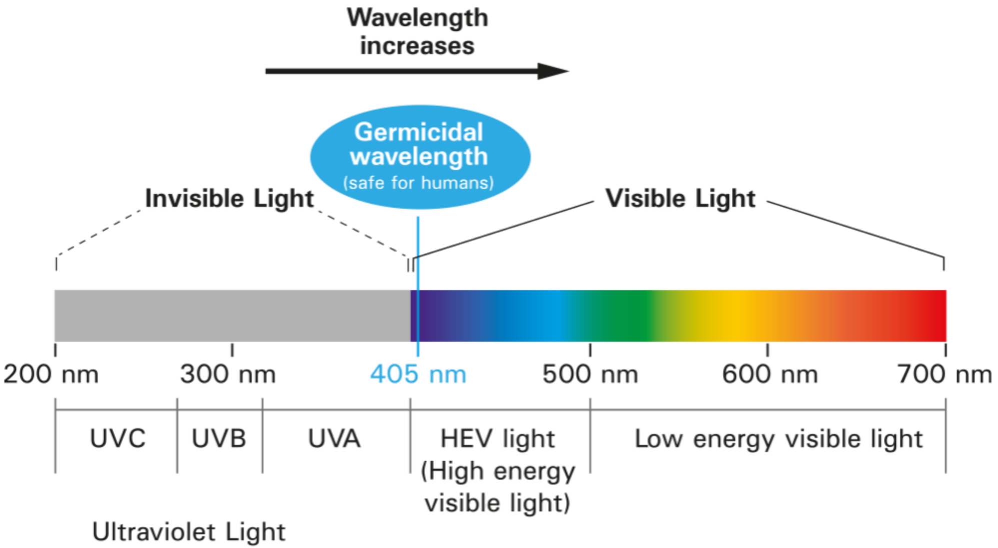
wt% = weight percent

- The percentage of the total weight that a particular molecule makes up

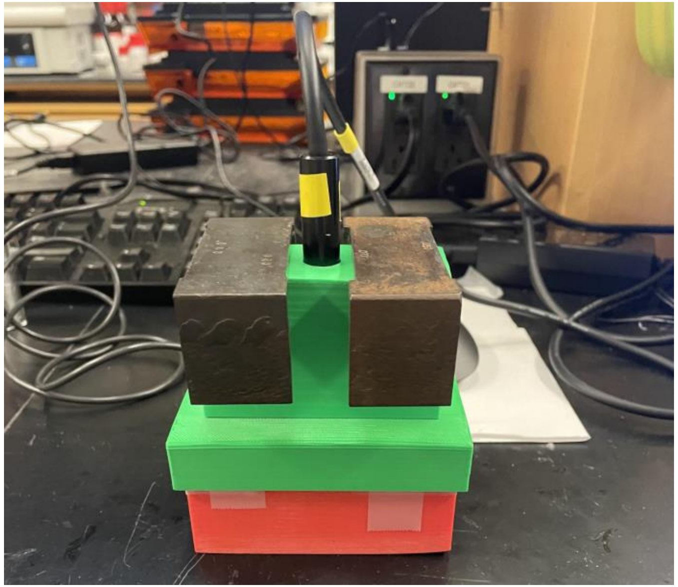


UV Irradiation

- UV Irradiation: Short wave ultraviolet light is emitted in a focused area
- An important part of photopolymerization, activating crosslinking
- Can also be used to clean and disinfect objects

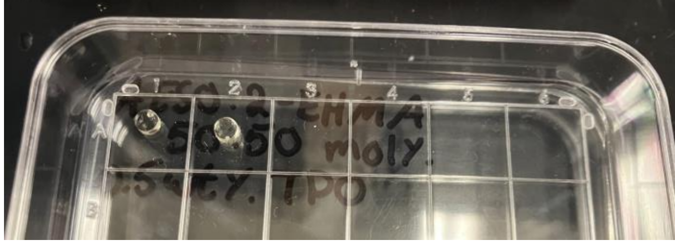


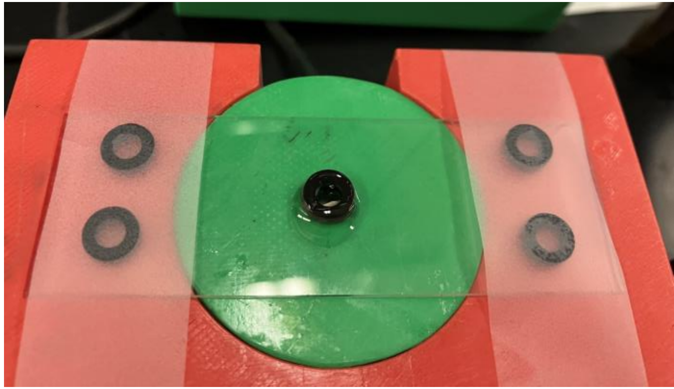
UV Irradiation in the Lab

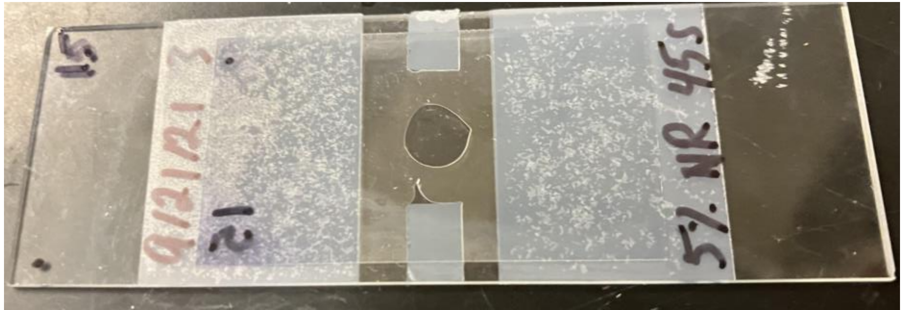


UV Irradiation Research Applications

- UV Irradiation is used to cure the monomer resin into a solidified sample
  - It is currently used to make compression test and DMA samples using molds
  - It will eventually be used to make SLA 3D printed objects
- UV Transmittance tests tell us how much light transmits through the sample
  - It also tells us if there is microscopic phase separation

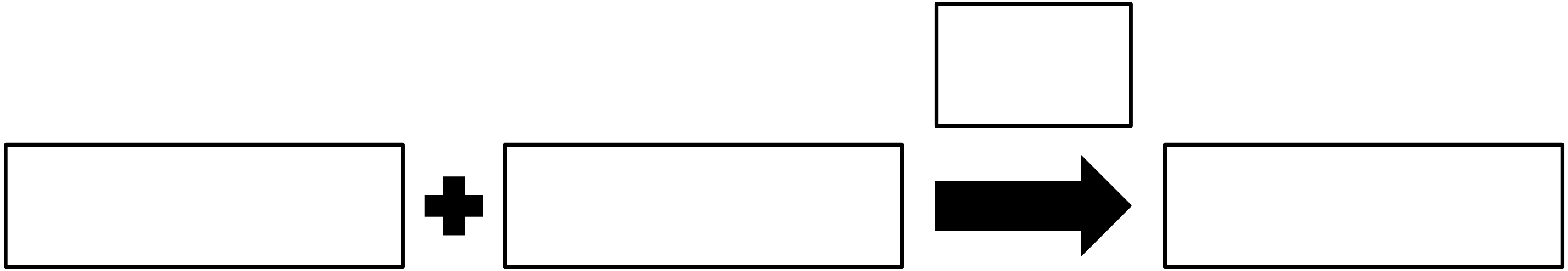






Review!

Fill in the blanks for the process of photopolymerization below.



Monomer(s)

Polymer

UV Light

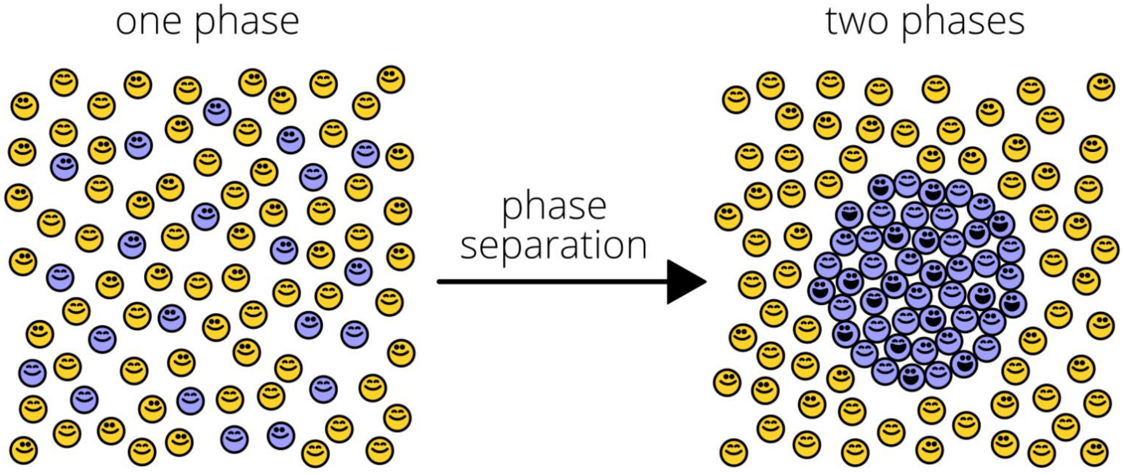
Photoinitiator

Review!

Fill in the blanks for the process of photopolymerization below.

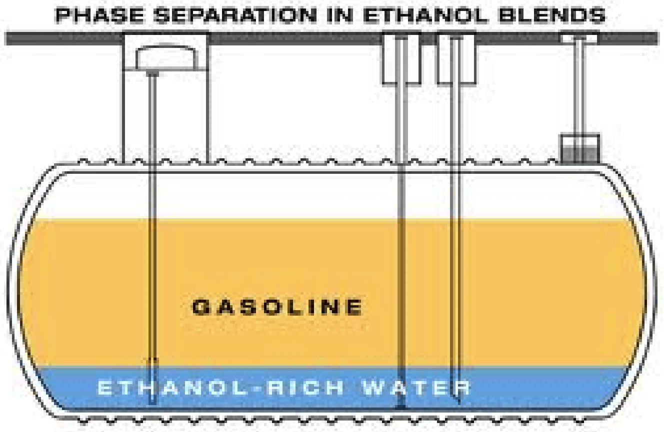
Phase Separation

- Homogenous mixture: Composition is the same throughout the whole mixture
- Phase separation (heterogeneous mixture): The creation of two distinct phases from one homogeneous mixture
- Phase separation can occur based on differing *densities* & *miscibilities/solubilities* (how much one molecule “likes” another)



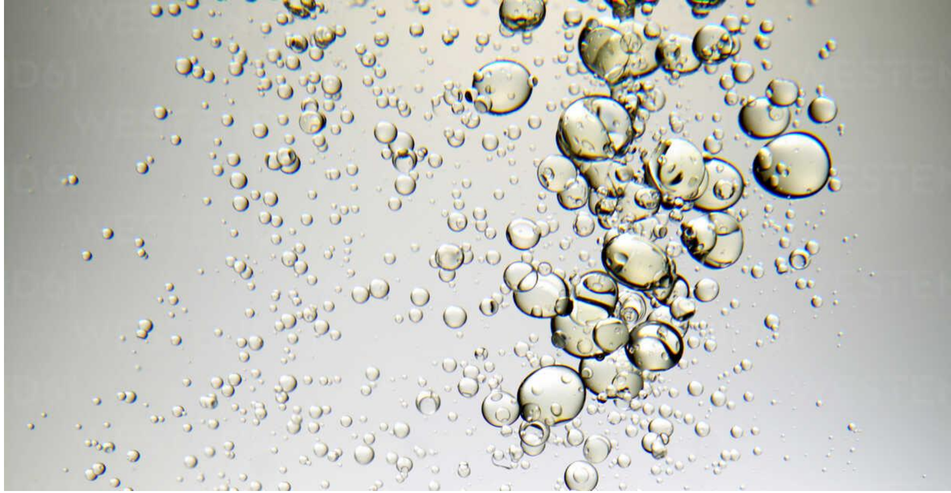
Phase Separation Causes

- Gravity separation: Differing densities in the components in the mixture lead to one part sinking to the bottom, and the other rising to the top
- A good example of this is oil and water
  - Oil is less dense, it floats on top of water
  - Water is more dense, it sinks below oil
- If water contaminates gasoline, phase separation occurs, with gasoline rising to the top of the tank, and water sinking to the bottom



Phase Separation Activity

- Take a cup of water and pour in a little bit of oil (olive, canola, or vegetable)
- Stir it together into a homogeneous mixture
- Stop stirring and observe the oil rise to the top



In-Lab Phase Separation Demo

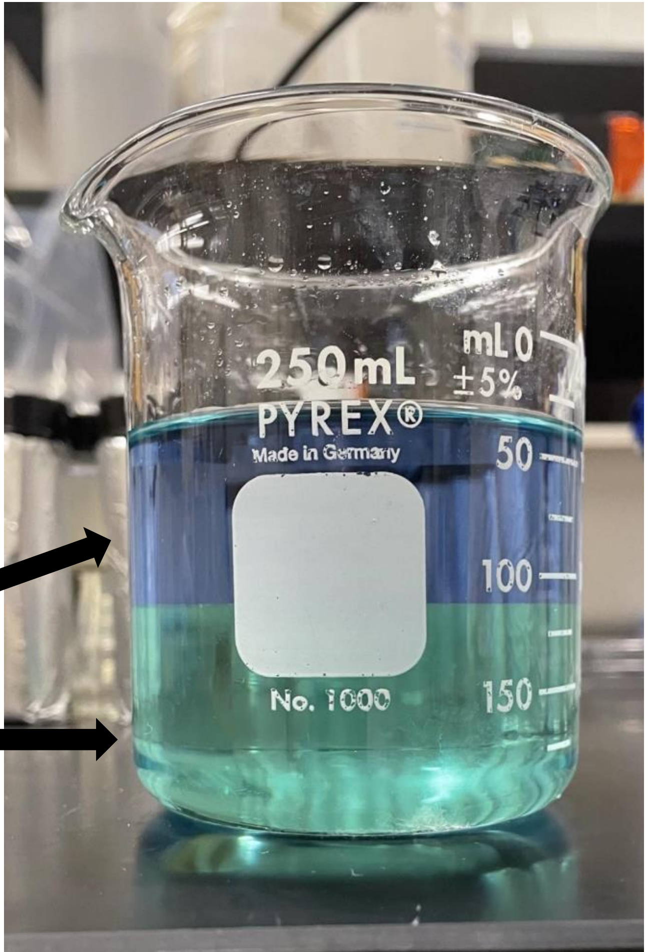
In the lab we can combine liquids with different densities:

- Olive oil
- Isopropyl alcohol (IPA aka rubbing alcohol)
- Salt water

Sharpie is used for dying purposes

IPA

Salt water



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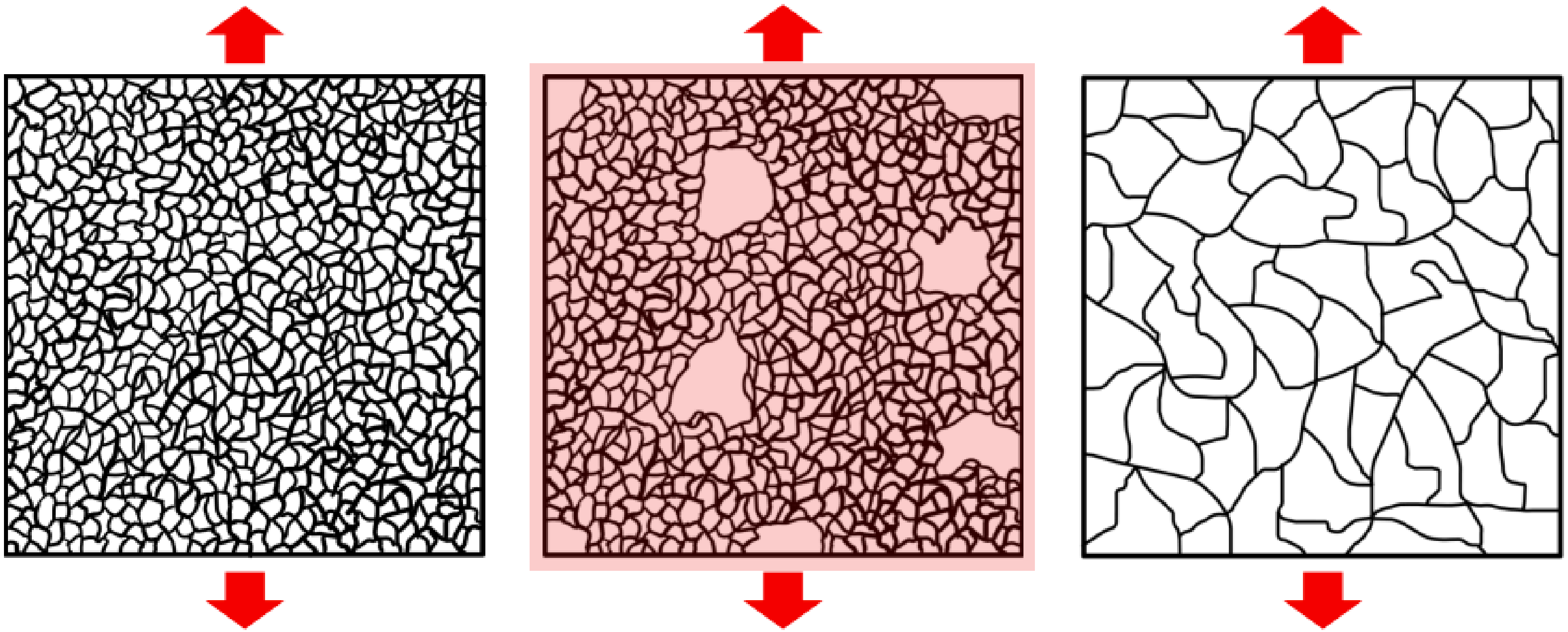
Phase Separation Research Applications



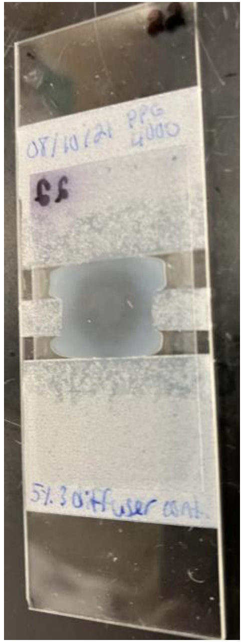
Stiff/Brittle
(Not Flexible/Extendable)

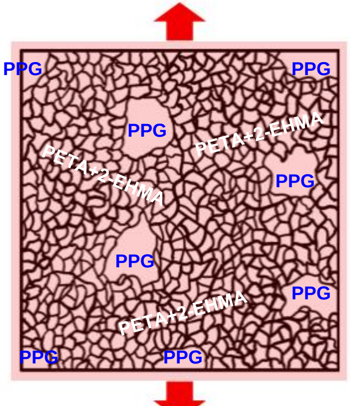
Stiff/Brittle @ Smaller Strain
Flexible/Extendable @ Higher Strain

Flexible/Extendable
(Not Stiff/Brittle)

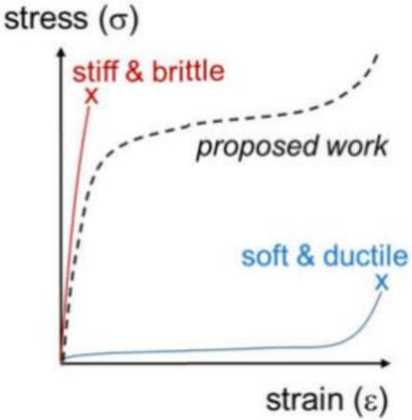
Phase Separation Research Applications

- Photopolymerization Induced Phase Separation (Photo-PIPS)
  - Multiscale structure with stiff (PETA+2-EHMA network) and soft (PPG chains) regions
- Pore size in the material will vary based on length of PPG chain length
  - The physical and mechanical properties of the material will change with pore size
- Finding a middle ground between stiff and brittle versus soft and ductile
- Microscopic phase separation causes light to scatter, leading to an opaque sample

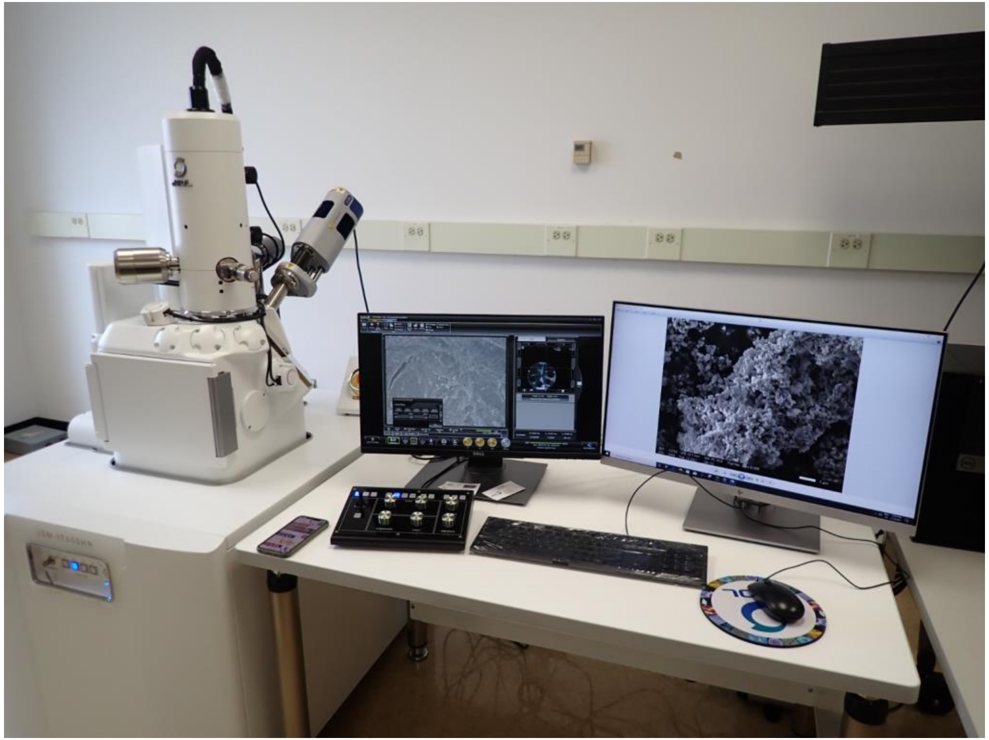




Stiff/Brittle @ Smaller Strain
Flexible/Extendable @ Higher Strain



Scanning Electron Microscopy



- SEM can identify external and internal properties of a specimen by directing a beam of high energy electrons at it
- Identifies external texture, crystalline structure, and chemical composition

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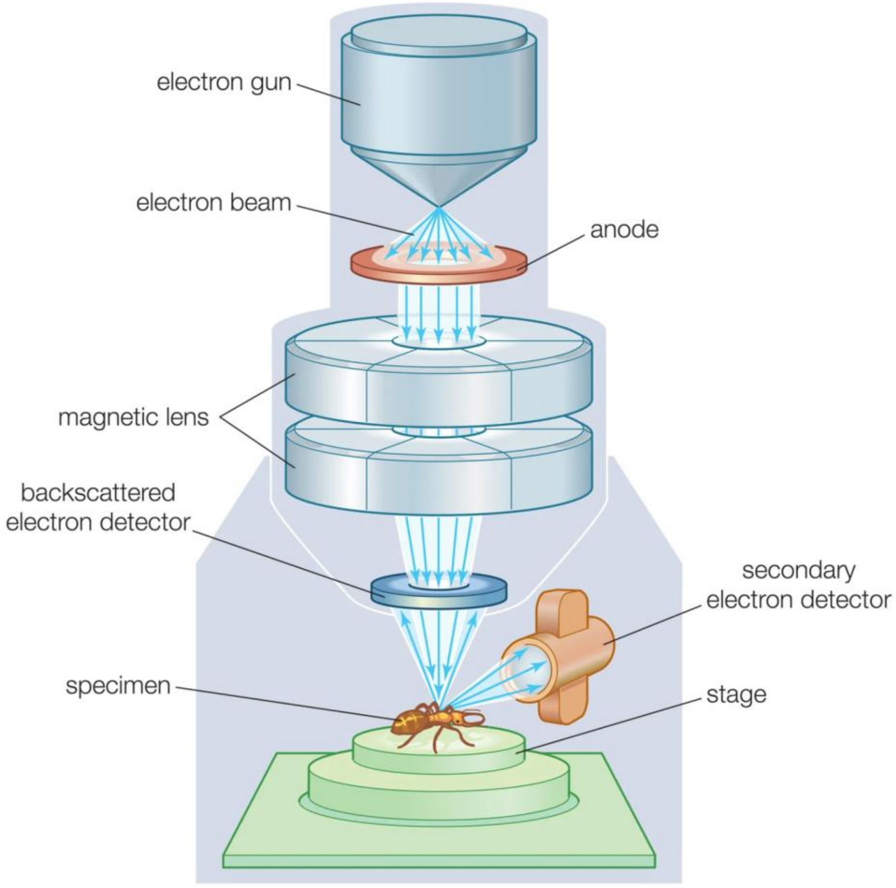
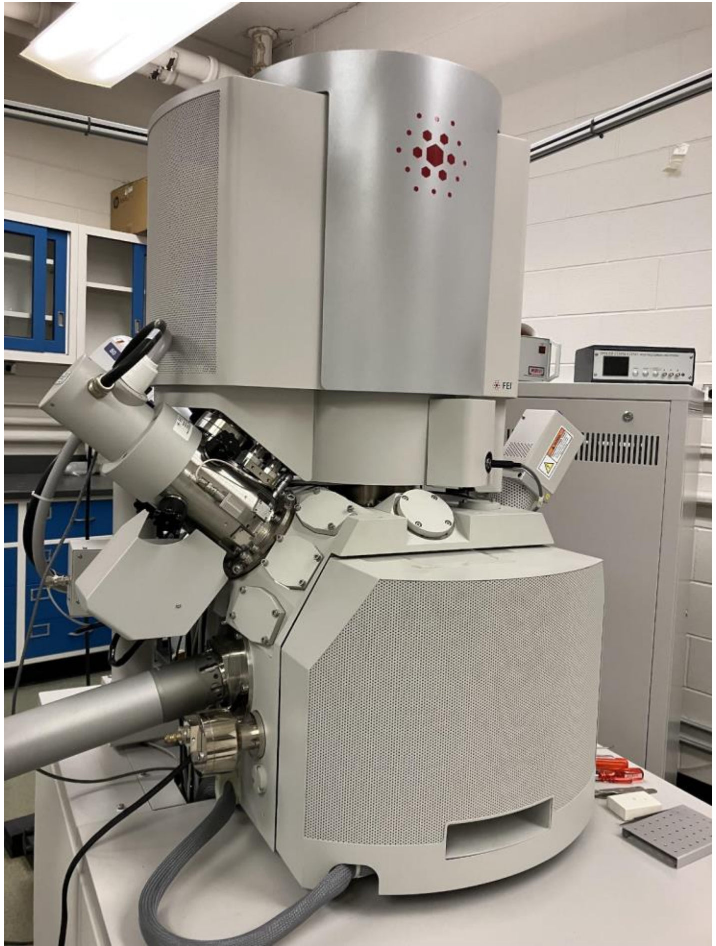
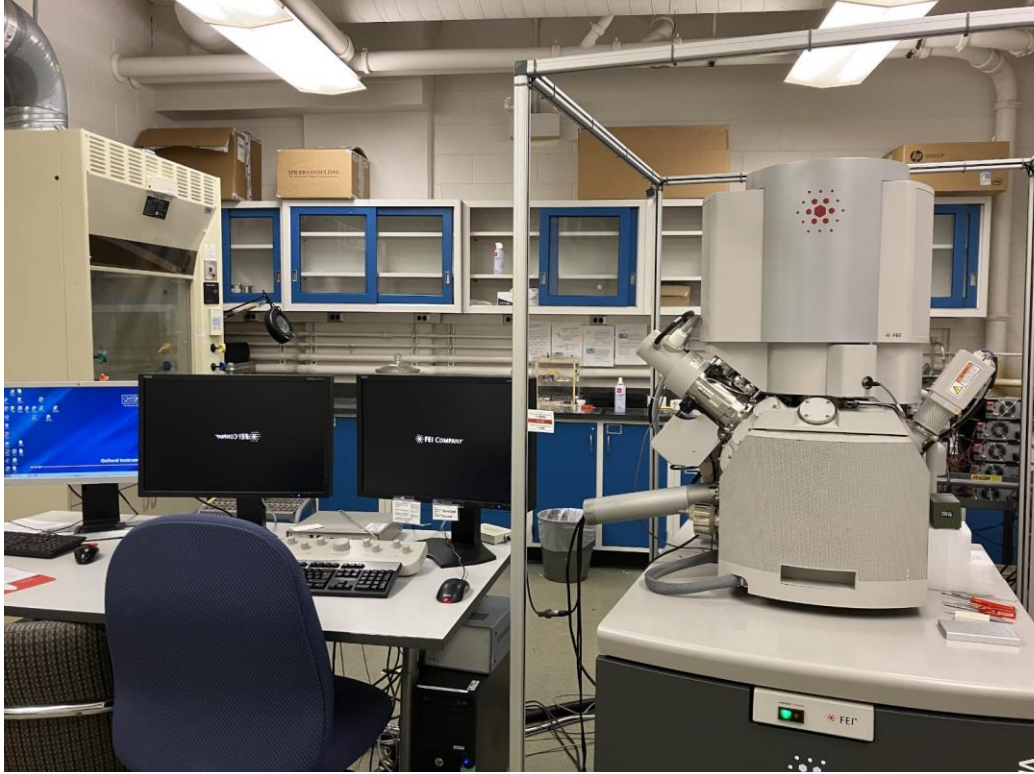
How SEM Works



- Electrons are accelerated, and they are directed into a beam
- When that beam hits the object, the electrons interact with the atoms in the object
- This releases multiple signals, like secondary electrons, and backscattered electrons which provide images of the sample

SEM in the Lab





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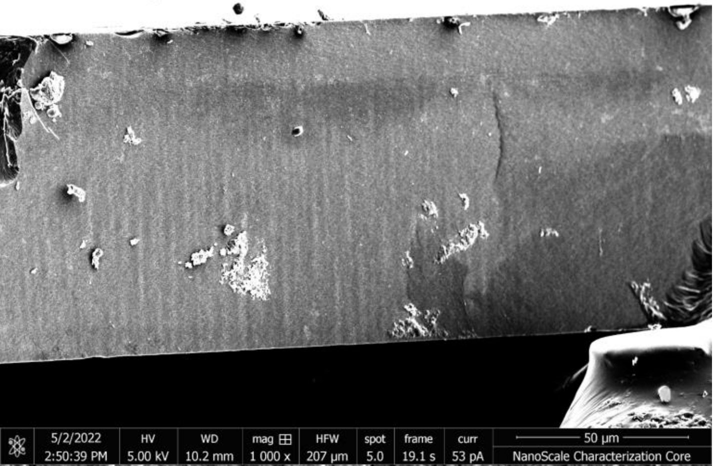
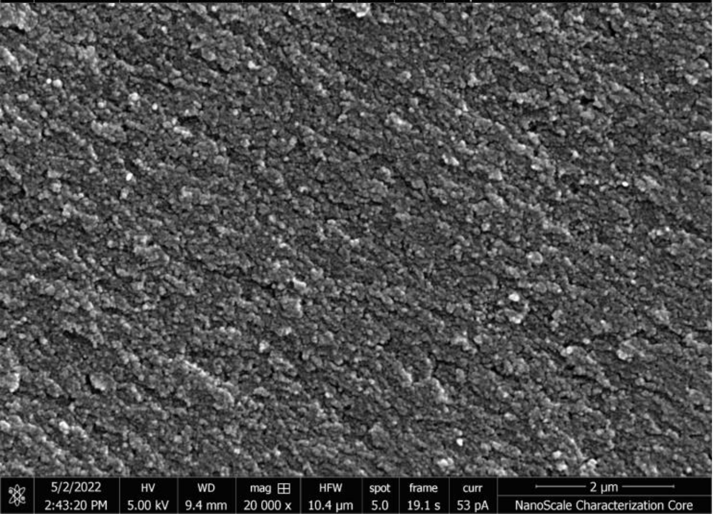
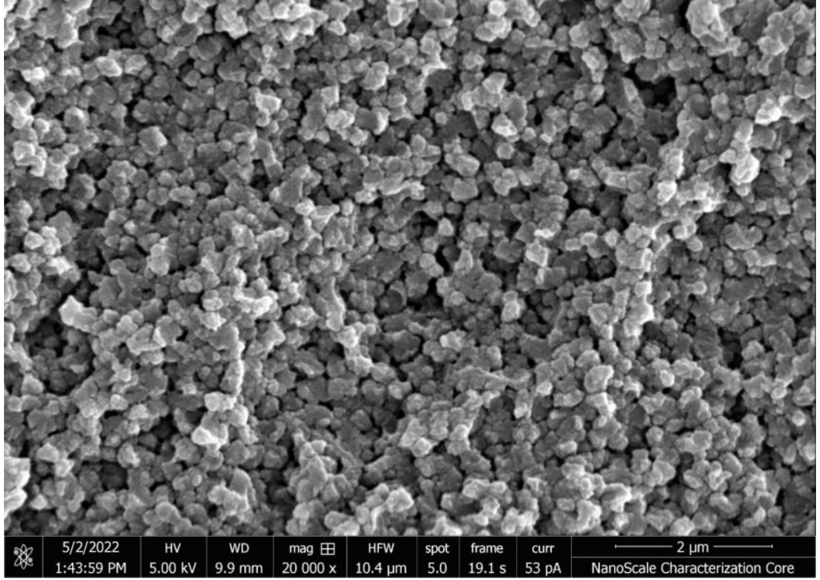
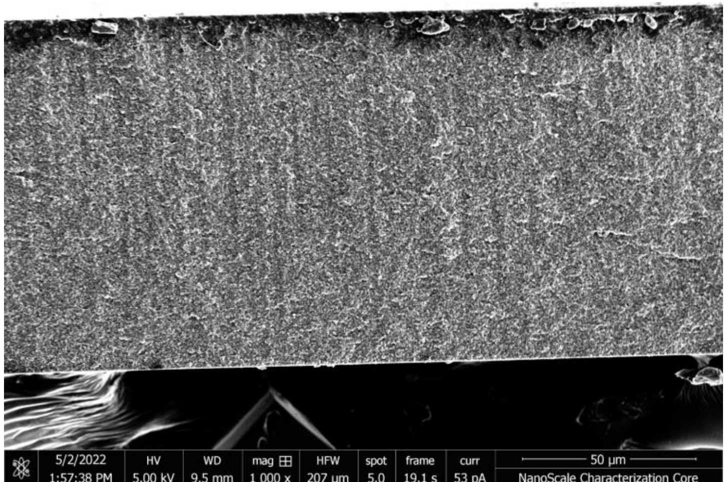
SEM Lab Images



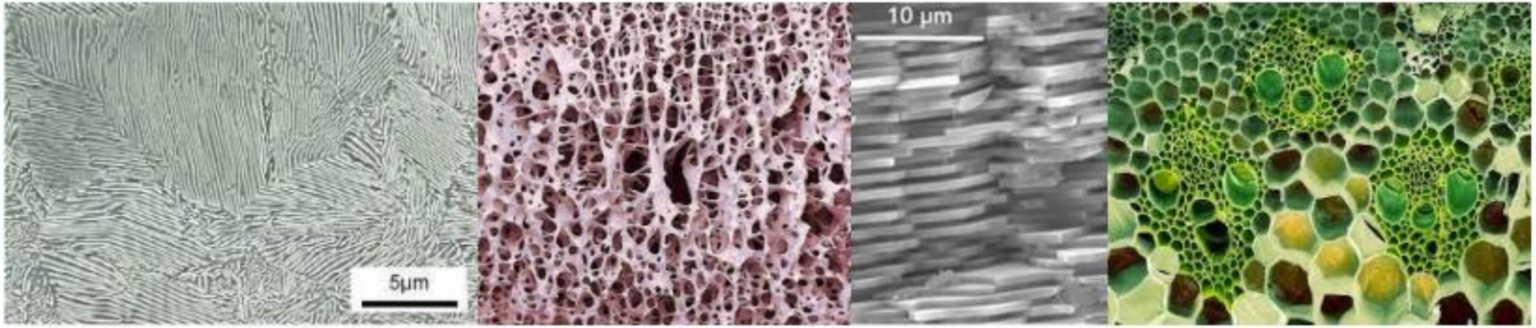






Nature and Nano-Structures

- Recall that multiscale structures lead to varying levels of porosity
- These stiff and soft regions can mimic structures seen in natural objects
- This leads to objects that have hardness and flexibility
- Examples of naturally occurring objects with complex multiscale architectures include:
  - Pearlite Steels
  - Bone
  - Nacre
  - Bamboo

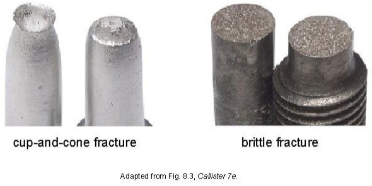




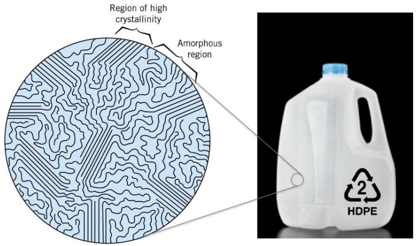


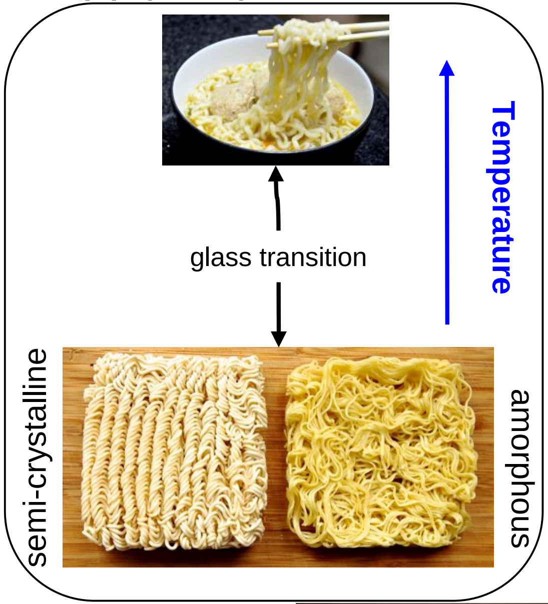

Thinking of Potential Real-Life Applications

What is something that you can take away from this week and apply to your life and/or career someday?



High Density Polyethylene: Milk Cartons





STRESS STRAIN CURVE