LECTURE 7:
Old Strategies with Biopolymers

Sanjana Gopalakrishnan

Sustainable Materials, Fall 2024

Artwork made using Gemini,
a Large Language Model by Google.
Generated June 4, 2024.

Announcements and Housekeeping

- Assignment #2 due TODAY!!

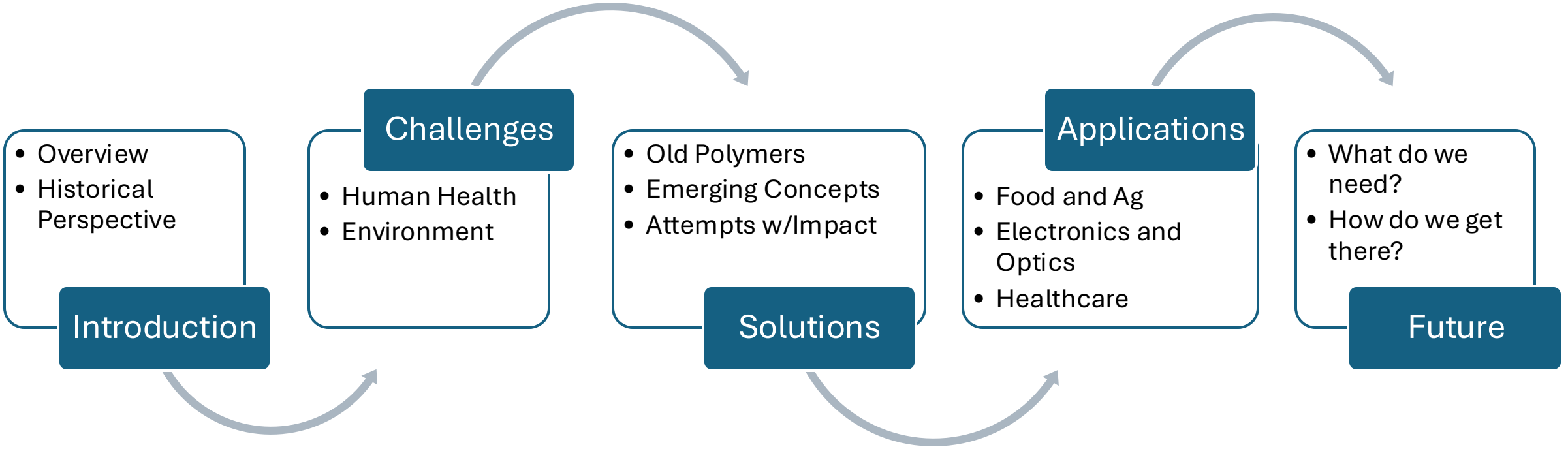
- Make your groups under People -> Groups -> Add group. This is important to ensure that all group members are graded.

Project Checkpoint #2: Work with your project group to prepare 1 slide to introduce your project. Slide should include your motivation and Scientific Hypothesis. Slides may include figures, graphics and text.

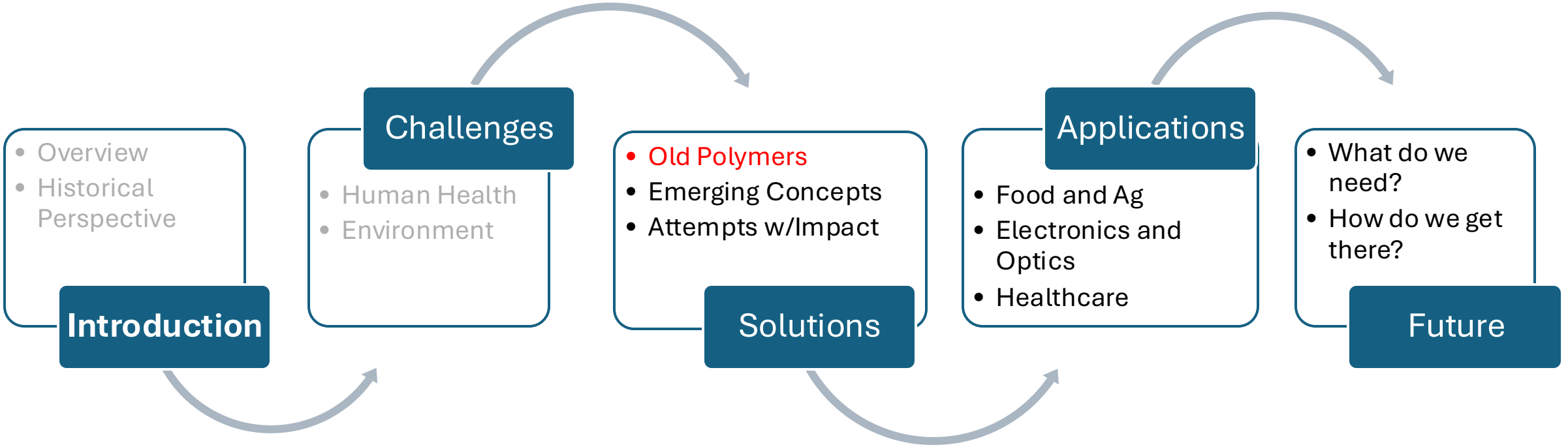
Include a second slide with the names of all group members.

Due next Wednesday on 10/02/24 at 11:59 pm

Course Overview



Lecture 6-7

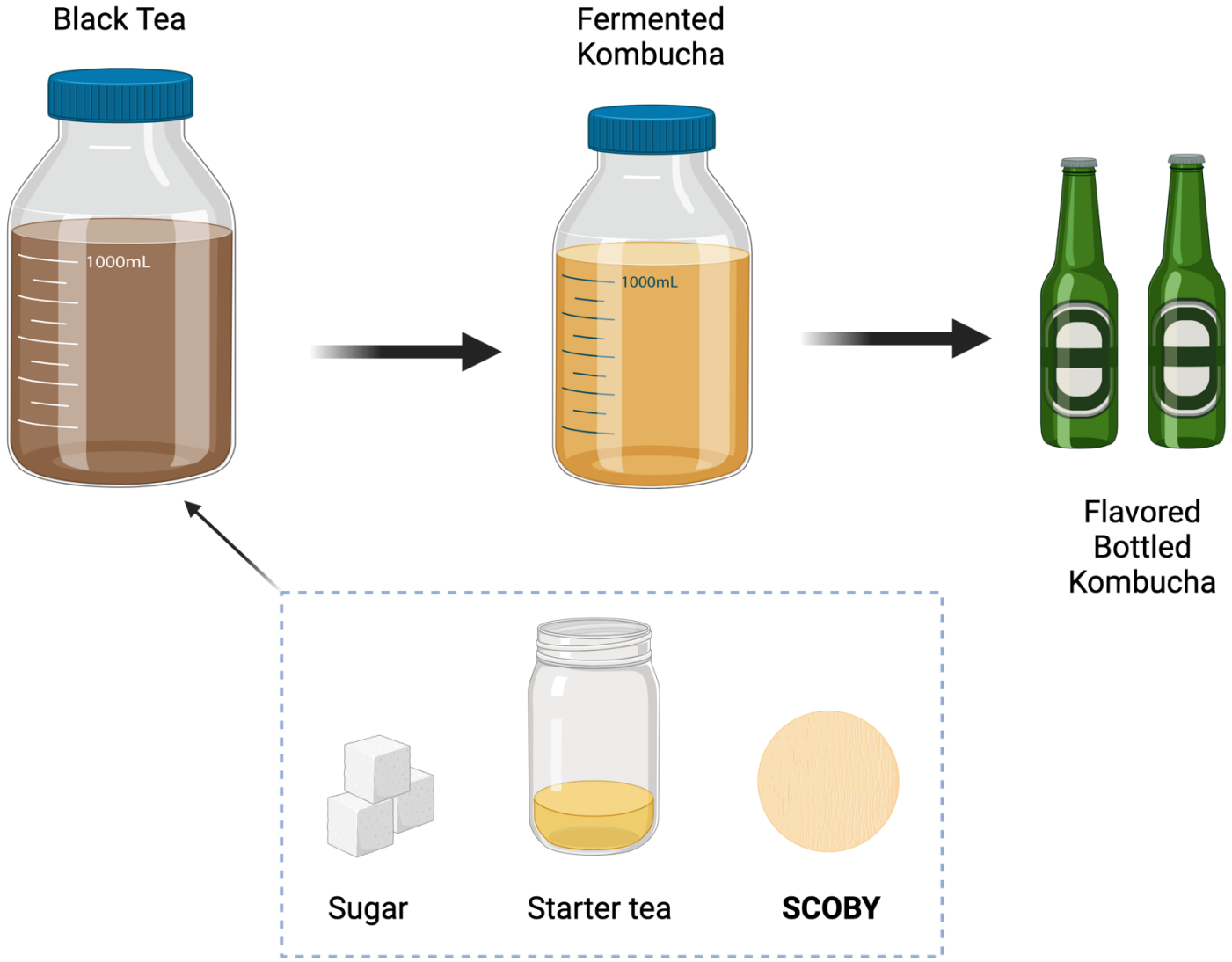

Introduction
Overview
Historical Perspective
Challenges
Human Health
Environment
Solutions
Old Polymers
Emerging Concepts
Attempts w/Impact
Applications
Food and Ag
Electronics and Optics
Healthcare
Future
What do we need?
How do we get there?

Kitchen Material Science: My Kombucha makes a Sustainable Material

SCOBY: Symbiotic Culture of Bacteria and Yeast

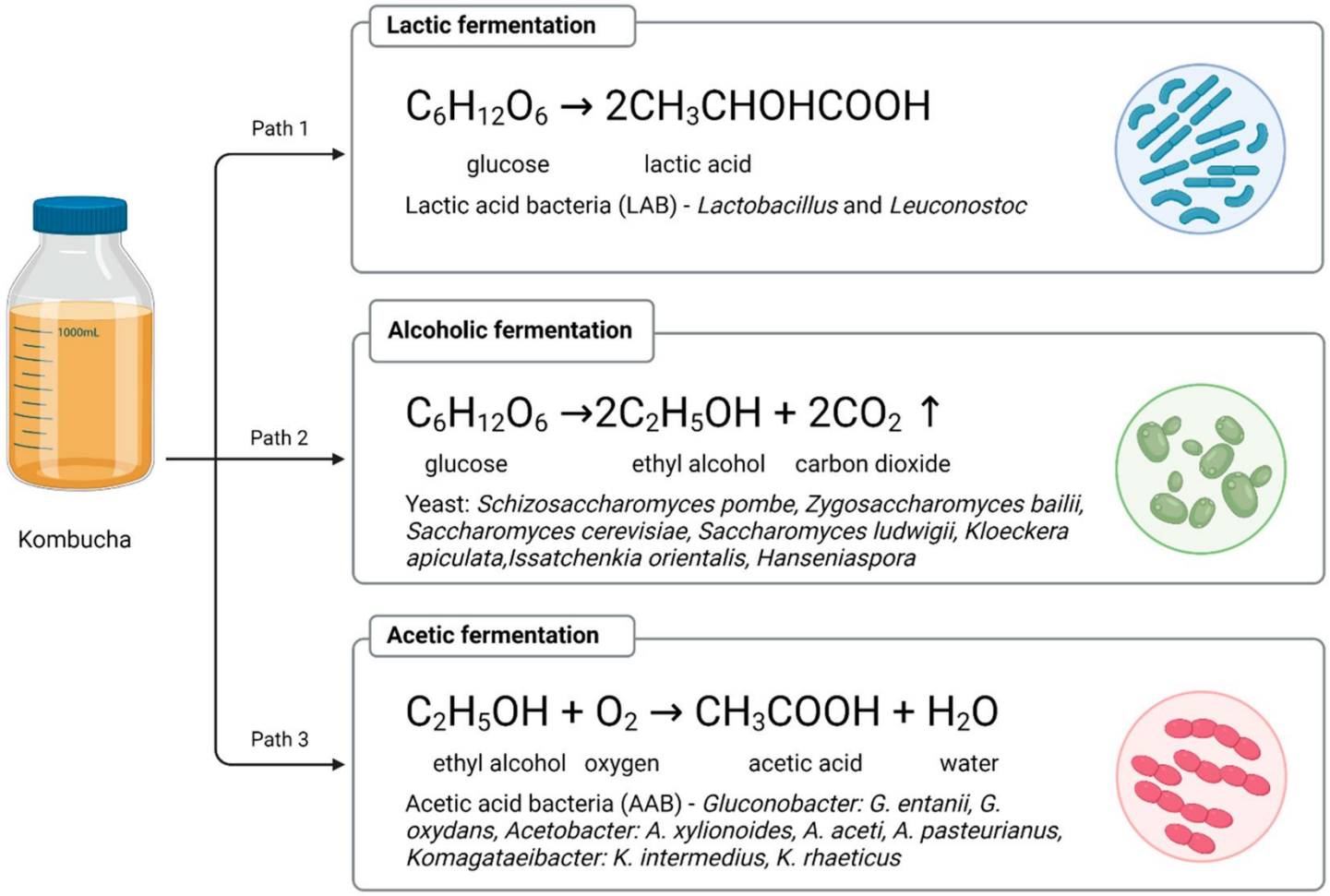
- Kombucha is a fermented tea drink made with a scoby

Kitchen Material Science: My Kombucha makes a Sustainable Material



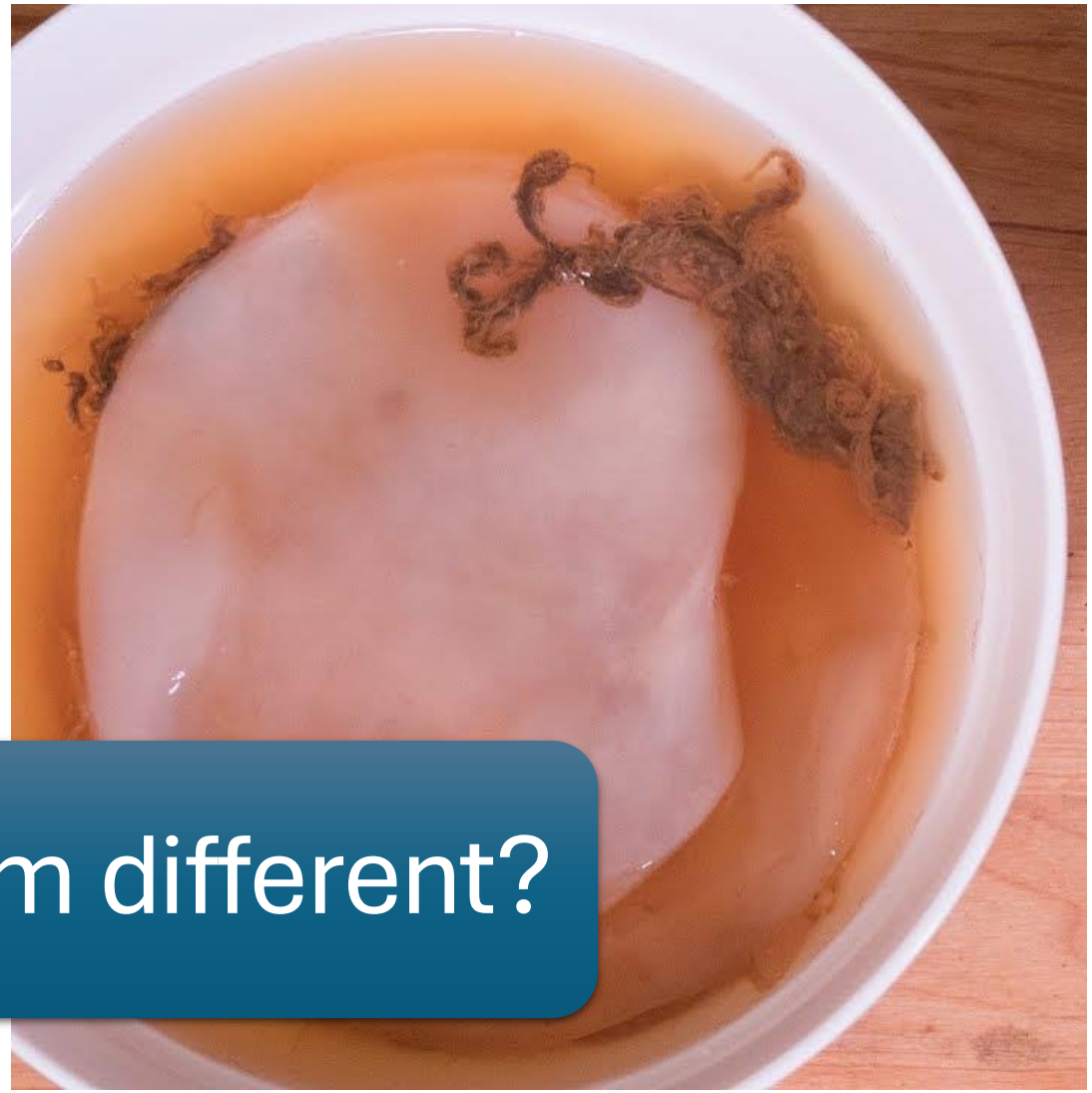
- Culture of yeast and bacteria is inoculated into a sugary tea
- SCOBY digests the sugar to produce kombucha
- Additionally, the SCOBY is re-produced

What is the SCOBY doing?



- Yeast and bacteria digest the sucrose to produce alcohol, organic acids and CO_2
- **Cellulose** is produced to form a pellicle which houses the cultures
- Cellulose producing bacteria – *Acetobacter xylinium*

Jakubczyk. K et al. *Nutrients* **2022**

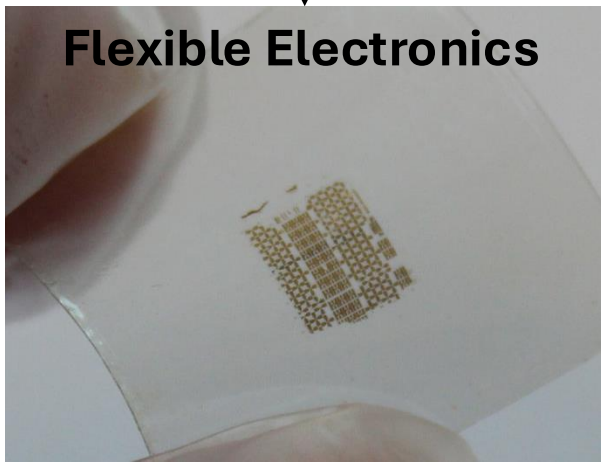


What makes them different?

Applications of SCOBY: How do we get here?

Food packaging

Flexible Electronics



Wound-healing

Outline for the Next two Classes

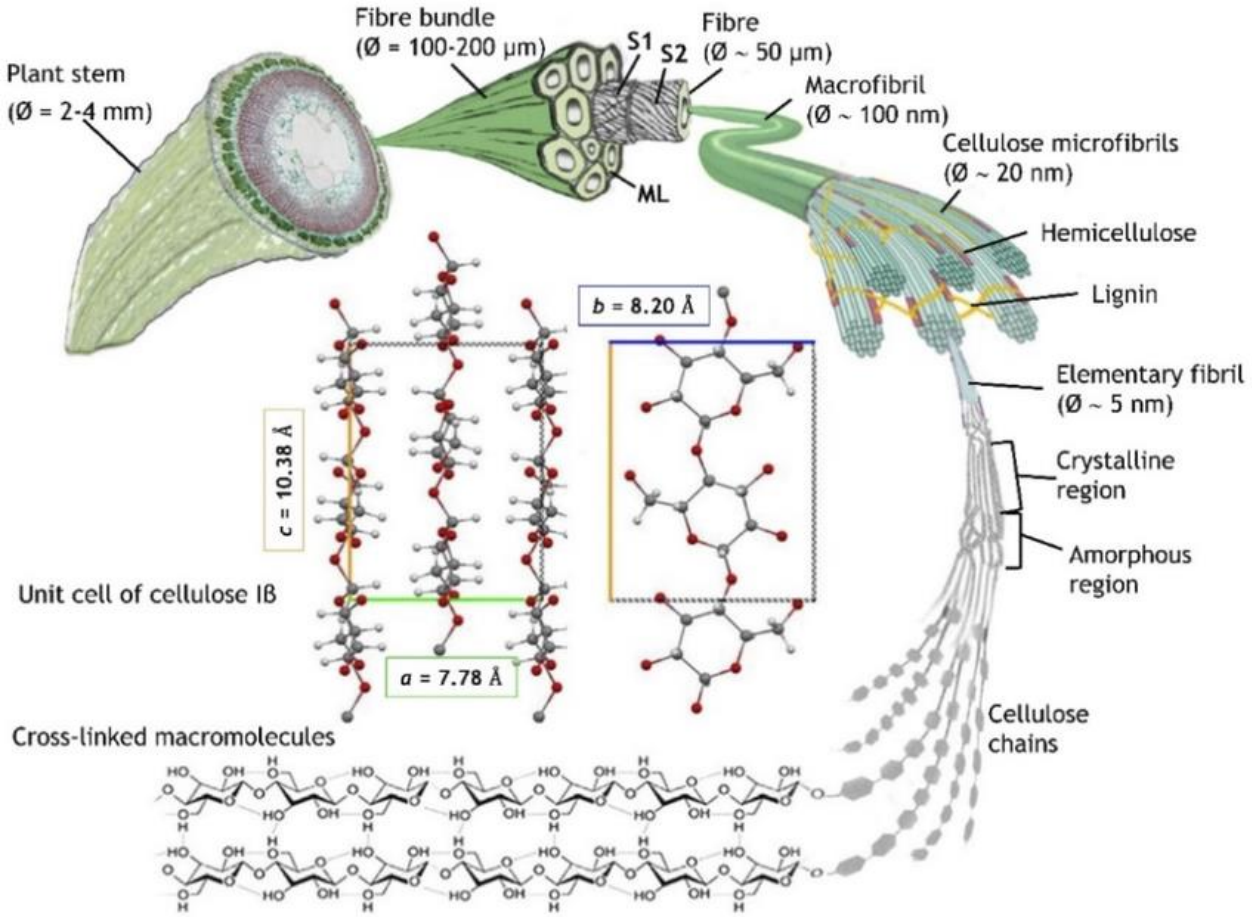
TODAY:

- What are Biopolymers?
- Chemistry and Structure
- Salient Features
- Process of Extraction
- Past Applications
- Key Limitations

NEXT WEEK:

- New design features
- Modification Techniques
- Applications

Biopolymers: Nature's building blocks

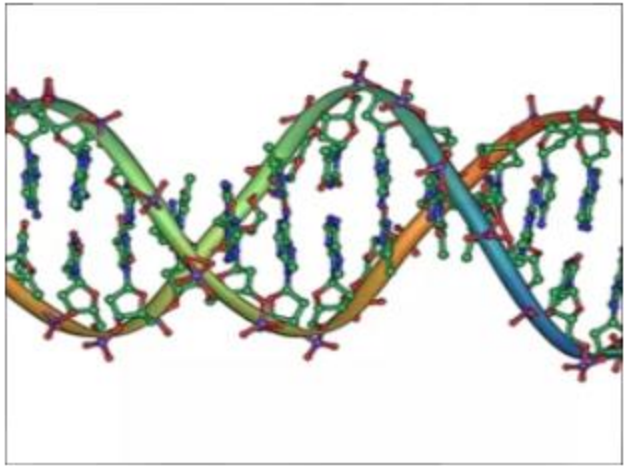


- Naturally-occurring Polymeric substances synthesized by living cells
- Naturally occurring monomeric units synthesized into polymers
- **Hierarchical Organization:** Polymeric chains further organized into secondary and tertiary structures
- Three main classes– carbohydrates, proteins and nucleic acids

Fovo, A. D. et al. *RSC Advances* **2022**

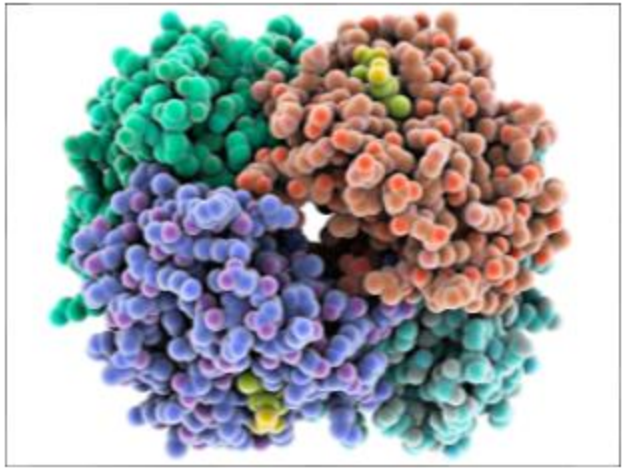
Types of Biopolymers

Nucleic Acids



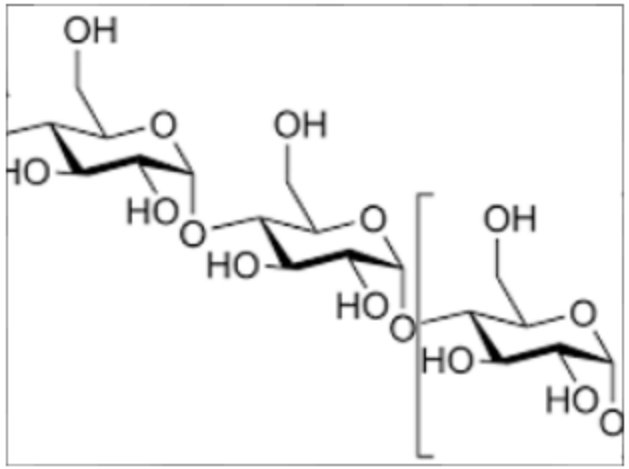
- Polynucleic acids
- Assembled into single or double strands
- 5 monomeric units – A,T,G,C and U

Proteins



- Polypeptides
- Assembled into globular or structural proteins
- 22 monomeric units – amino acids

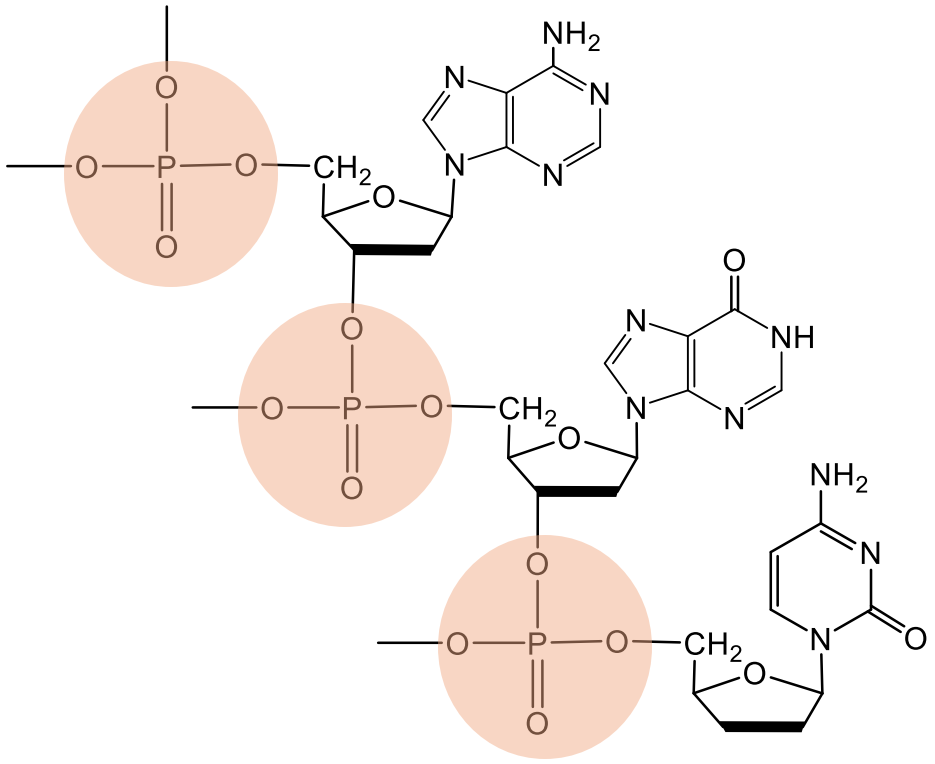
Carbohydrates



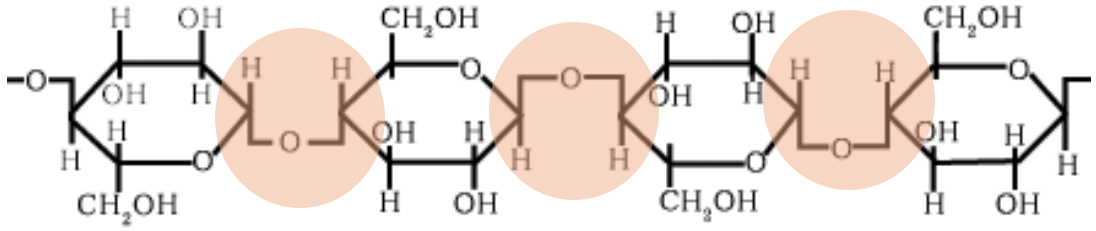
- Polysaccharides
- Linear or branched. Assemble into fibrils
- Monosaccharides - Glucose, fructose

Primary Structure of Biopolymers

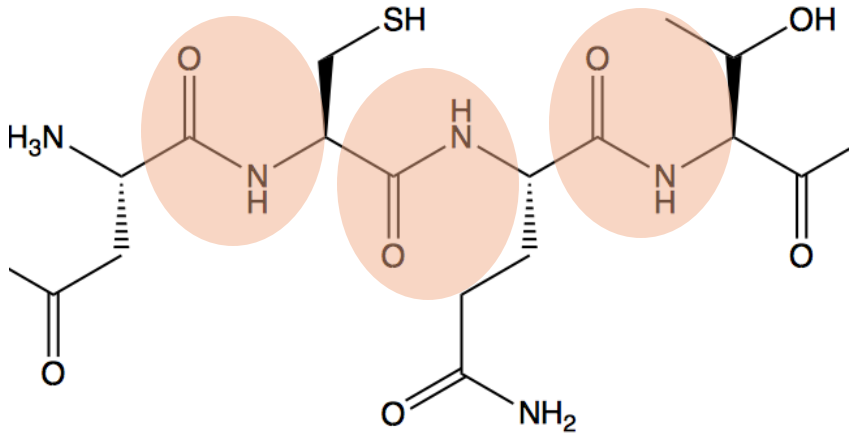
Polynucleotides:



Polysaccharides:

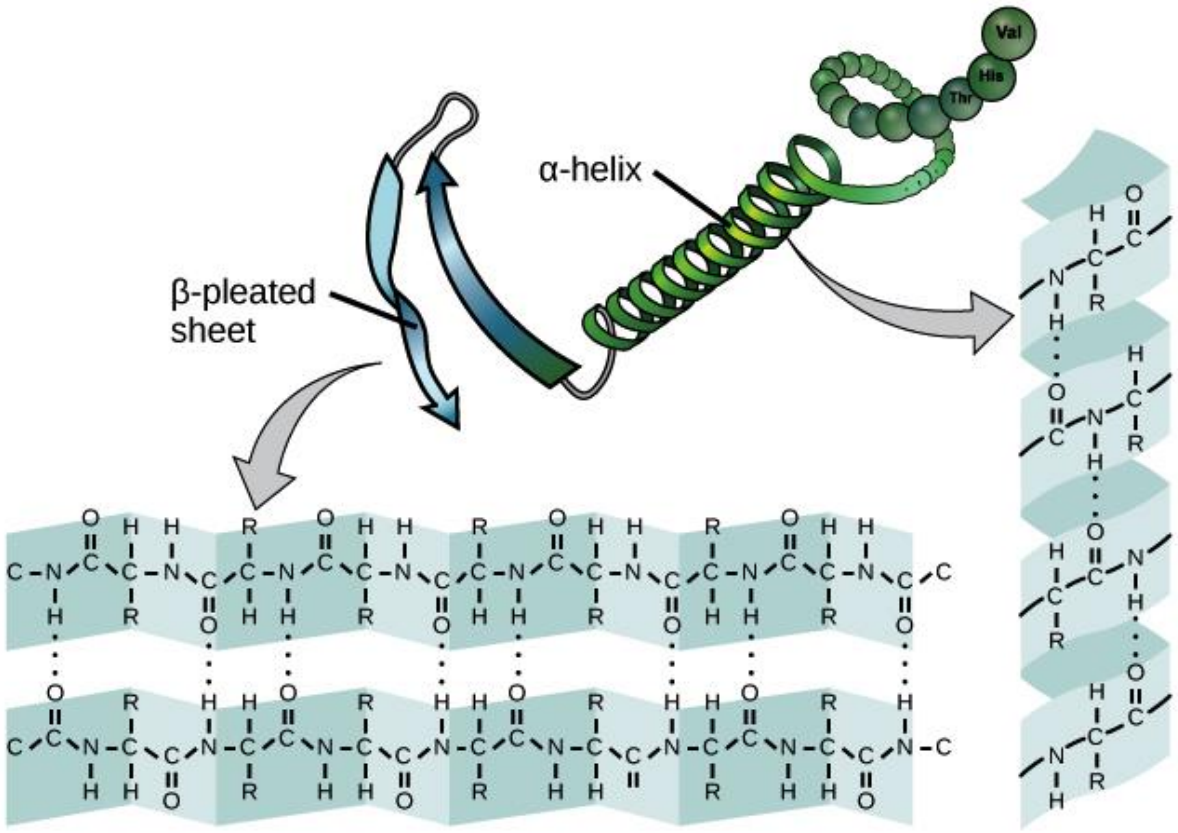


Polypeptides:



- Usually linked by ether, ester or amide bonds
- Groups that hydrogen bond produce hierarchical structures

Hydrogen Bonding Dictates Secondary Structure

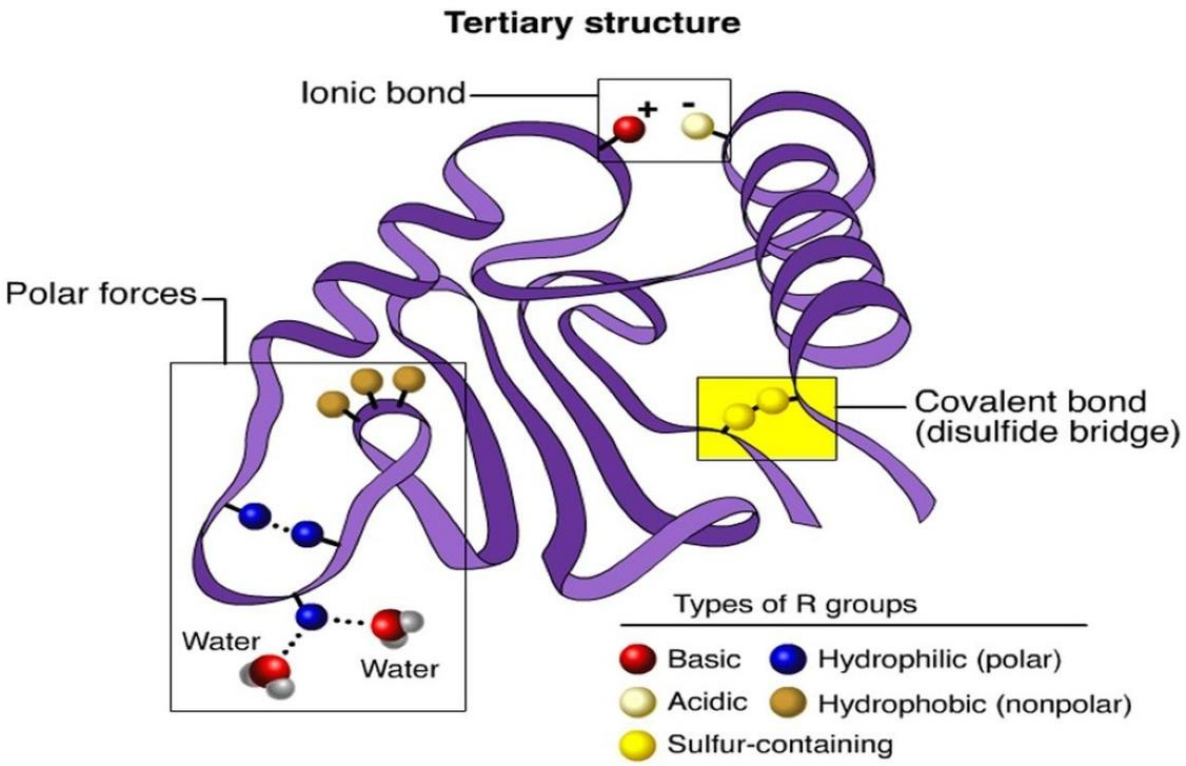


Parker, N. et al. *7.4 Proteins - Microbiology OpenStax*, **2016.**

Hydrogen Bonding:
Inter/Intramolecular dipole-dipole interactions between a Hydrogen atom and an electron donor

- Dictates –
  - Orientation
  - Supramolecular Arrangement
  - Crystallinity
  - Interaction with other biopolymers

Weak Interactions play a Significant Role in Protein Tertiary Structure



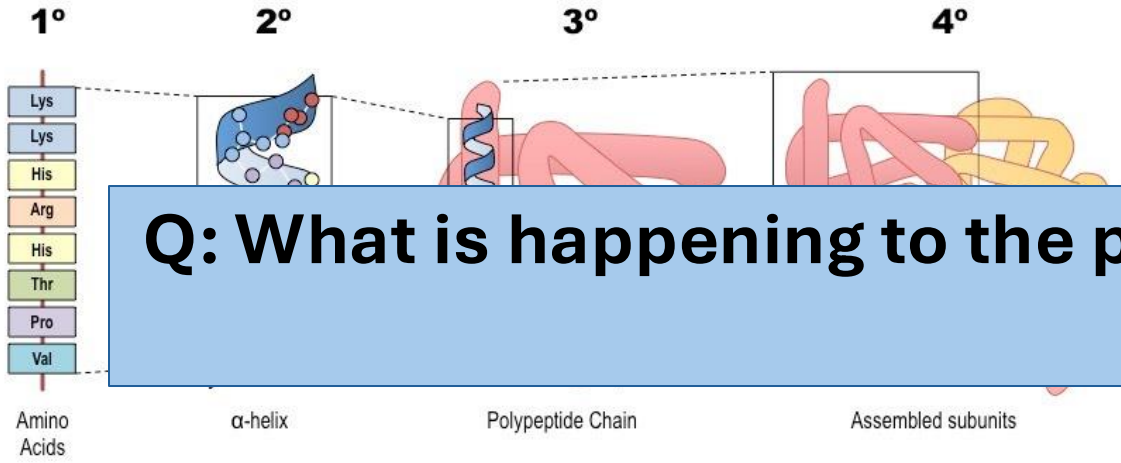
Facts.Net 17 Surprising Facts about Tertiary Structure

Van der Waals Interaction: Weak interactions between polarized carbon atoms within biopolymer structure and environment

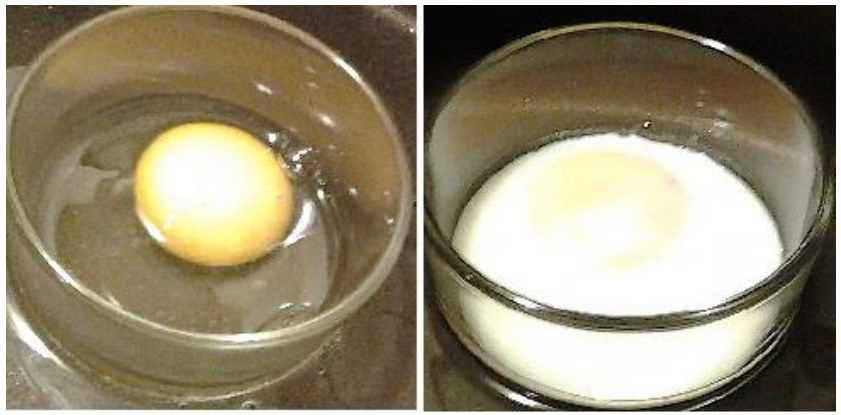
Hydrophobic Effect: Non-polar regions within a polymeric structure form aggregates to minimize interaction with water

- Primarily govern the orientation of amorphous regions within protein chain

Molecular Structure Affects Properties & Function



Q: What is happening to the protein when you fry an egg?



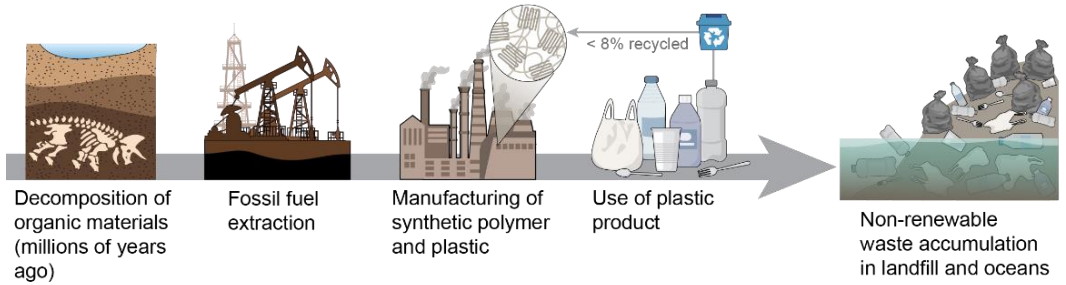
Structure :

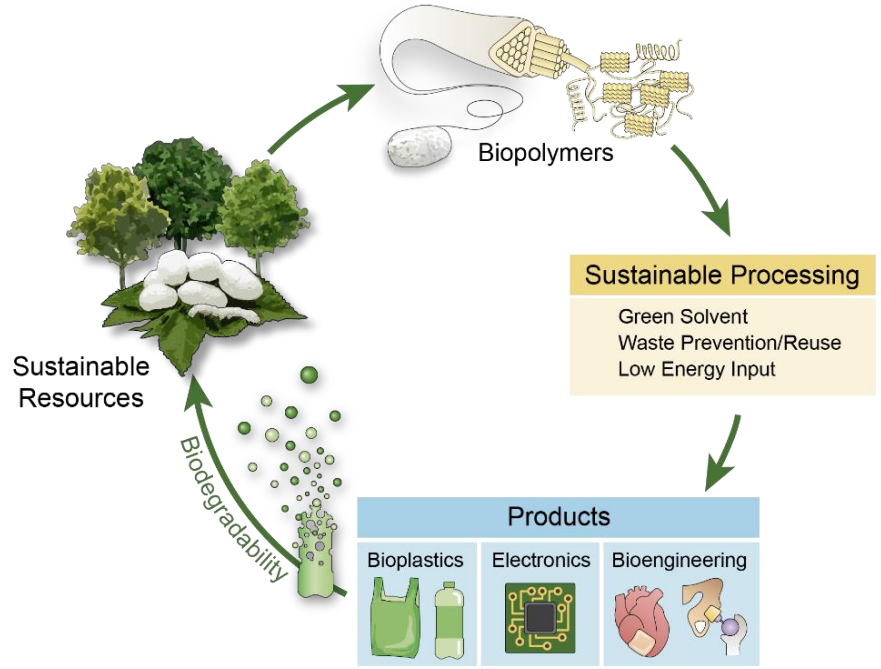
- Polymer chain length
- Side-chain functionality

Property :

- Mechanical strength
- Flexibility
- Degradability
- Hydrophobicity
- Biological Function

Salient Features of Biopolymers

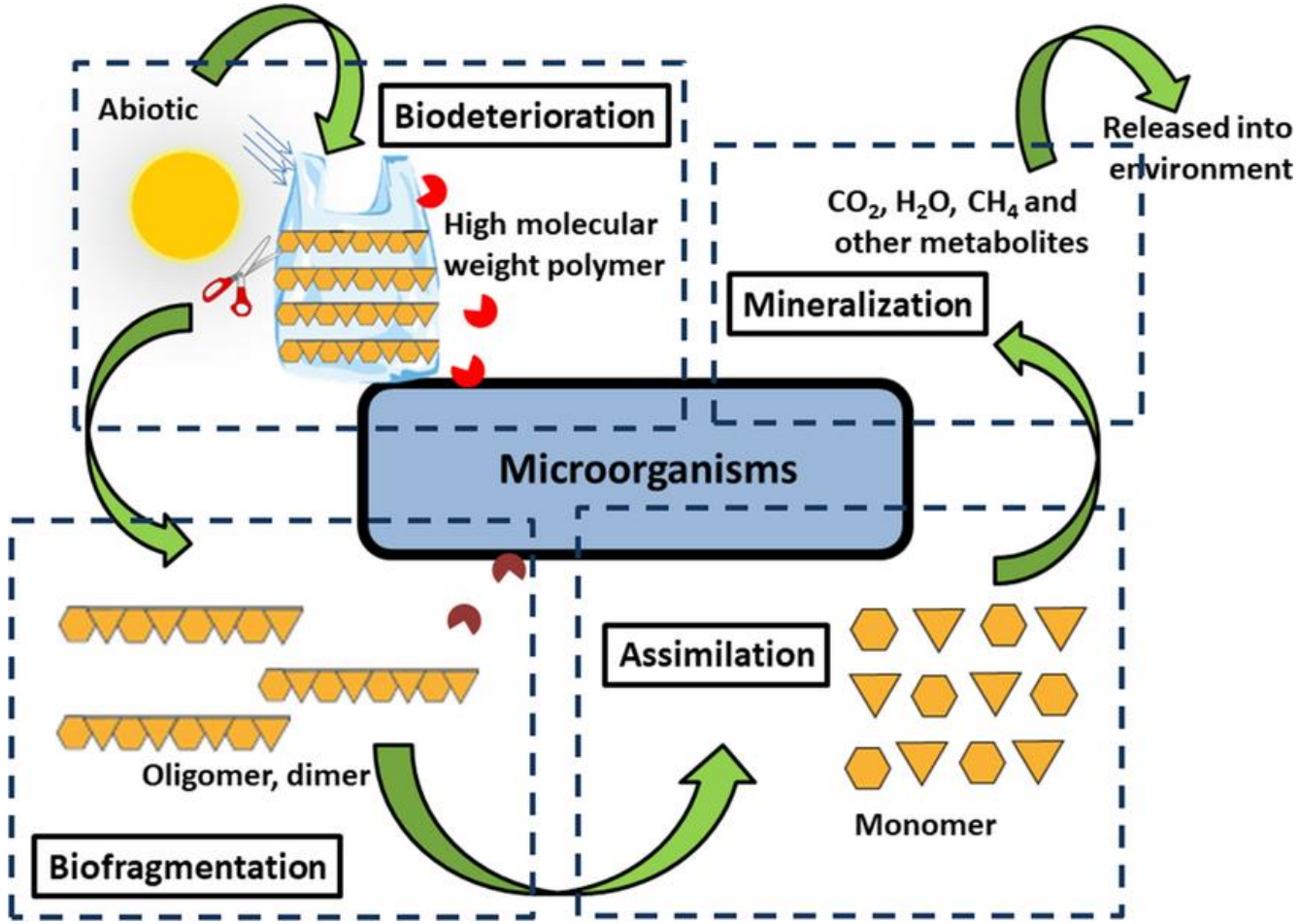




- Sustainably-sourced
- Structural diversity
- Functional diversity
- Aqueous processing
- Low energy input
- **Biodegradability**

Li et al., ***Advanced Matls,*** 2021

Why are Biopolymers Degradable?

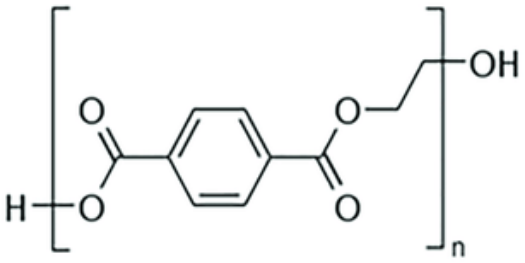


Solanki, S. et al. *Biodegradation* **2022**

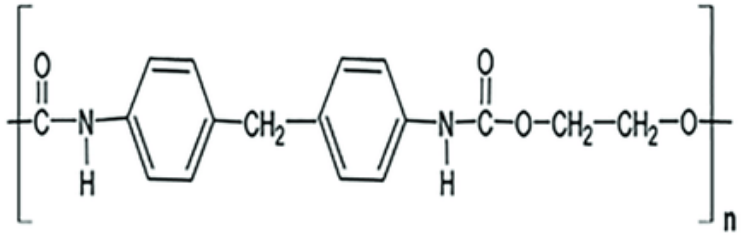
- Breakdown into naturally-occurring components
- Conducted by abiotic factors as well as microbes
- Microbes have evolved over million years to use metabolites as nutrient
- **Microbes can breakdown ester, ether and amide bonds**

Why are Synthetic Polymers not Degradable?

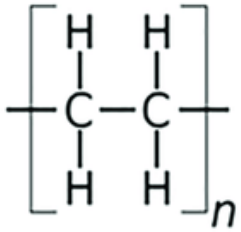
Polyethylene terephthalate (PET)



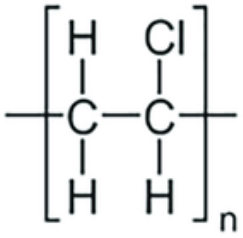
Polyurethane (PU)



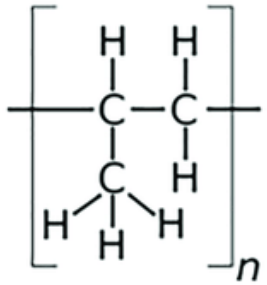
Polyethylene (PE)



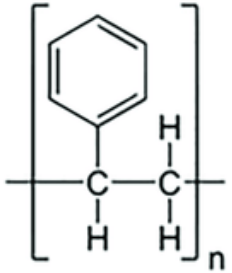
Polyvinyl chloride (PVC)



Polypropylene (PP)

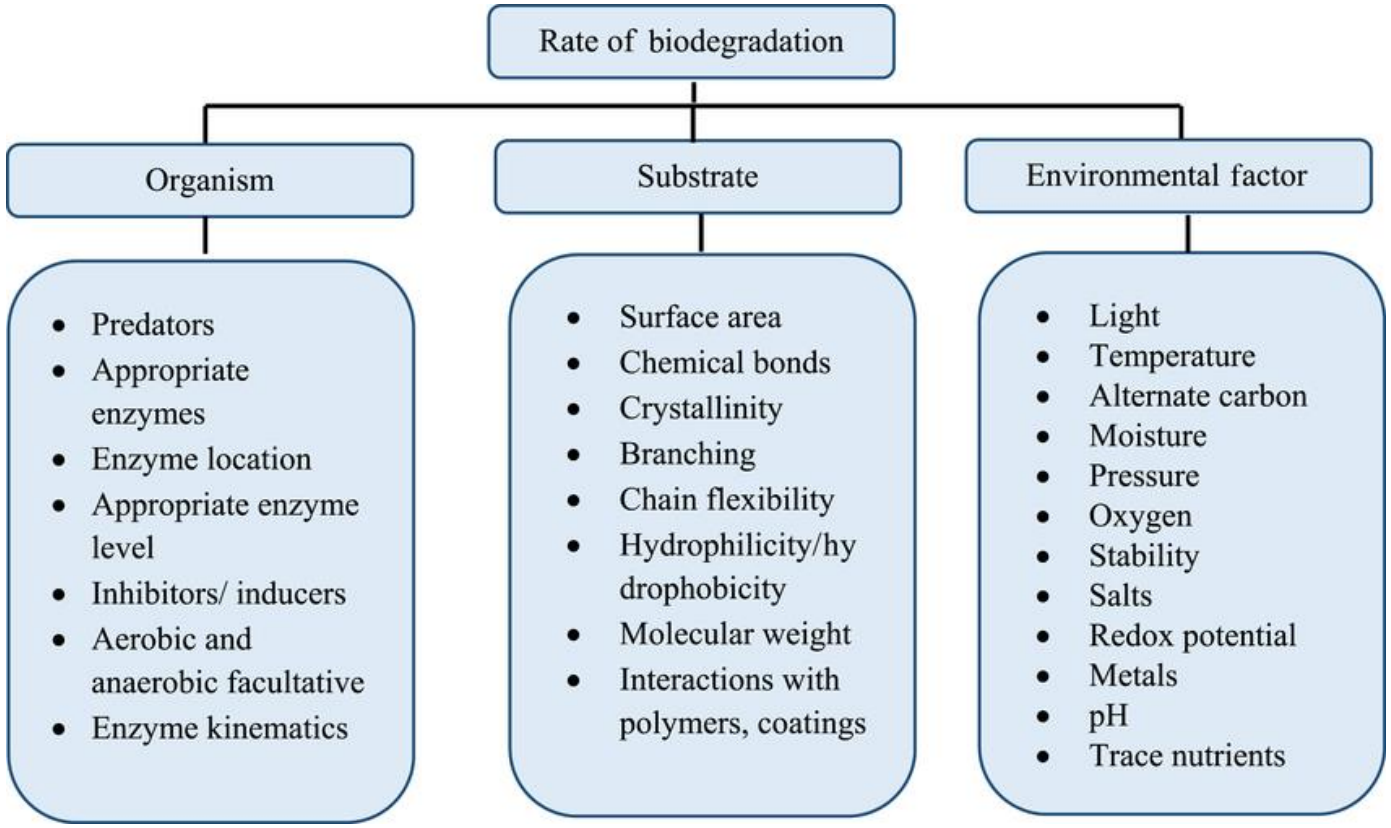


Polystyrene (PS)



- Still susceptible to abiotic deterioration
- Breakdown fragments cannot be metabolized by microbes
- Predominantly C-C linkages which are not broken down by microbial enzymes

Factors Affecting Degradation



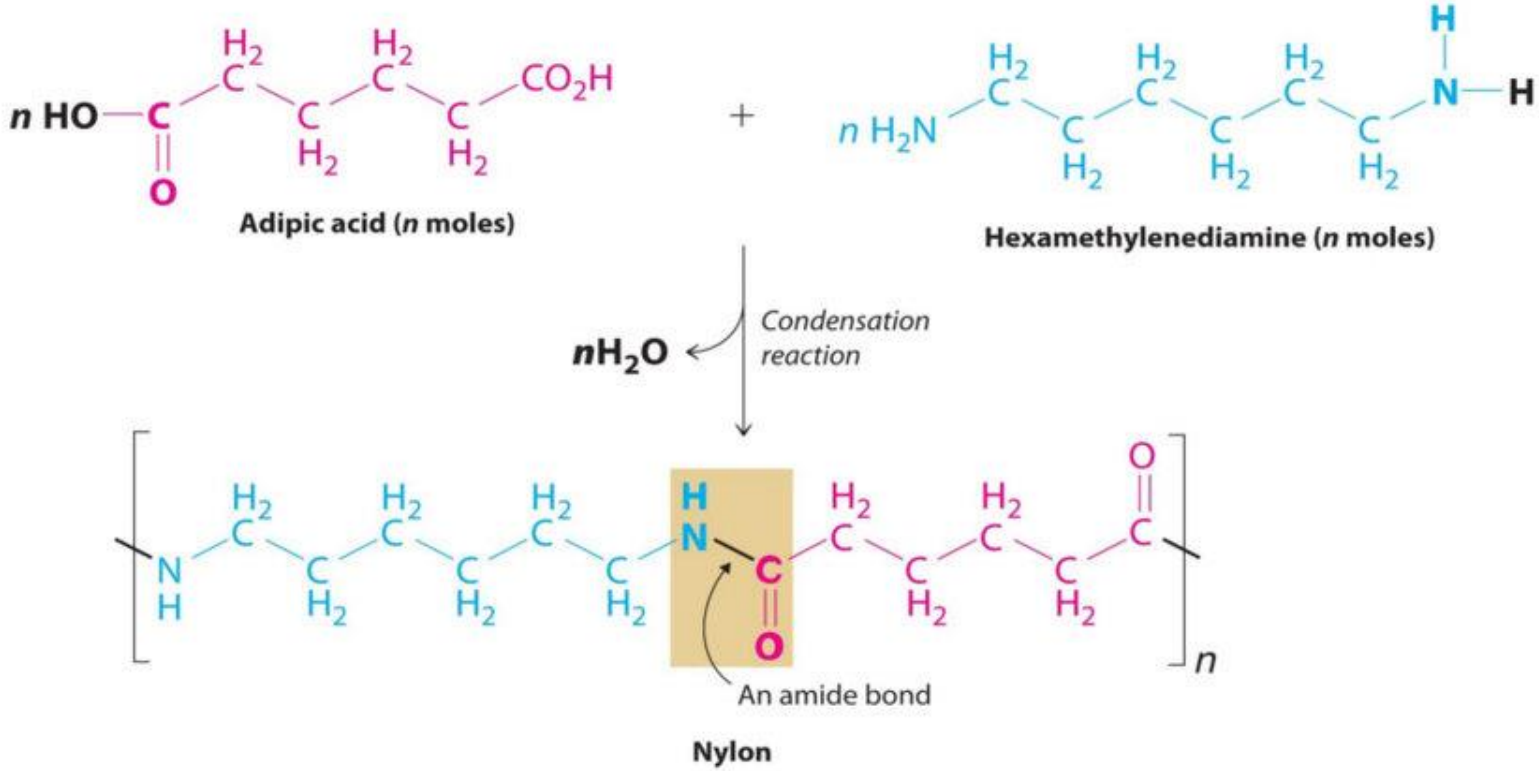
Birania, S. et al. *Food Process Engineering*, **2021**

- Environmental factors such as aerobic vs. anerobic degradation should be considered
- Biopolymer properties will modulate degradability
- Types of organism dictates enzyme eg. Protease, amylase etc
- Biopolymer amount and type can affect microbial populations as well as local flora and fauna

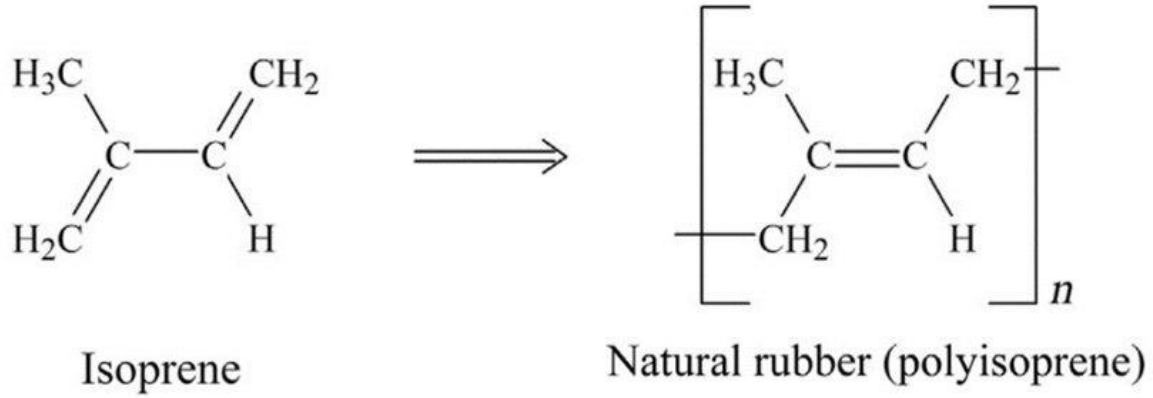
Just because something is **Biodegradable** doesn't mean it won't cause environmental damage

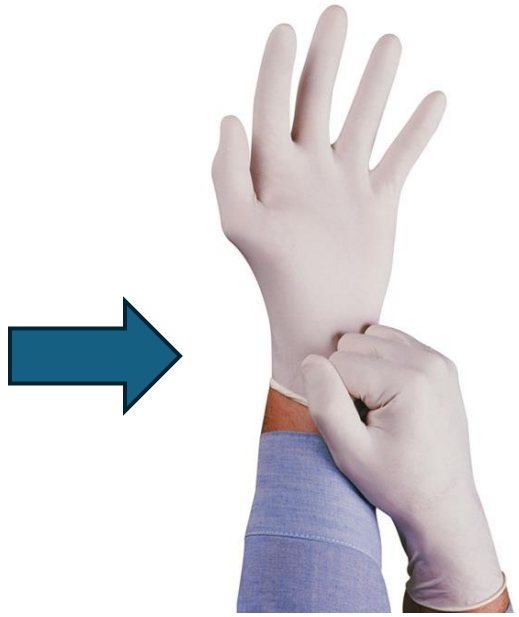
Q: Why is nylon not degradable?

- Research at home
- Answer will be discussed in the next class



Other Types of Biopolymers: Rubber

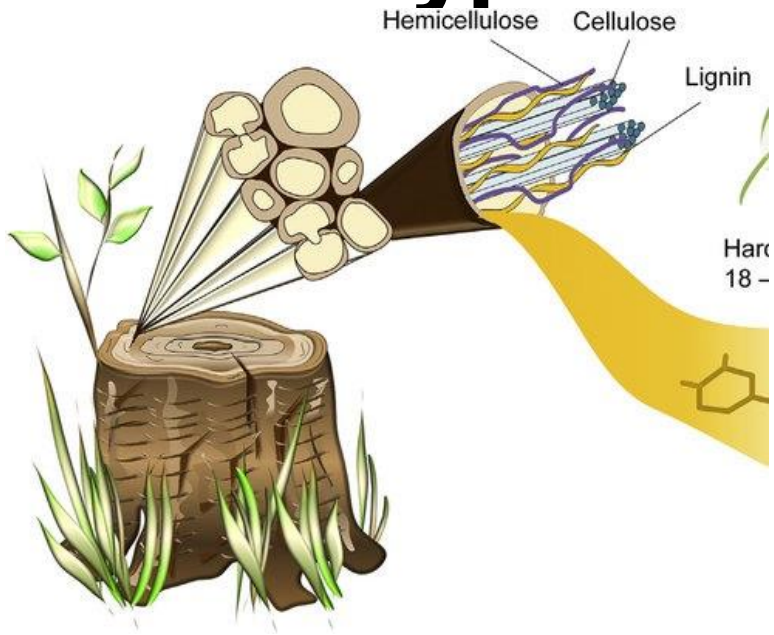


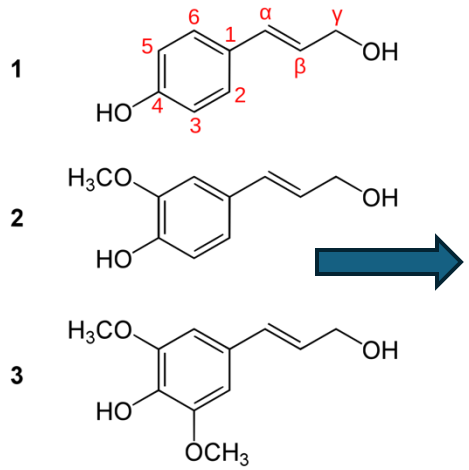


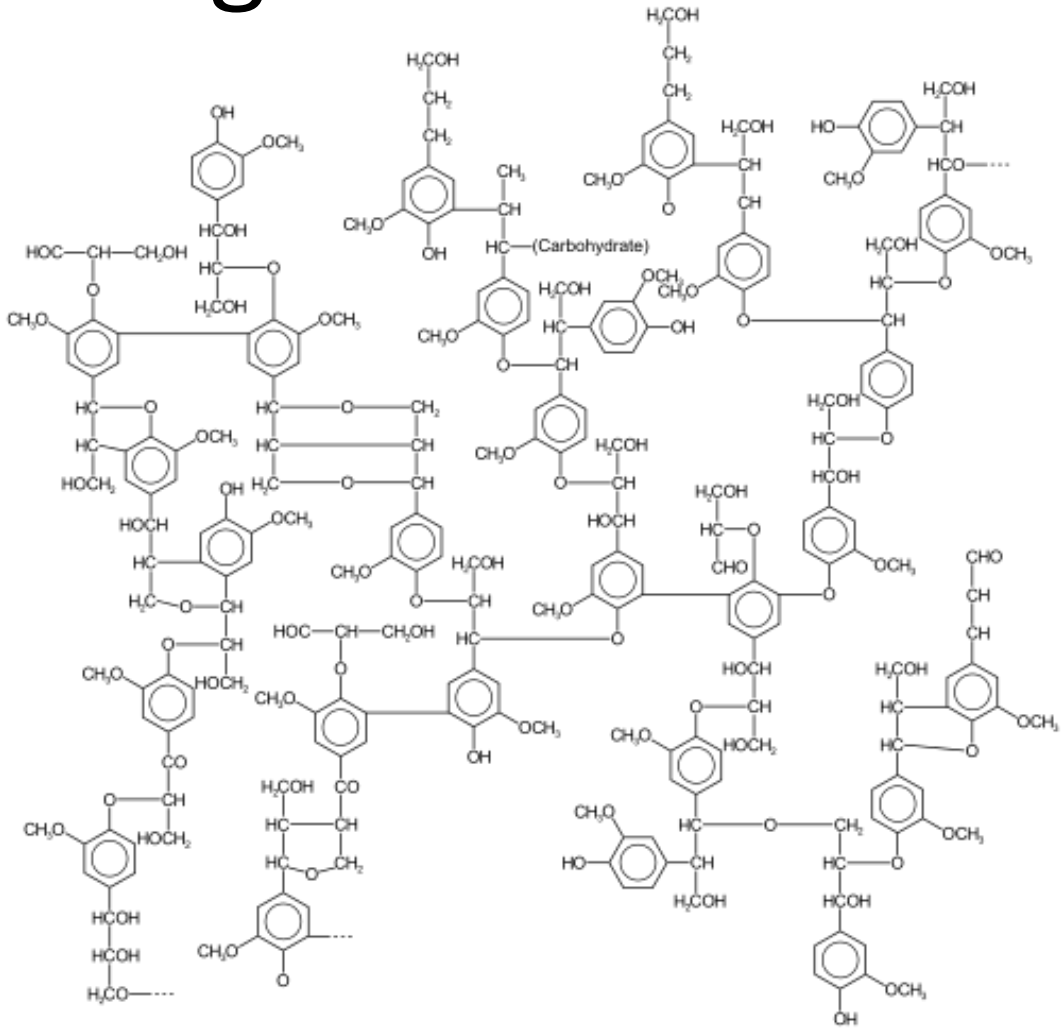
Fazli, A. et al. *Materials* **2020**

- Natural rubber extracted from rubber tree is a class of molecules known as terpenes
- An elastomer that is biodegradable
- Rubber is often blended with synthetic variant or vulcanized
- **Vulcanization:** Irreversible chemical crosslinking of rubber using sulfur and heat

Other Types of Biopolymers: Lignin

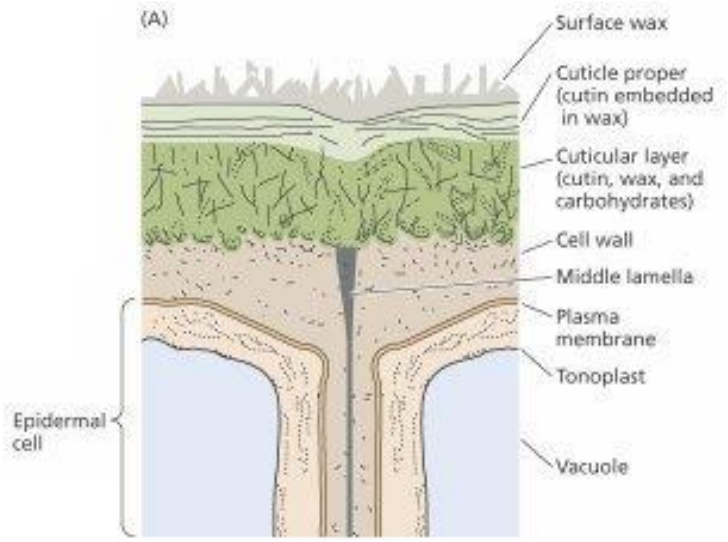




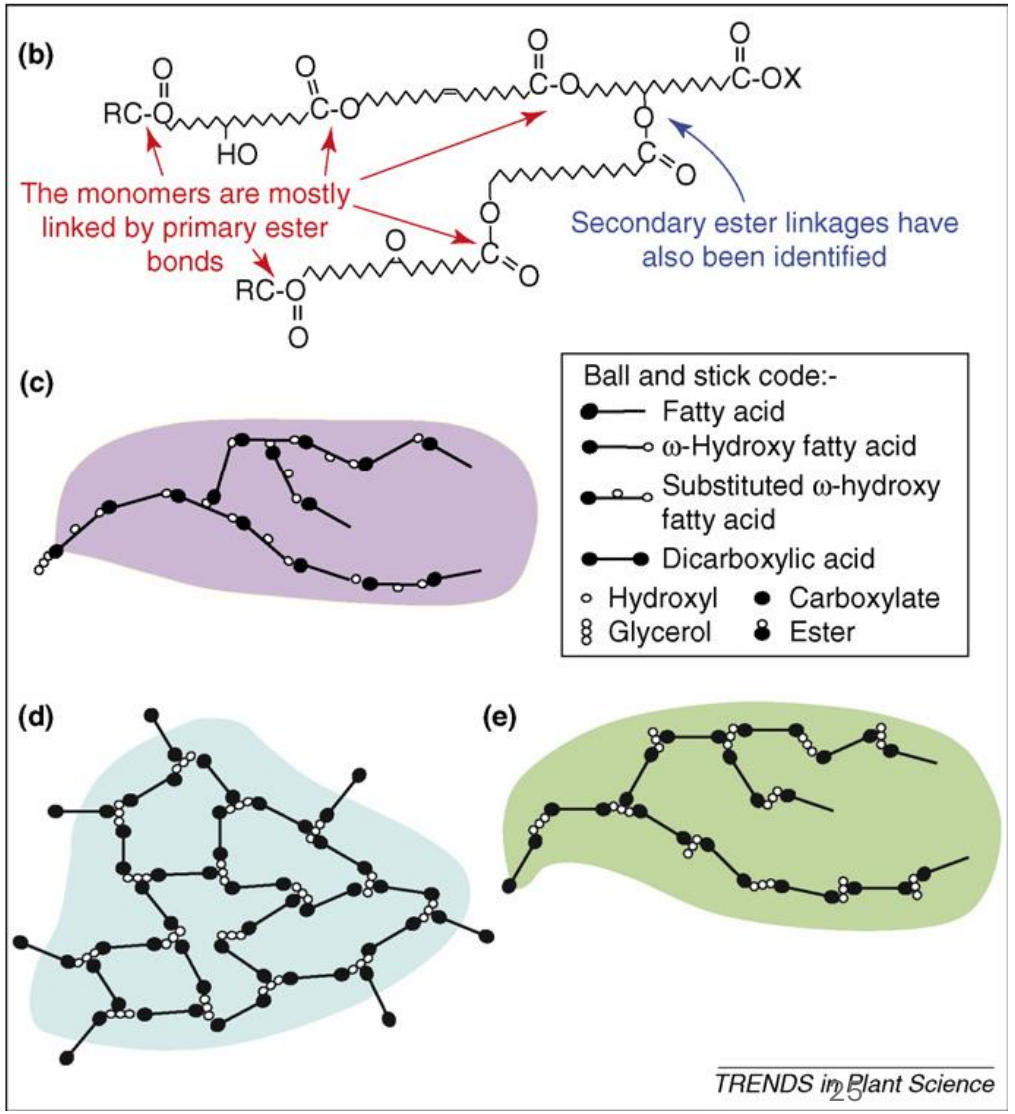


- Third most abundant biopolymer after cellulose and hemicellulose
- Found in most wood providing rigidity and structural support
- Removal of lignin from wood pulp is a challenge

Other Types of Biopolymers: Cutin



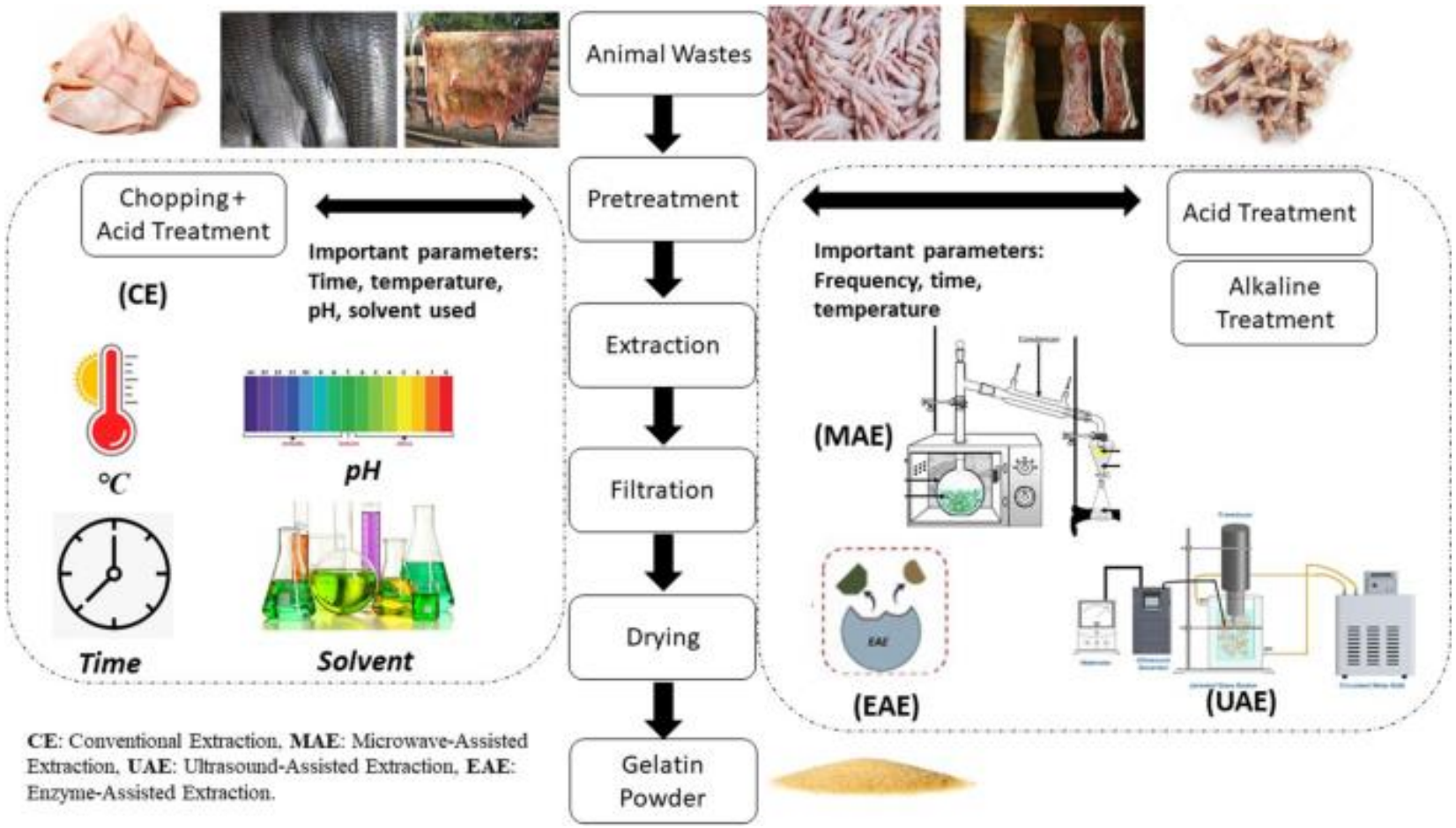
- Component of plant cuticle imparting waxy hydrophobic coating
- Prevents water log and water damage
- Monomeric unit – fatty acids



How does the Isolation of Biopolymers from their Sources Impact the Environment?

- **Things to consider –**
  - Source of material
  - Process of extraction – removal of impurities
  - Use of solvents, acids and other chemicals
  - Energy consumption
  - Waste stream

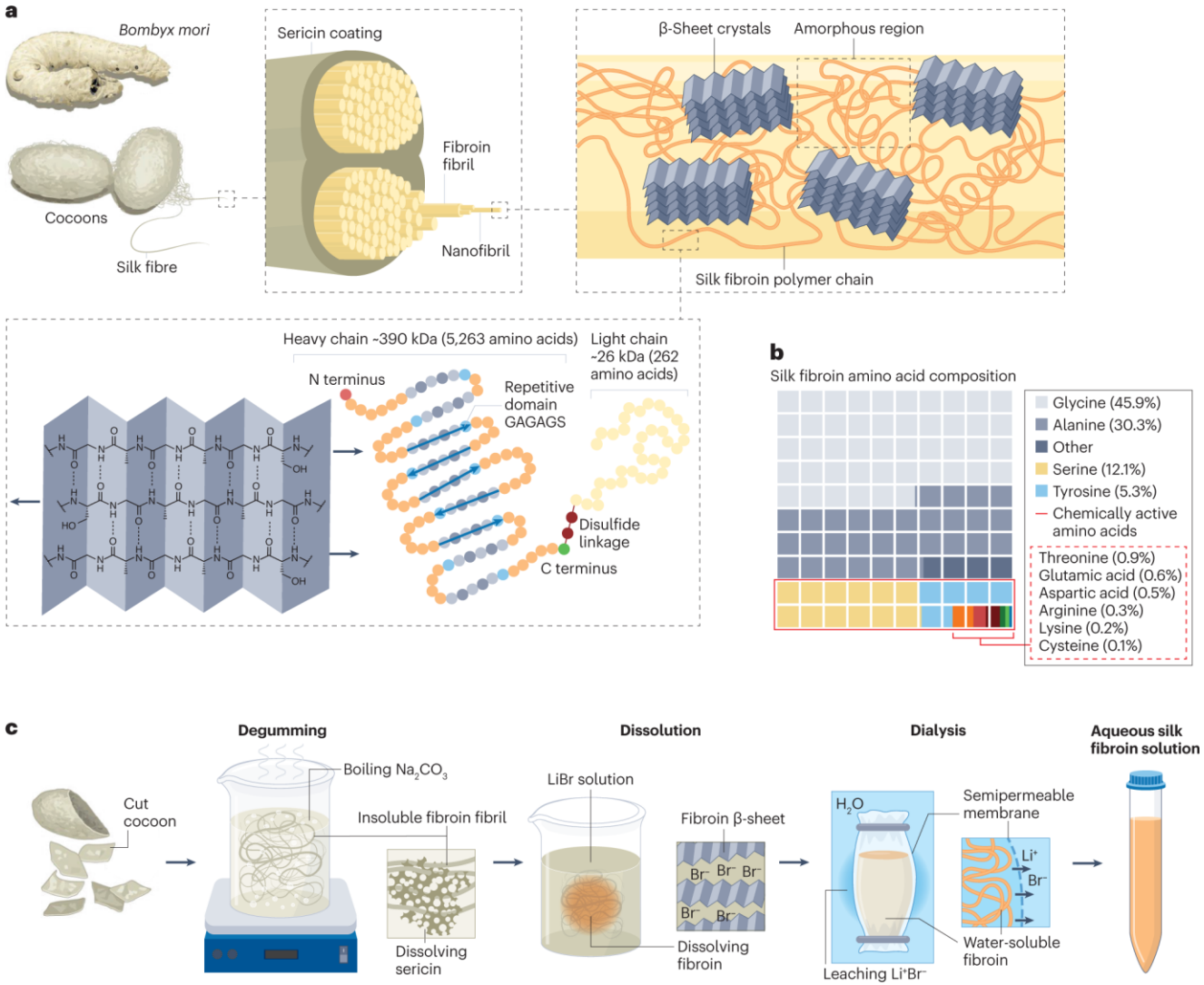
Gelatin is Extracted from Meat and Poultry Waste



- Green source – Meat waste and by-products
- Water-based processing approaches available
- Some strategies may require organic solvents
- Use of acidic and alkaline treatments

Usman, M. et al. *Biomass Conversion and Biorefinery* **2023**

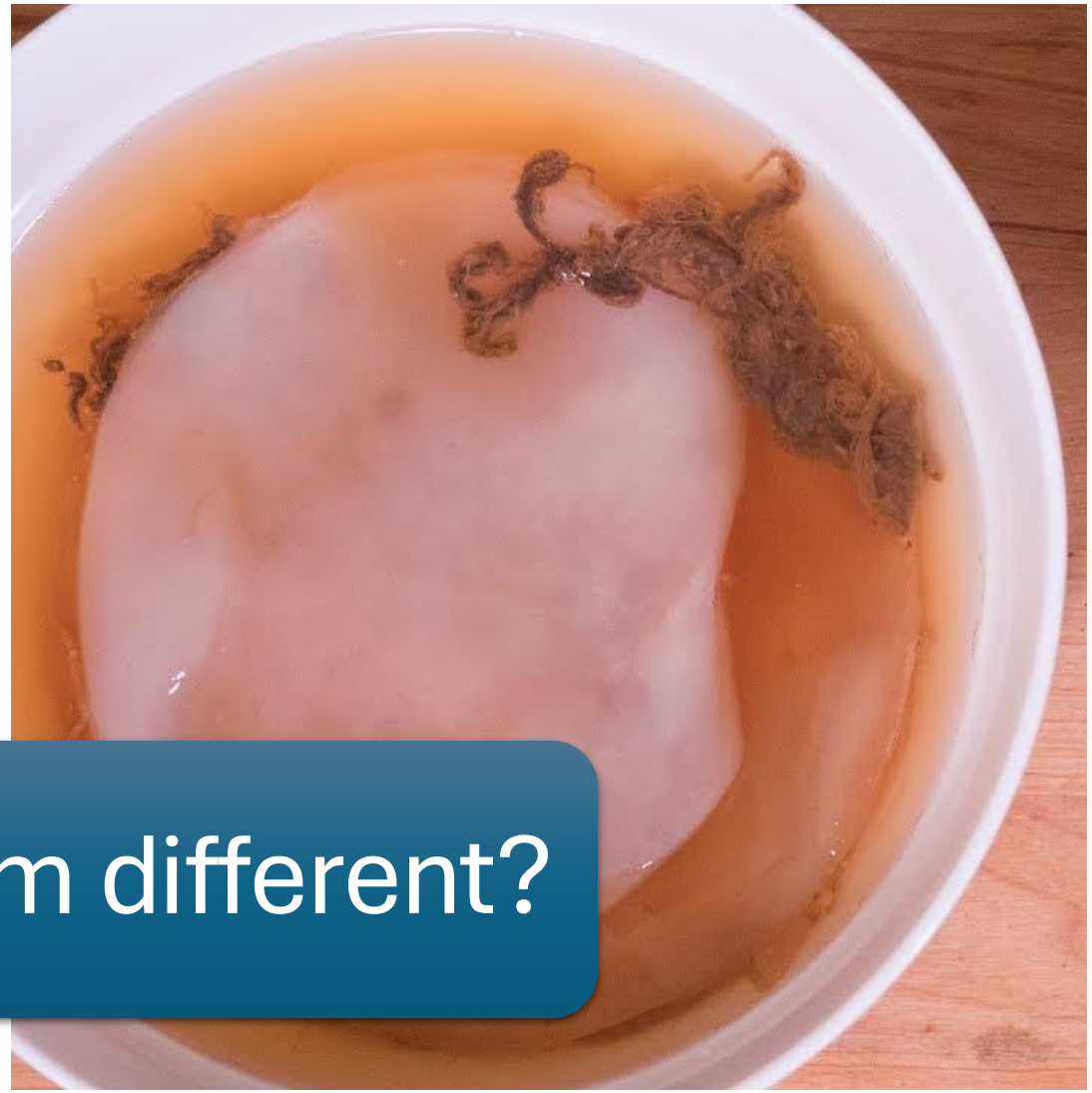
Silk Fibroin is Extracted from *Bombyx mori* Silk Cocoons



- Extracted from silk cocoons
- Processing is fully in aqueous media
- Minimal use of toxic chemicals
- LiBr can be potentially harmful in wastewater streams at high concentrations

Sahoo, J. K. et al. *Nature Reviews Chemistry* **2023**

Discussion:



What makes them different?

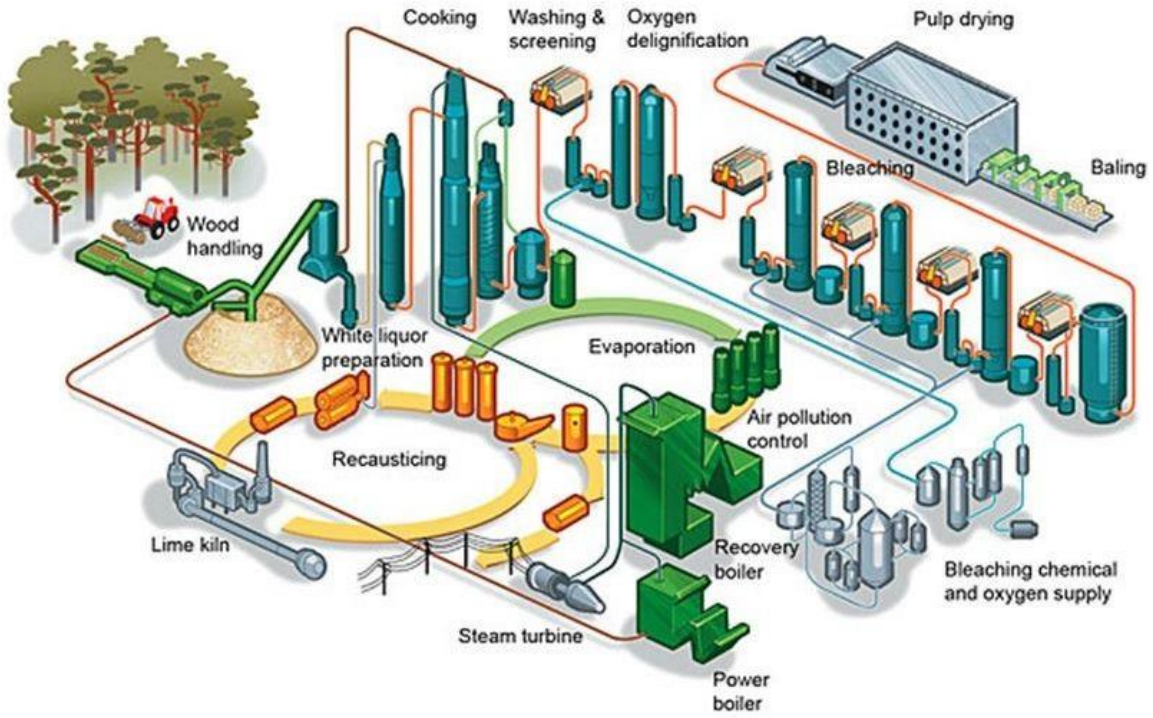
Breakout Session:

In groups of 2-3, discuss the following for 10 min:

- What lignocellulose is – molecular structure, supramolecular structure, various components
- What is bacterial cellulose – structure and components
- Compare similarities and differences
- Discuss methods of extraction for both
- What is more sustainable?
- What is more cost effective?

- Discussion with the whole class

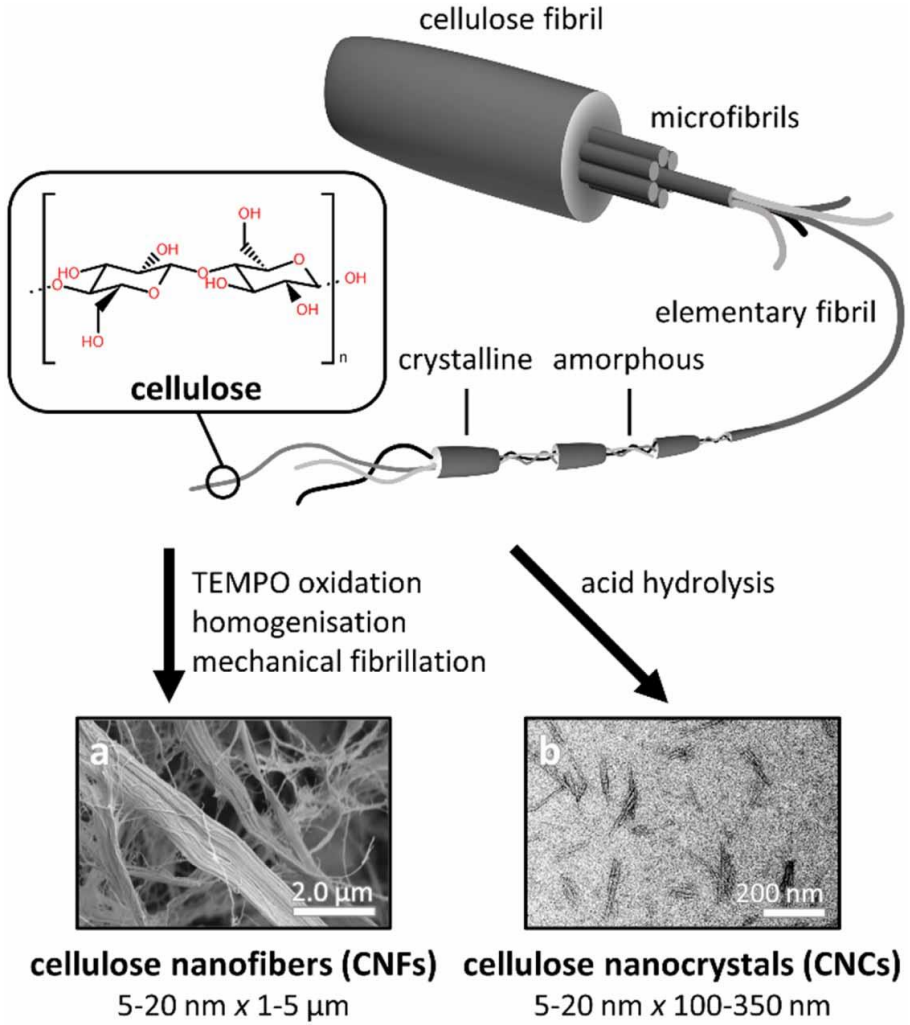
Lignocellulose is Extracted from Wood Pulp



Onarheim, K. et al. *International Journal of Greenhouse Gas Control* **2017**

- Cellulose is extracted from wood through the kraft process
- Involves corrosive alkali material (white liquor) to separate lignin
- Bleaching process for materials like paper
- Highly energy intensive process

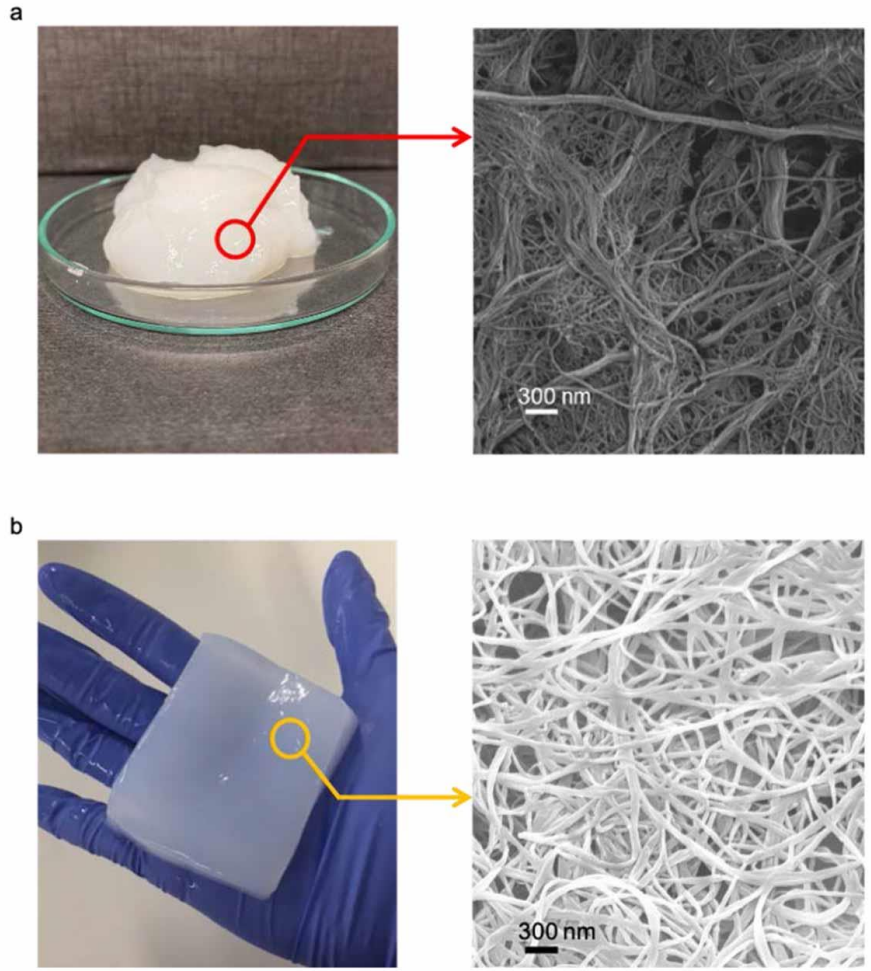
Nanocellulose Production is Not Sustainable



- Nanocellulose – nanocrystalline cellulose or cellulose nanofibers
- Wide ranging applications – reinforcement in paper and plastic packaing, absorbent in hygiene products, food additive
- Process of fabrication involves strong acids and high energy consumption ~ 30 MWh/tonne!

Onarheim, K. et al. *International Journal of Greenhouse Gas Control* **2017**

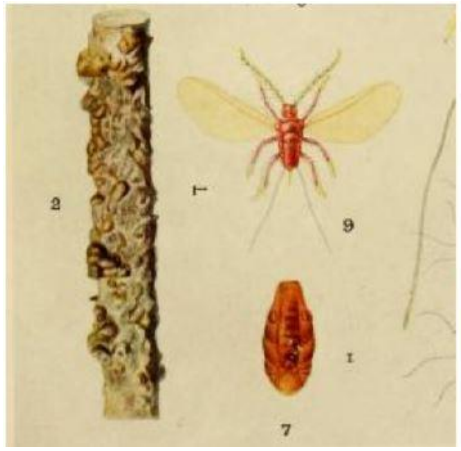
Bacterial Cellulose is an Alternative to Lignocellulose



Titirici, M. et al. *Journal of Physics: Materials* **2022**

- Bacterial cellulose has the same molecular structure as lignocellulose
- Forms similar nanocellulose fibrils
- However, process of lignin extraction, hydrolysis and bleaching avoided
- Producing through biofermentation processes involving *A. xylinium*

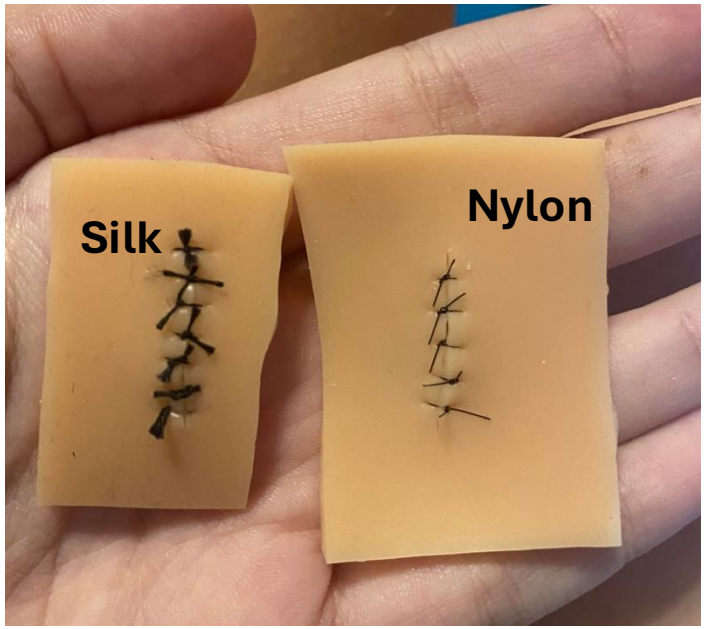
Biopolymers were Widely Utilized Pre-plastic

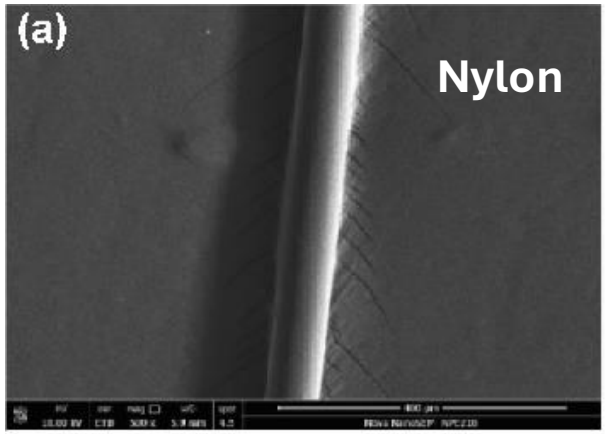


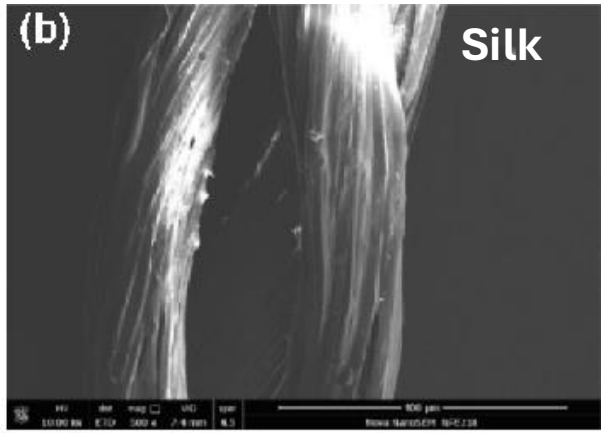
- Silk fibers used as suture materials since 600 BC
- Celluloid was the first thermoplastic developed from cellulose
- Shellac resin was used for making records prior to vinyl
- Latex gloves were made with natural rubber

Why did we stop using Biopolymers?

Advent of Synthetic Polymers: Silk vs. Nylon



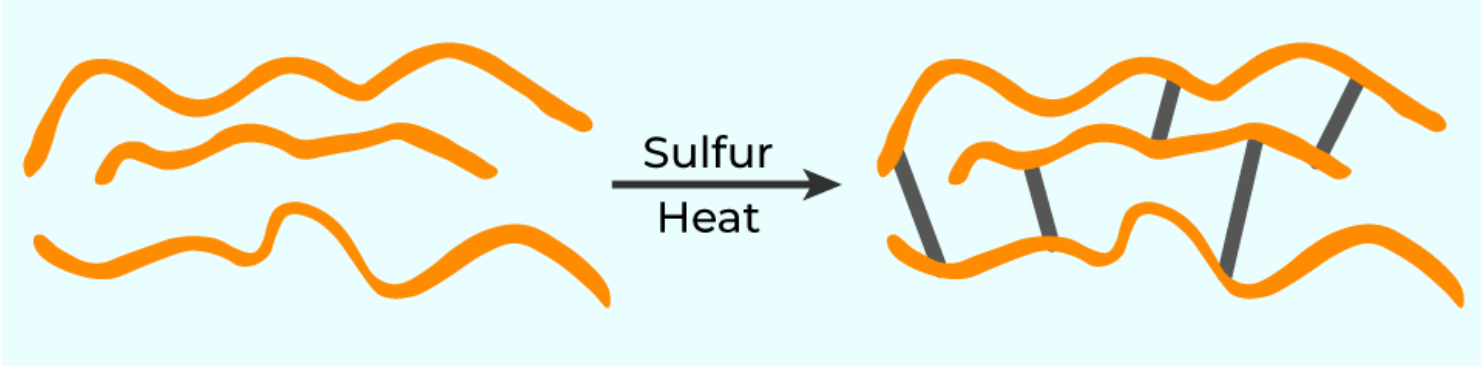


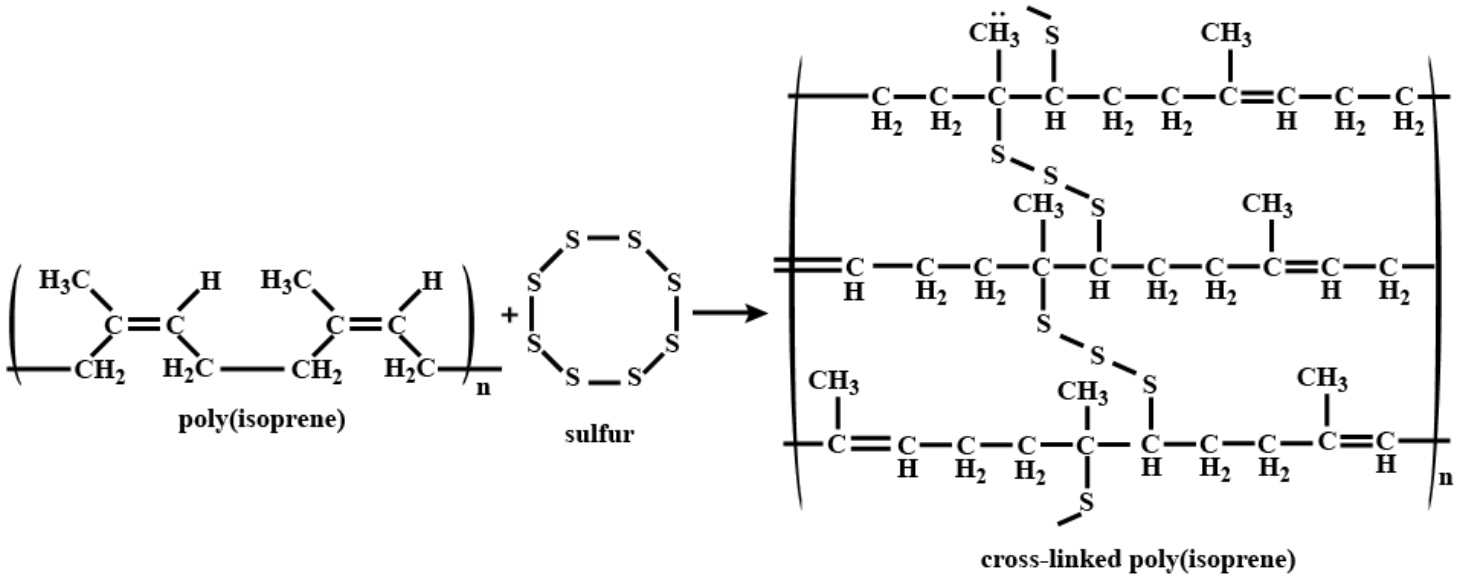


- Silk sutures are multifilament – multiple filaments of silk polymer woven together
- Nylon sutures are monofilament
- Monofilament sutures are smooth. Less visible scars
- Multifilament sutures are more likely to harbor microbes. Risk of infections

Zhang, G. et al. *Friction* **2017**

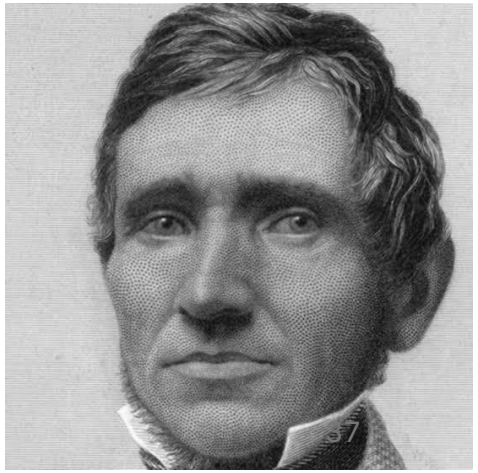
Vulcanized Rubber: Boon or bane?



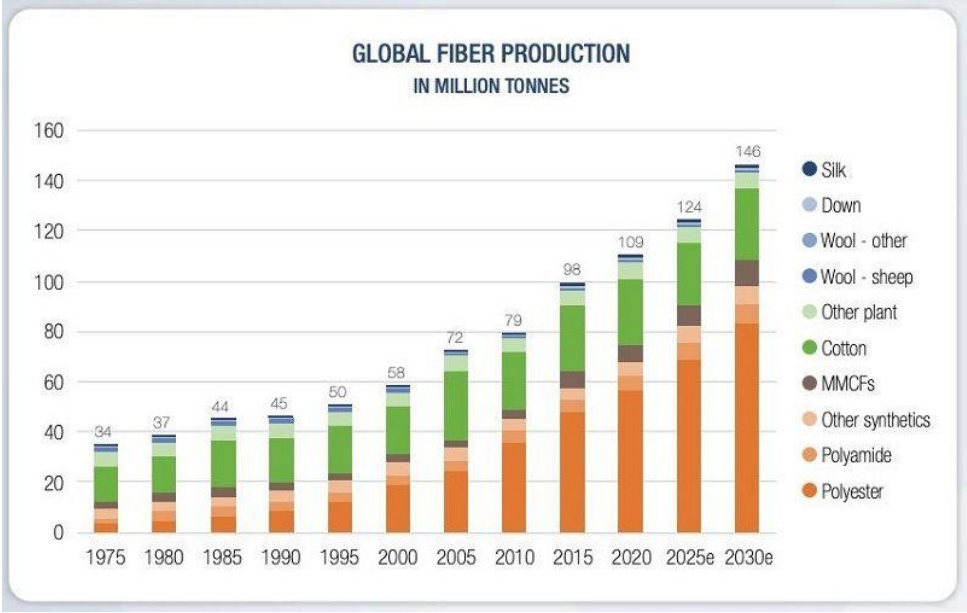


- Natural rubber grows brittle with time and exposure to the elements – temperature, humidity
- Crosslinking improves durability, strength and elasticity
- However, renders non-degradable

Charles Goodyear: Developed Vulcanization process



Critical Limitations of Biopolymers led to Synthetic Polymers



Source: https://www.textiletoday.com.bd/demand-for-preferred-fibers-growing-rapidly

- Cost of production and extraction.
- Aqueous, mechanical and thermal stability
- High propensity for degradation
- Immunogenicity – latex causes allergies
- Likelihood of infections
- Batch to batch variations – location, weather etc.

How do we Adapt Biopolymers for a better future?

- Next class!

Biopolymer Metropolis: The Living City
Artwork made using Gemini, a Large Language Model by Google.
Generated June 4, 2024.