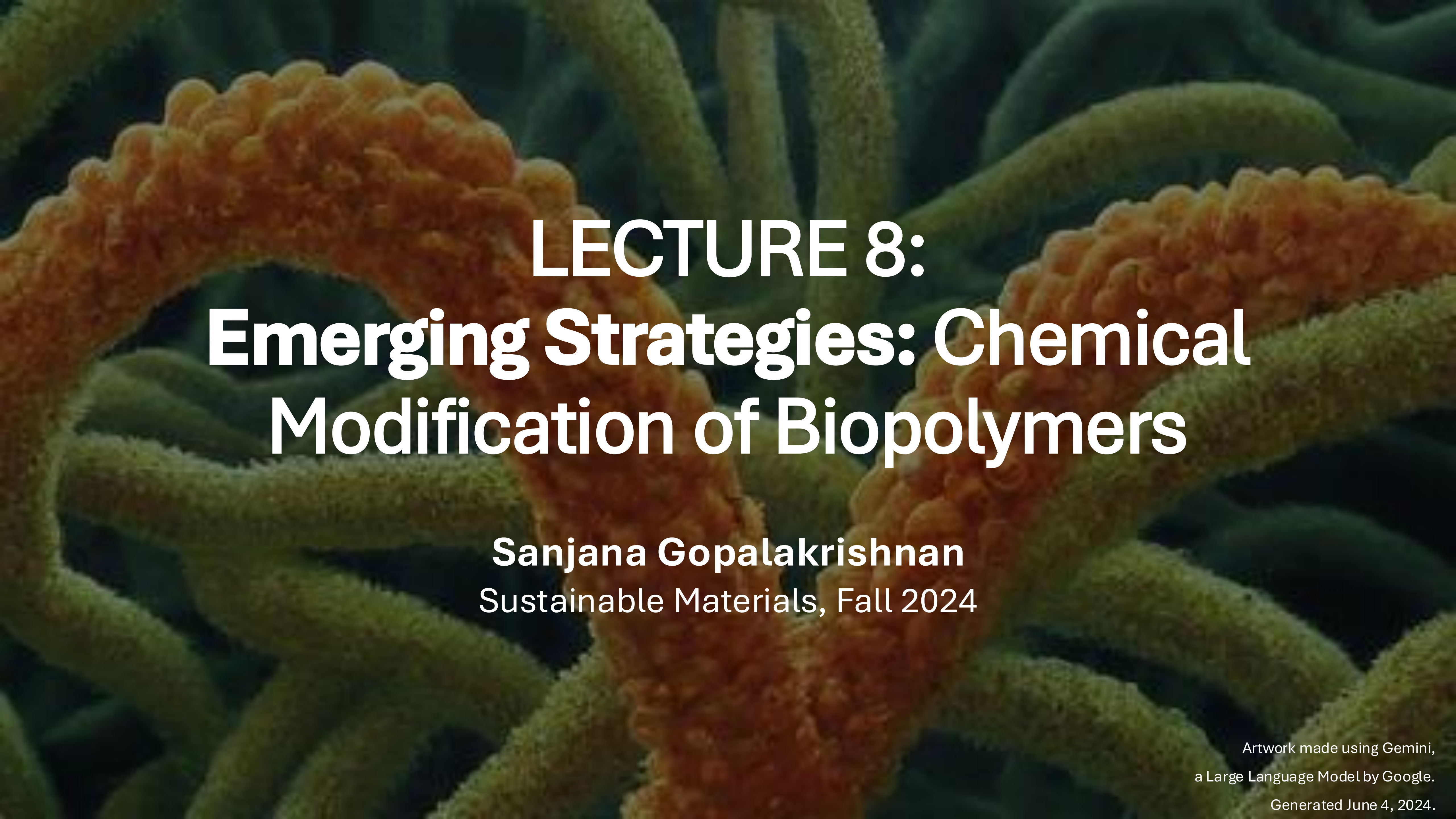

LECTURE 8:
Emerging Strategies: Chemical Modification of Biopolymers

Sanjana Gopalakrishnan

Sustainable Materials, Fall 2024

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

Course Overview

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?

Lecture 9-10

Introduction
- Overview
- Historical Perspective

Challenges
- Human Health
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Solutions
- Old Polymers
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Applications
- Food and Ag
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- Healthcare

Future
- What do we need?
- How do we get there?

Outline for this class

LAST WEEK:

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

TODAY:

- Brief Recap
- New design strategies
- Biosynthetic materials
- Biopolymer Modification Strategies –
  - Physical
  - Chemical
  - Additive-based

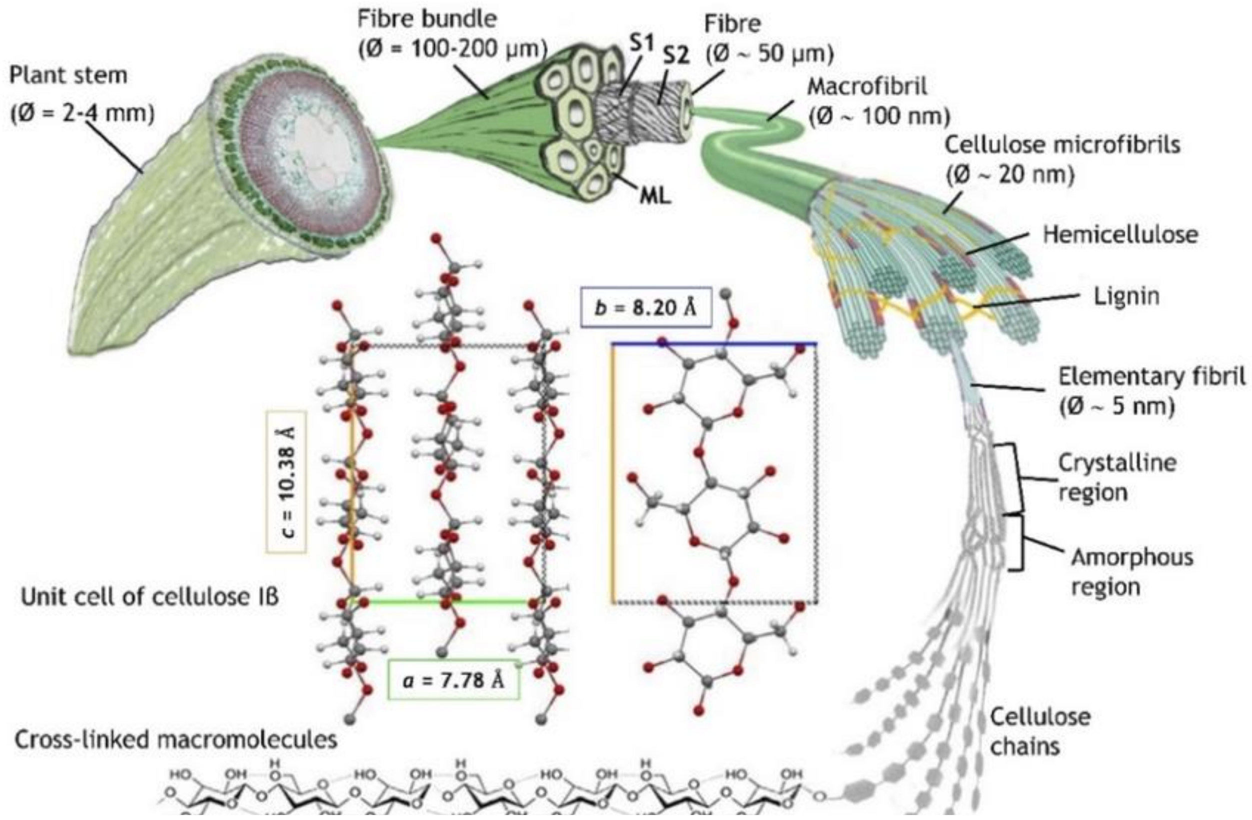
What are Biopolymers?

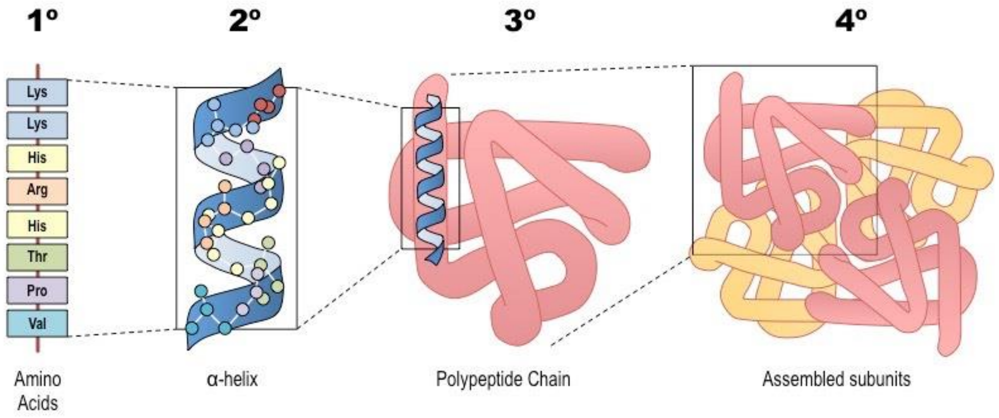
- Naturally-occurring Polymeric substances synthesized by living cells

- **Hierarchical Organization:** Polymeric chains (primary structure) further organized into secondary and tertiary structures

- Hydrogen bonding, van der Waals' interactions dictate organization

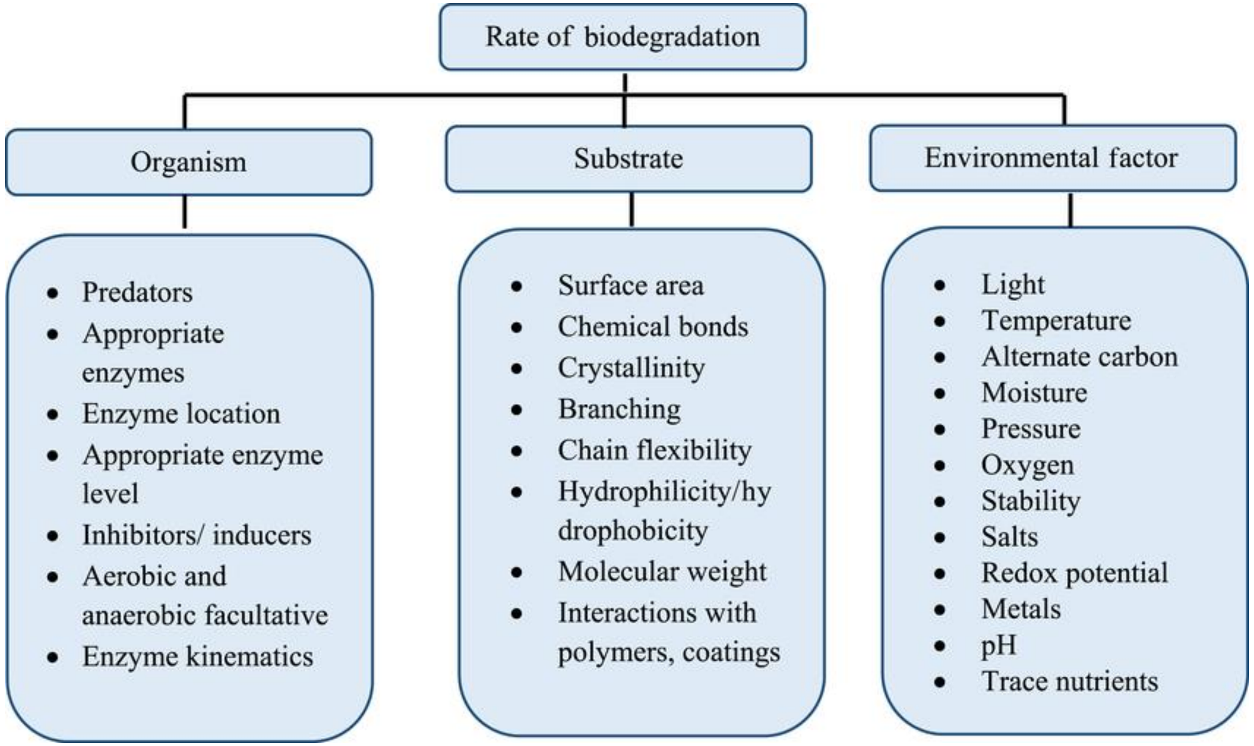
- Three main classes– carbohydrates, proteins and nucleic acids



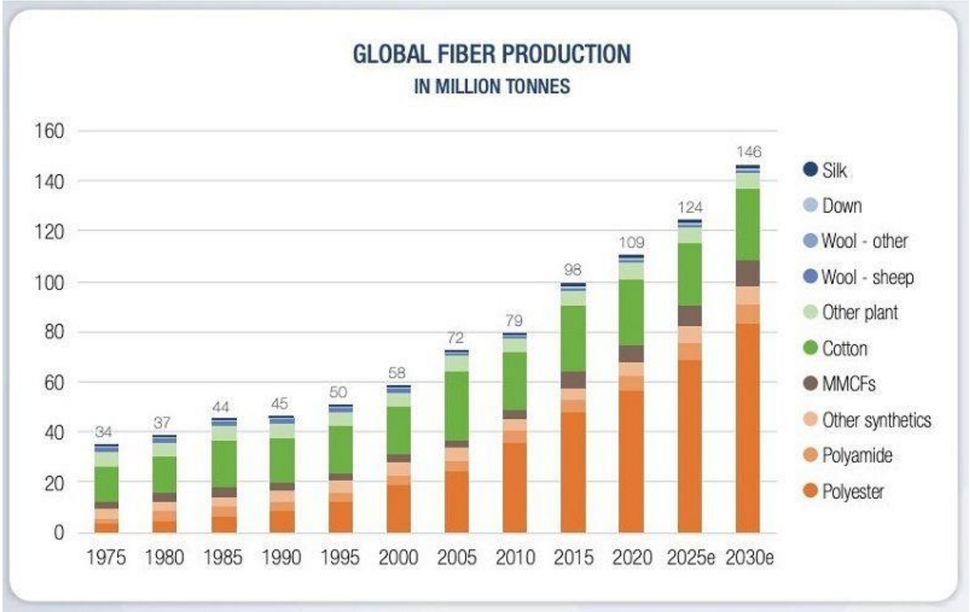


Biopolymer Degradability is Governed by Multiple Factors

- Microbial enzymes digest the ester, ether and amide linkages
- However, temperature, microbial populations, oxygen, etc. can impact degradability
- Additionally material properties can impact rate of degradation



Critical Limitations of Biopolymers led to Synthetic Polymers

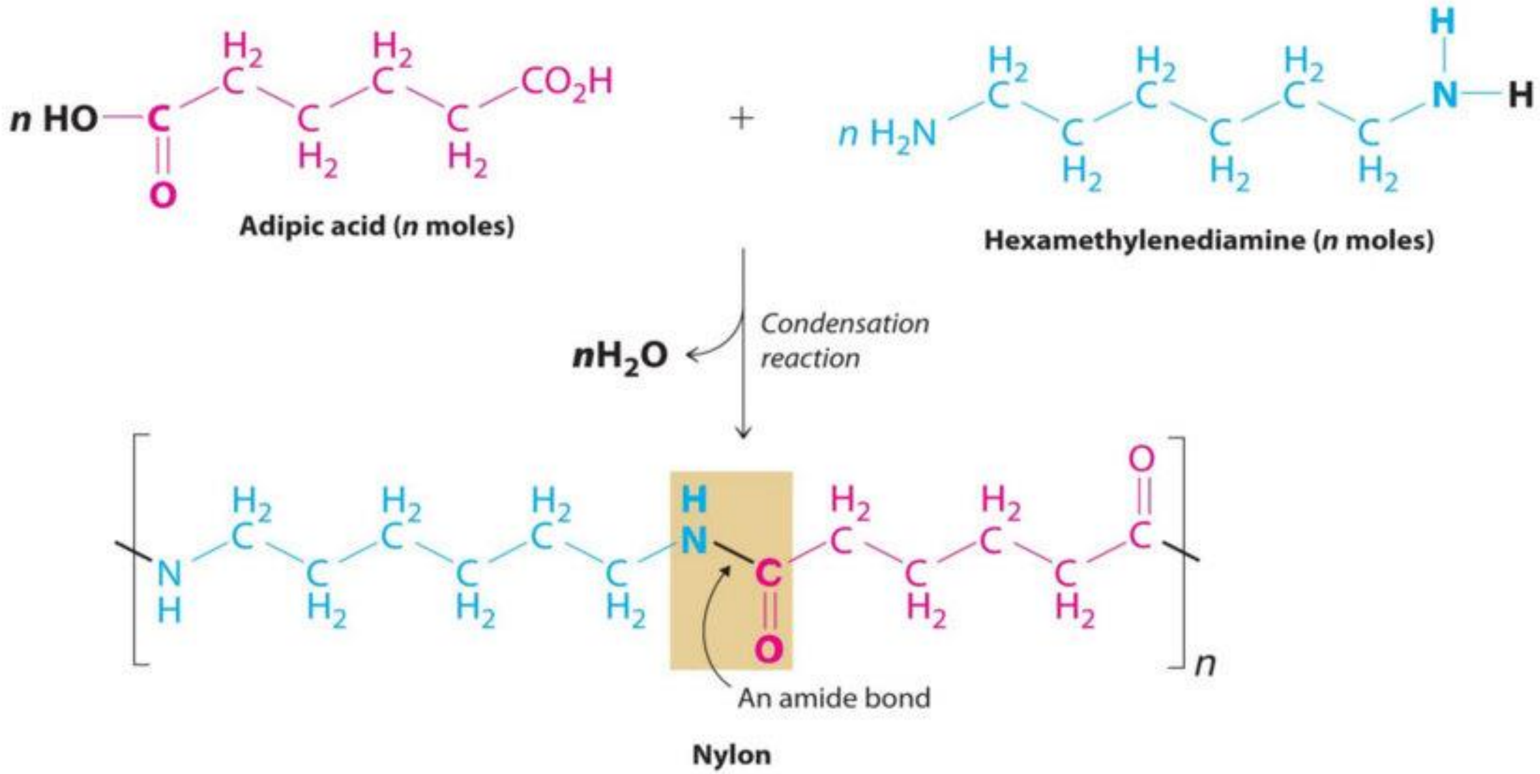


Source: https://www.textiletoday.com.bd/demand-for-preferred-fibers-growing-rapidly

- 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.

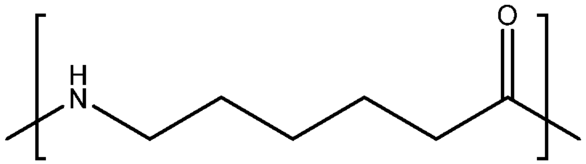
DISCUSSION OF HOMEWORK

Q: Why is nylon not degradable?

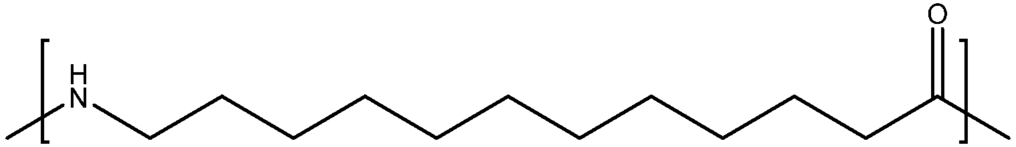


- Research at home
- Answer will be discussed in the next class

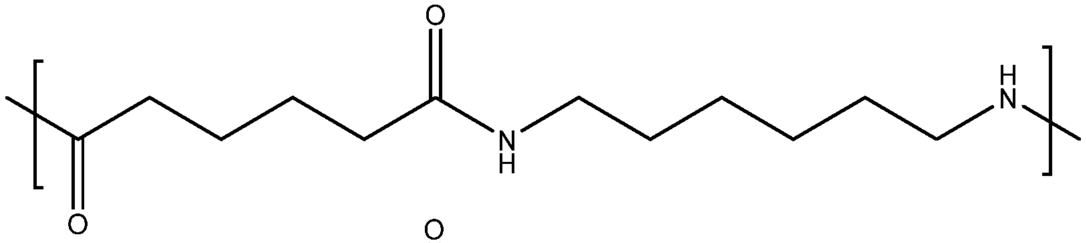
Non-degradable Nylon types:



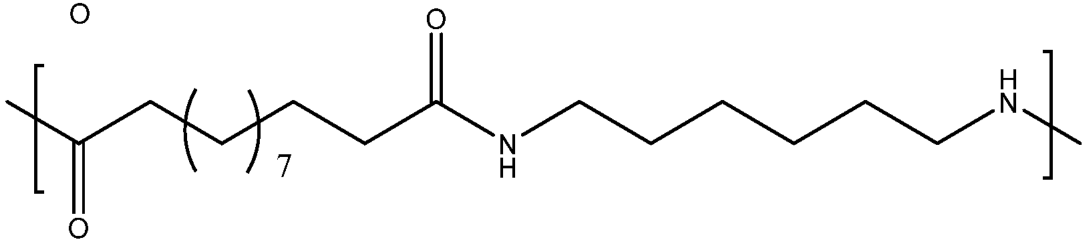
Nylon 6



Nylon 12

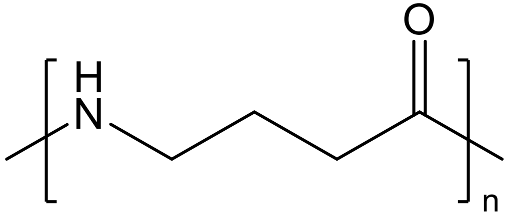


Nylon 6,6



Nylon 6,12

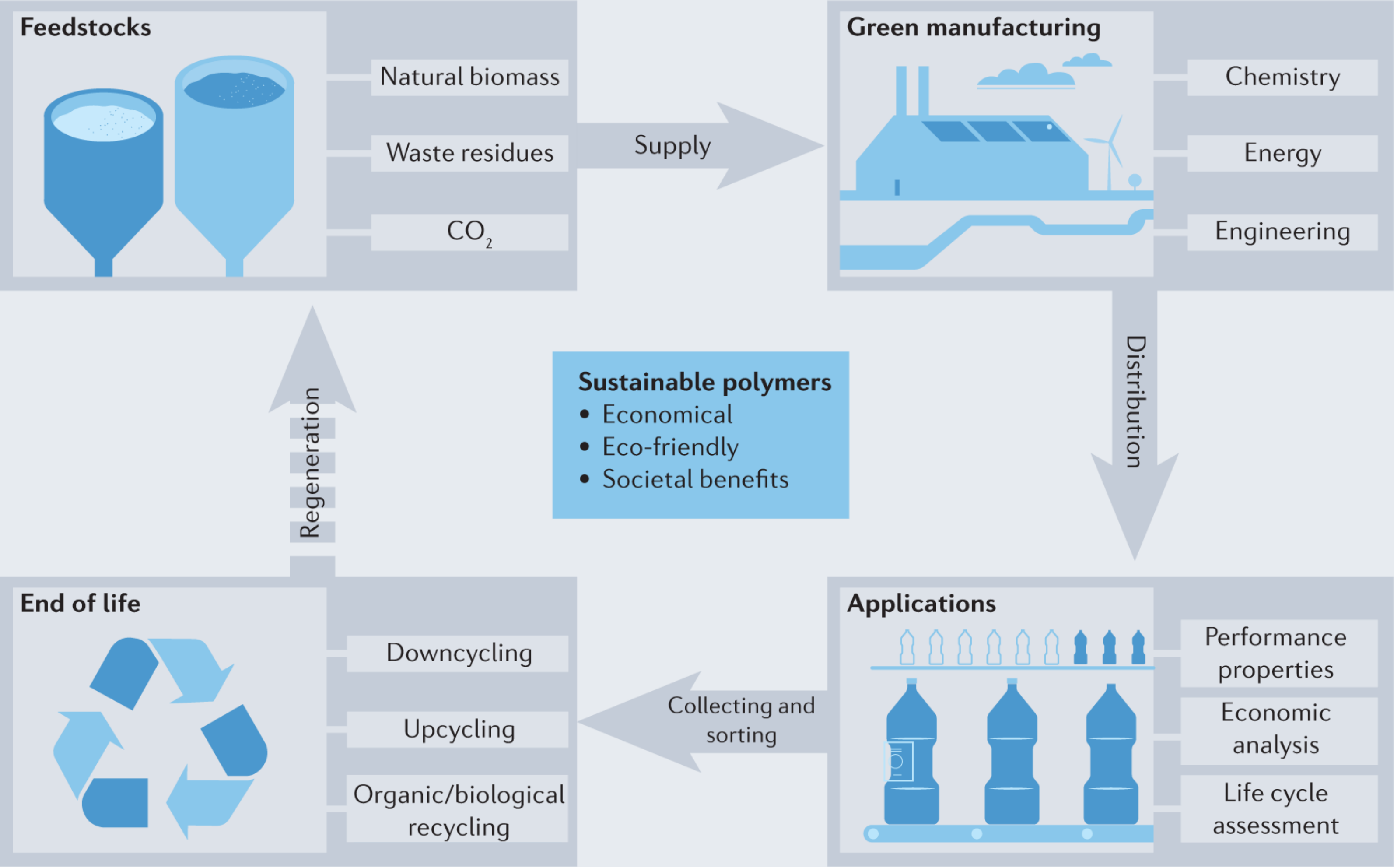
Biodegradable Nylon :



Nylon 4

- Long hydropohobic regions are not degradable
- Long hydrophobic regions result in tighter packing of chains leading to mechanical stiffness and poor enzymatic access

Novel Strategies *must* Optimize Several Parameters

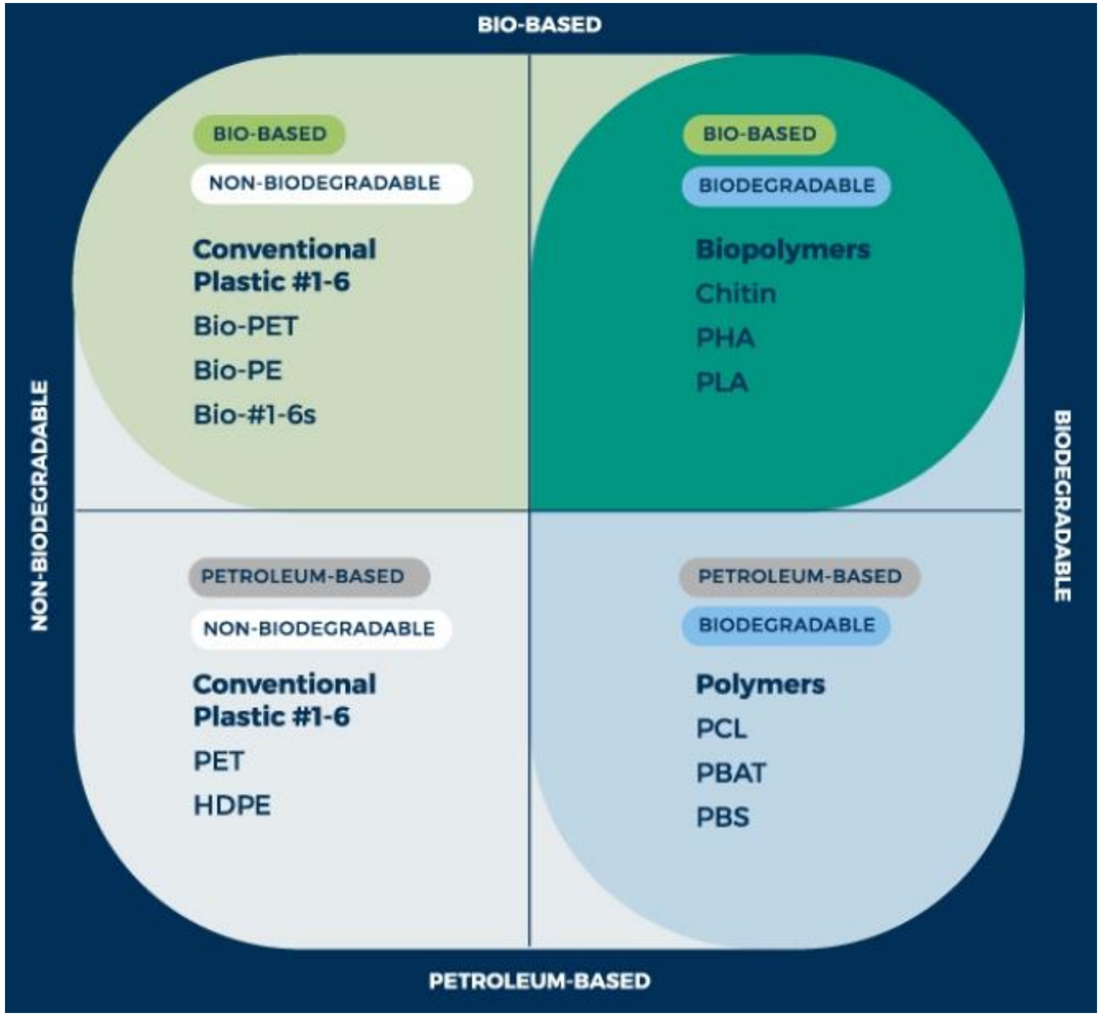


Optimize:

- Feedstock/ source
- Manufacturing Processes
- Material properties based on intended application
- End of life

Mohanty, A.K. et al. *Nature reviews methods primers*, **2022**

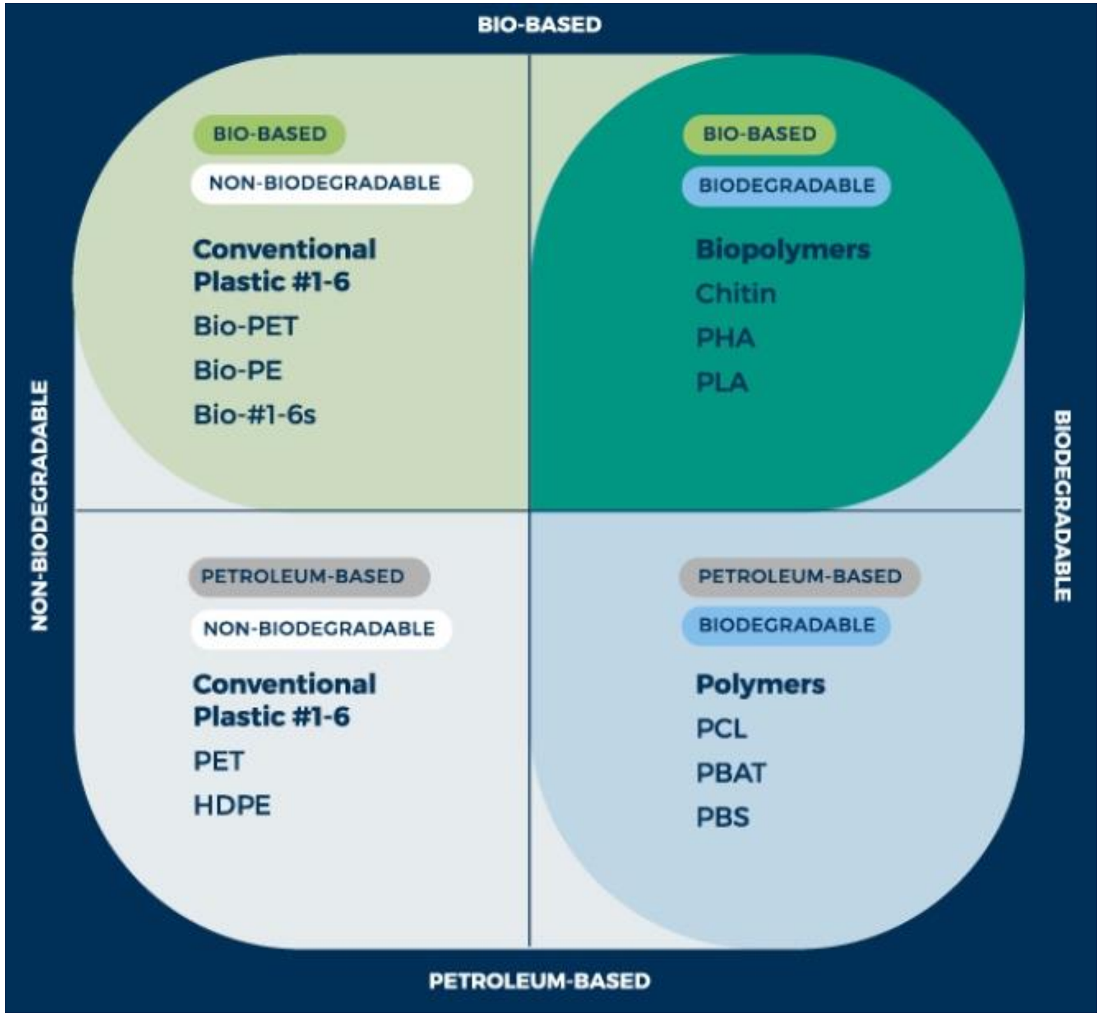
Bio-based Raw Materials as Alternative Feedstock



Goldstein, N. Demystifying Biopolymers and Compostable Packaing, *Biocycle,* **2020**

- Using petroleum-based feedstock to develop biodegradable polymers
- Using bio-based feedstock to develop conventional polymers
- Using bio-based feedstock to develop biodegradable synthetic polymers
- Using bio-based feedstock to extract biopolymers

Bio-based Raw Materials as Alternative Feedstock



Goldstein, N. Demystifying Biopolymers and Compostable Packaing, *Biocycle*, **2020**

- Using petroleum-based feedstock to develop biodegradable polymers
- Using bio-based feedstock to develop conventional polymers
- Using bio-based feedstock to develop biodegradable synthetic polymers
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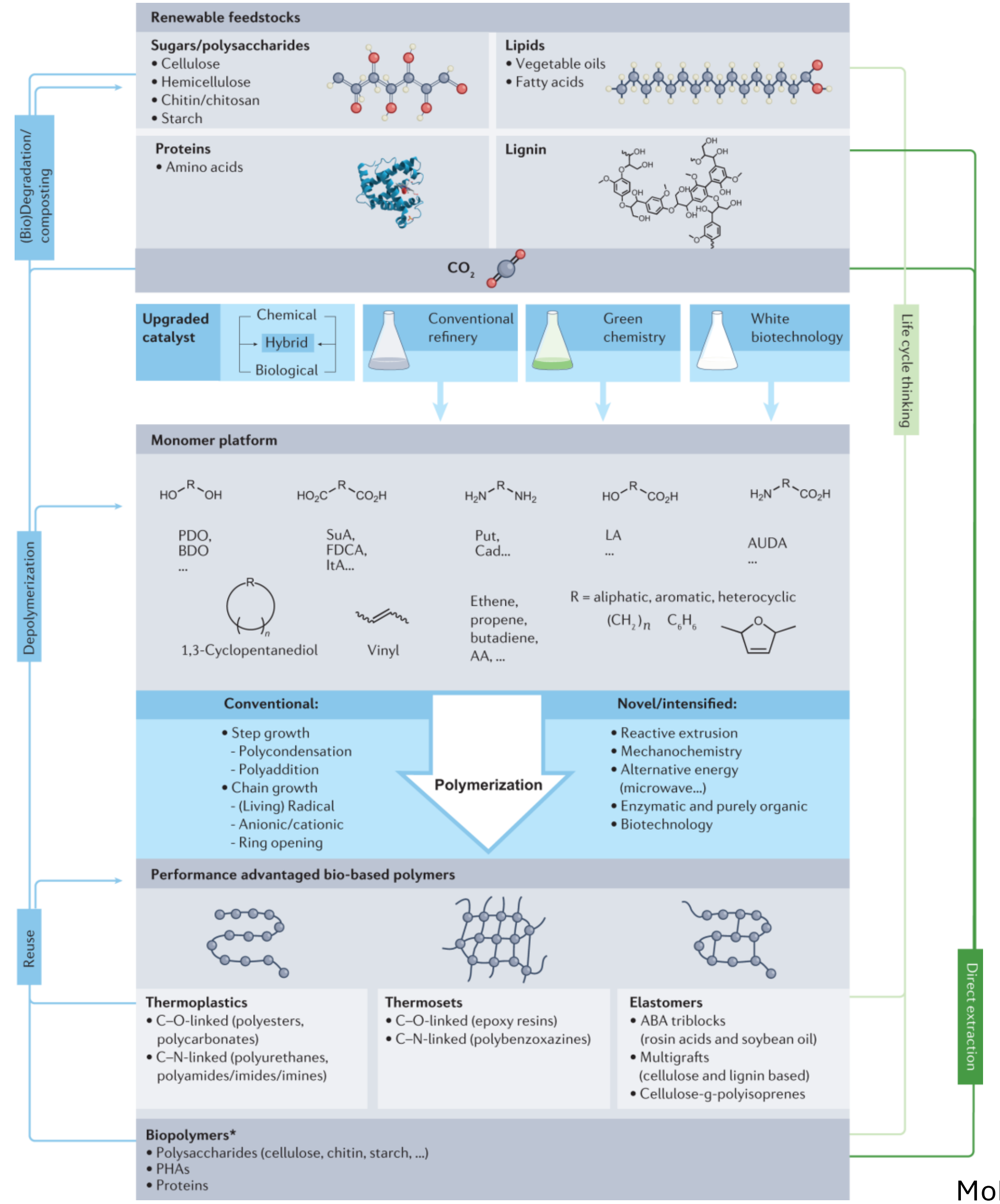
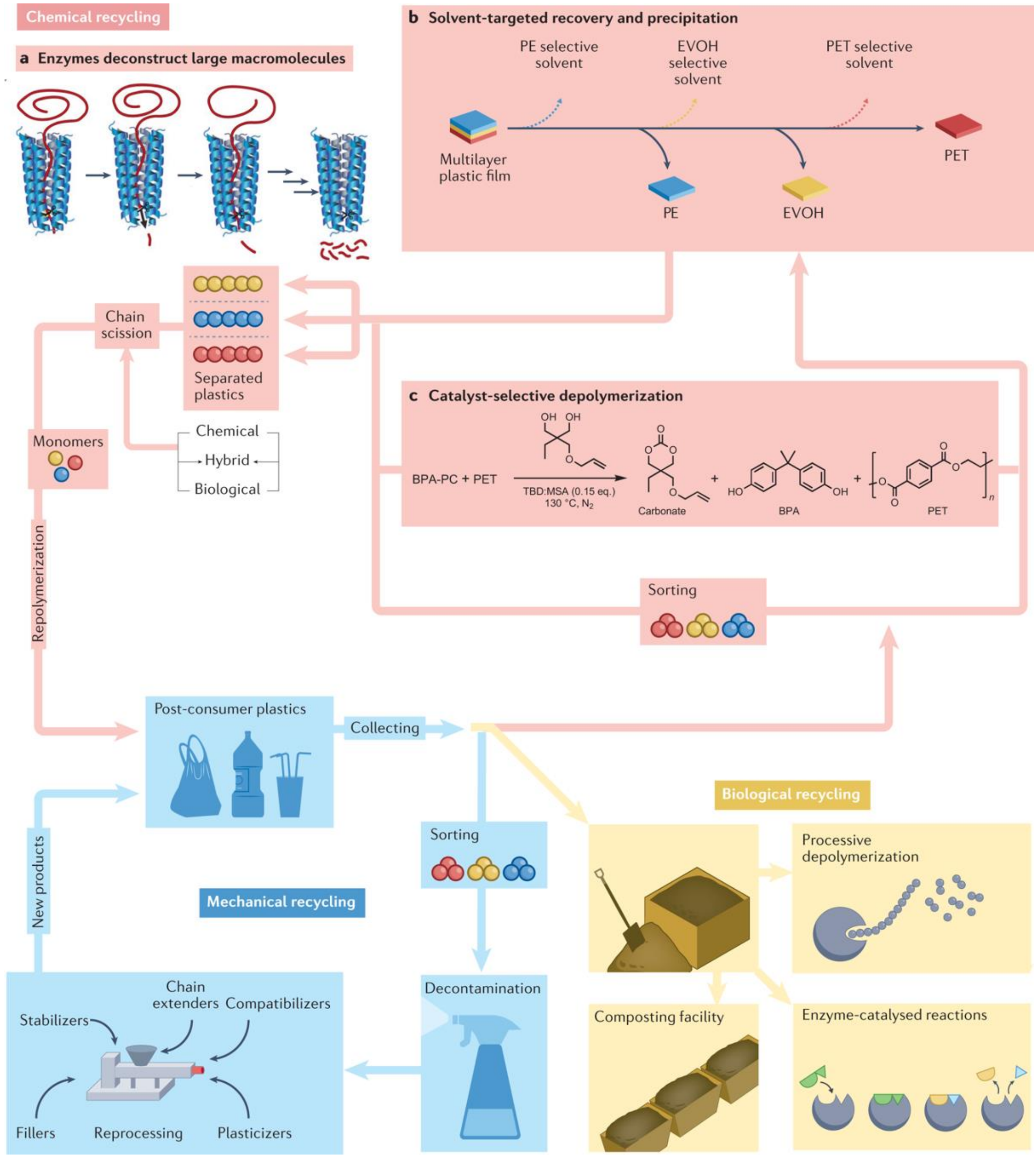
What's your favorite?



It Depends... Consider the LCA of your Material

- How are you processing your feedstock?
- If using as is, how are you manufacturing materials for intended applications
- If generating monomers, then how? How are you repolymerizing?
- Intended use – duration and repeated usage?
- **End of life**

Mohanty, A.K. et al. *Nature reviews methods primers*, **2022**



End of Life can be More than Biodegradation

- Mechanical/ Physical Recycling
- Chemical recycling or depolymerization into monomers using catalysts or enzymes
- Biological recycling or microbial degradation into CO_2, H_2O, CH_4 and other nutrients

Mohanty, A.K. et al. *Nature reviews methods primers*, **2022**


DW
Bioplastics
DEBUNKED

What’s better?

Bio-based, non-degradable, multi-use

Bio-based, compostable, single-use

What’s better?

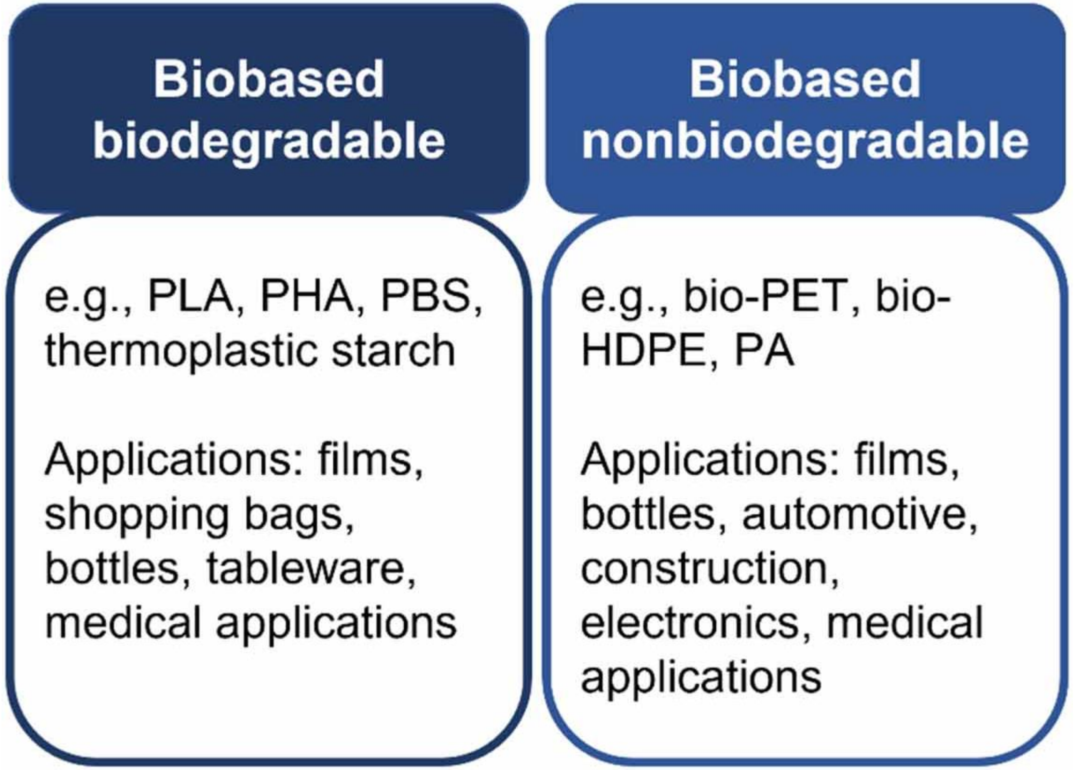
It’s complicated

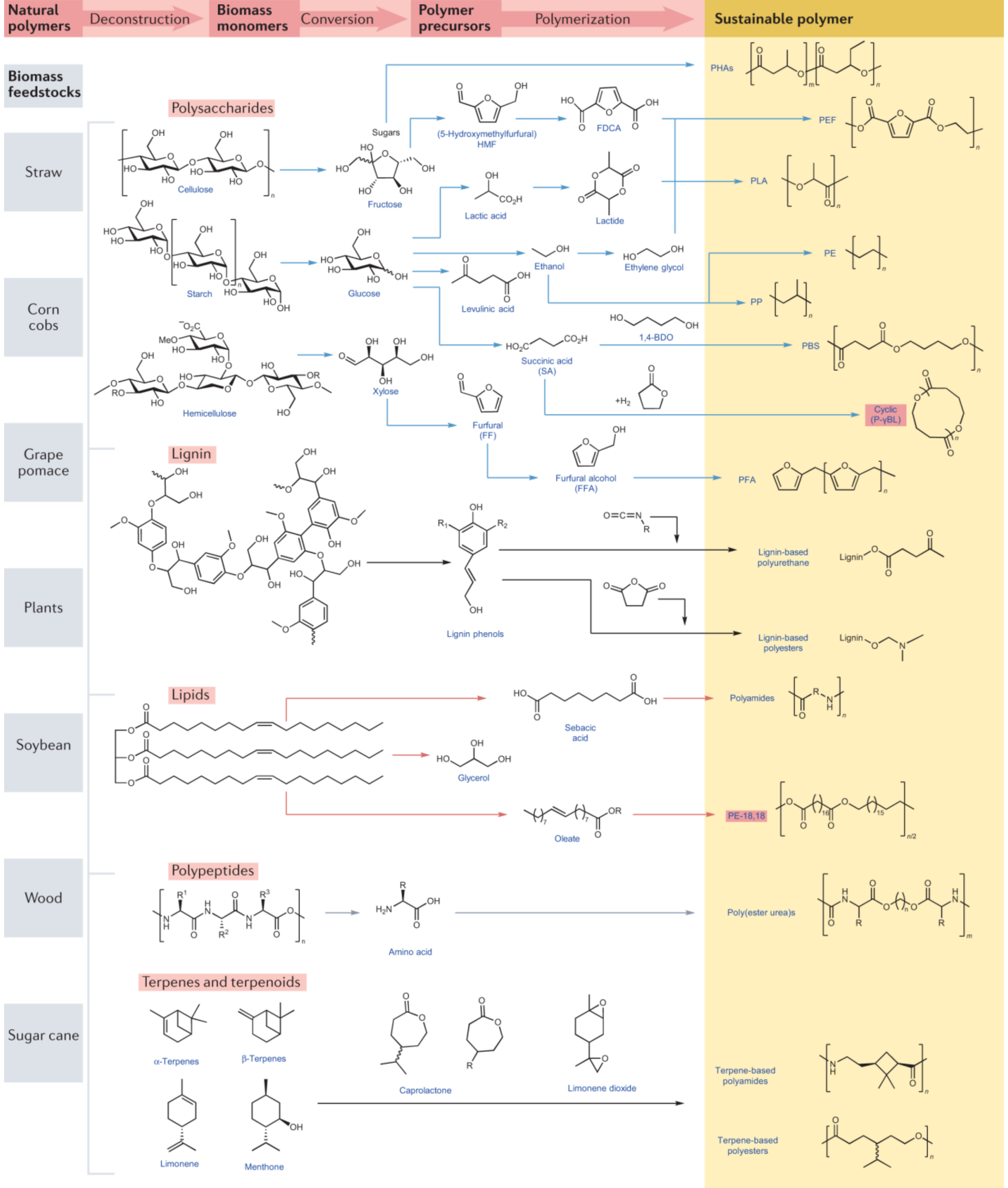
Bio-based, non-degradable, multi-use

Bio-based, compostable, single-use

Bio-synthetic Polymers as Alternatives to Traditional Plastics

- Bio-based feedstocks are broken down into monomeric units and then repolymerized
- **Monomeric units** – monosaccharides, lactic acid, glycolic acid, ethanol, propanol, ethylene glycol etc
- **Polymeric Linkages** – amides, esters, or C-C





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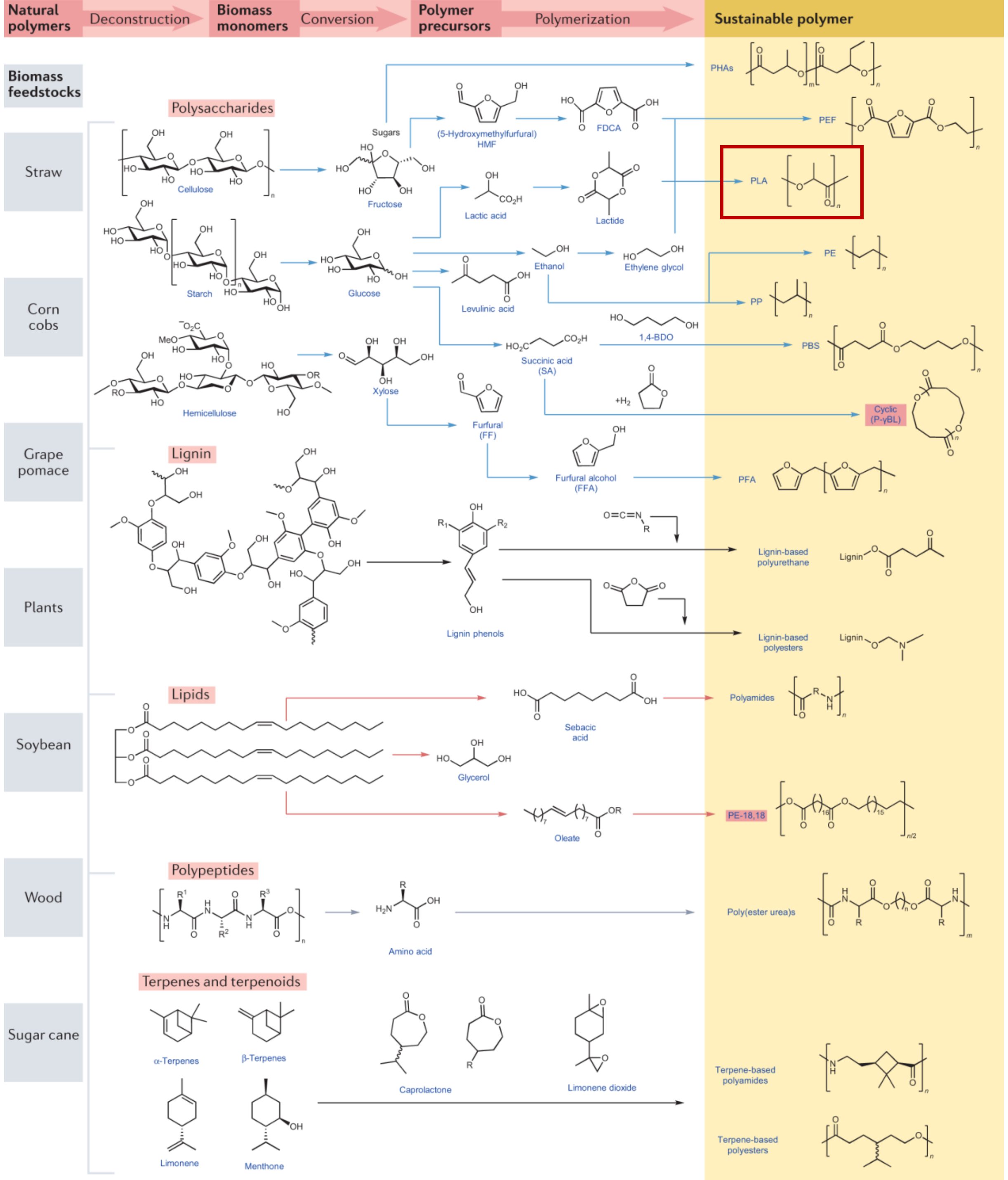
Mohanty, A.K. et al. *Nature reviews methods primers*, **2022**



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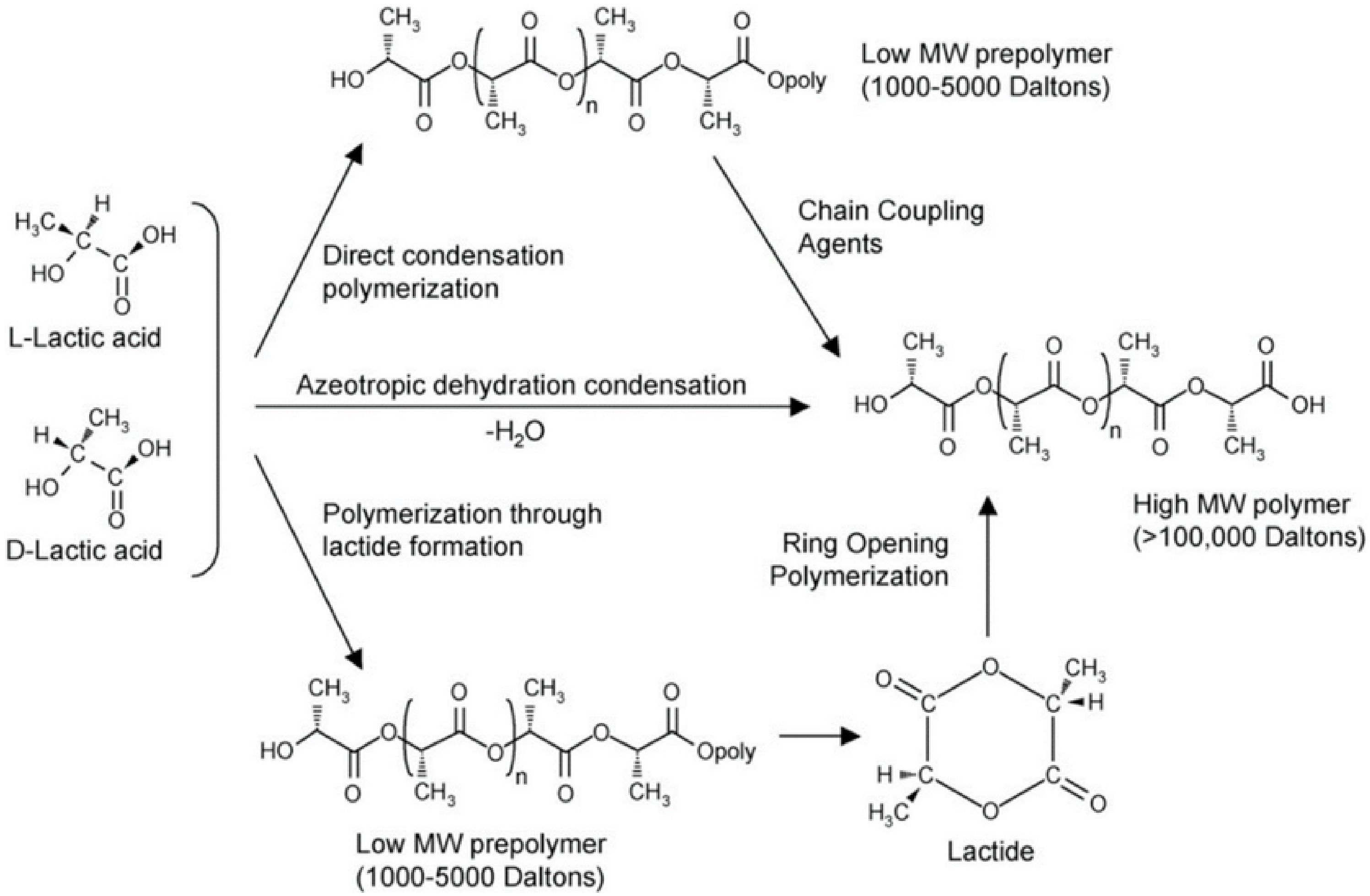
Mohanty, A.K. et al. *Nature reviews methods primers*, **2022**

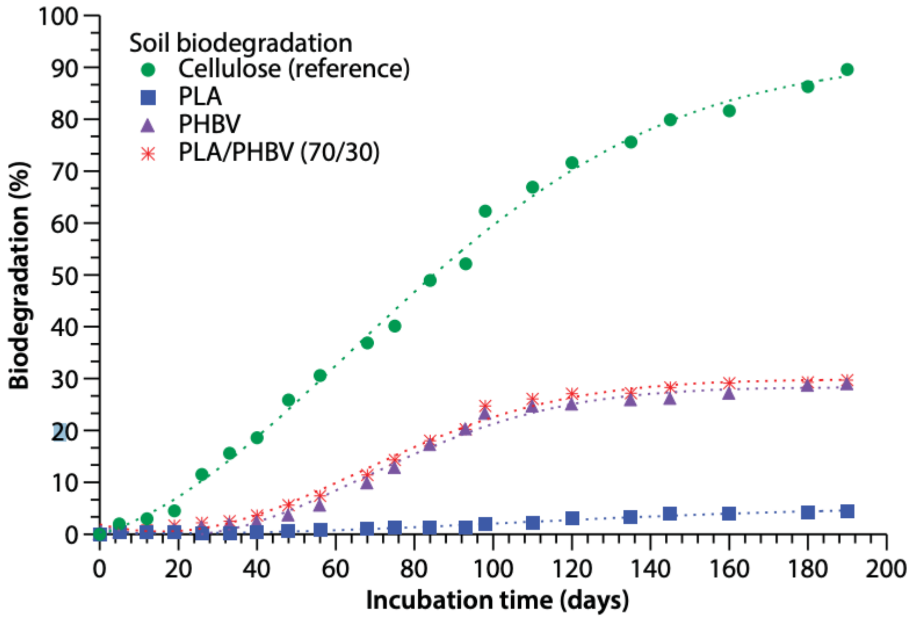
PLA: An Alternative to Single-use Plastics

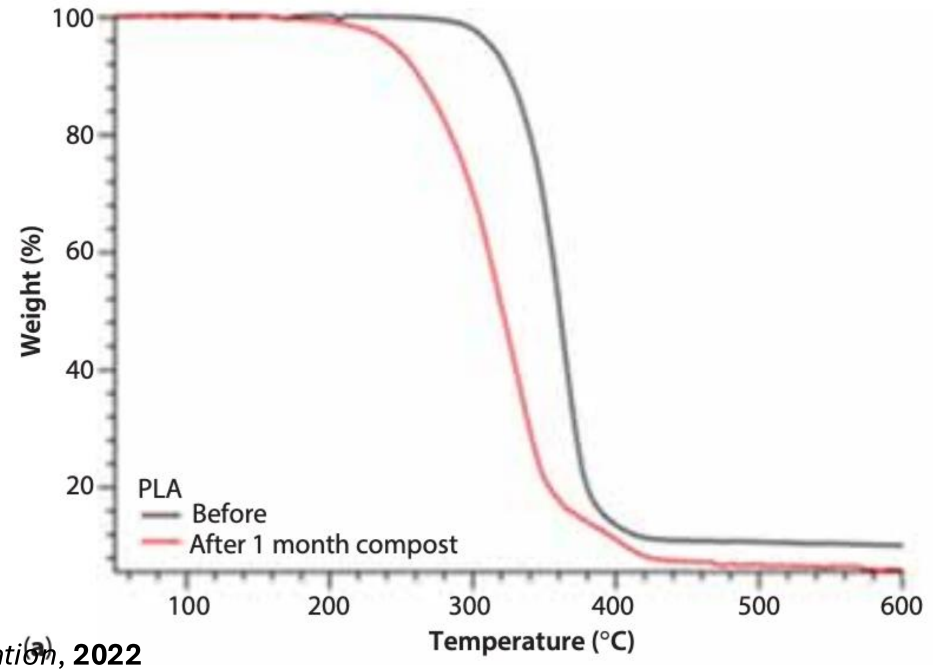


- PLA is a polymer synthesized from lactic acid using common strategies like ROMP
- Forms optically transparent bioplastic similar to PET
- Lactic acid is a bio-based monomer
- **PLA is biodegradable***

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

PLA Requires Industrial Composting

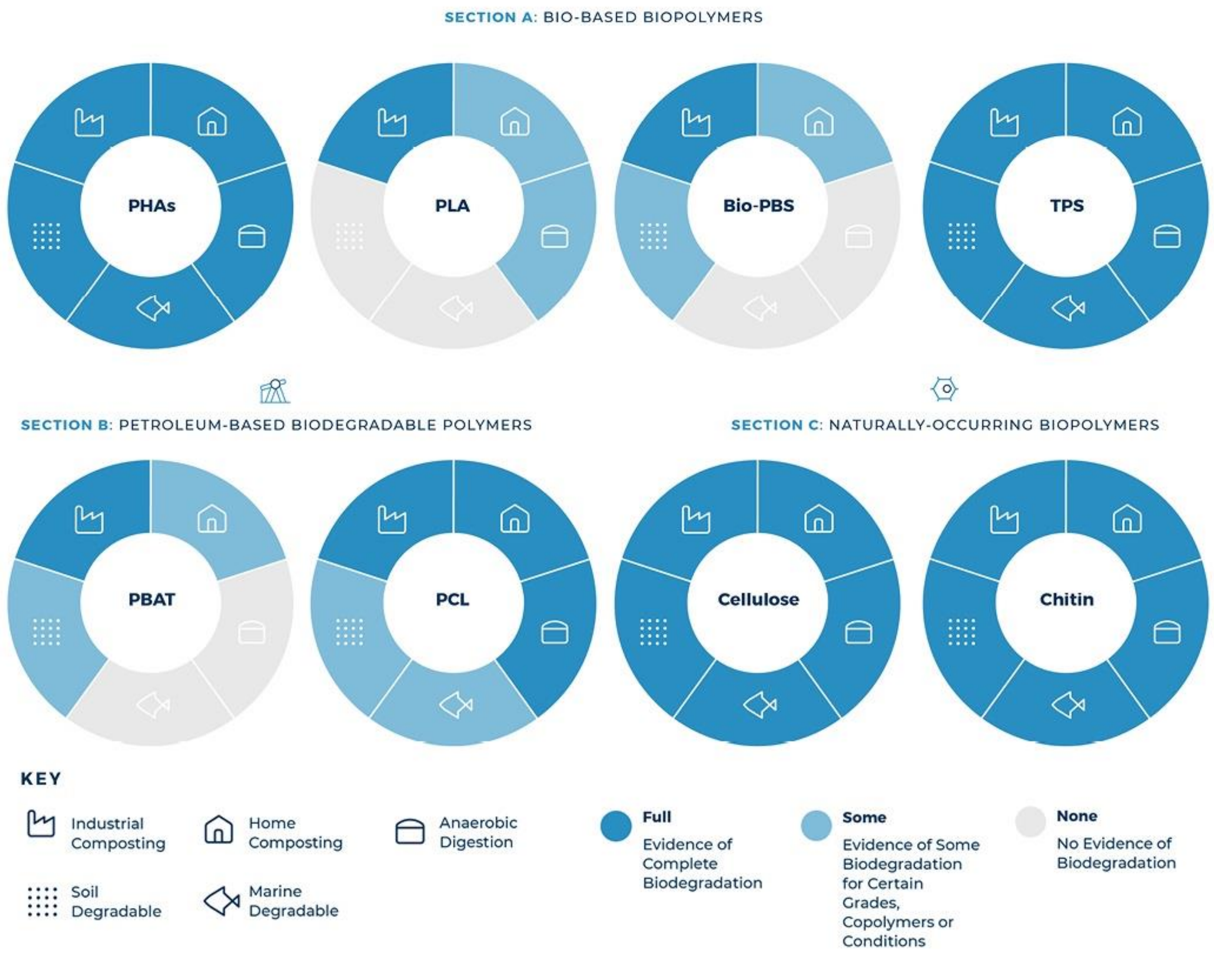




Solanki, S. et al. *Biodegradation*, **2022**

- PLA does not biodegrade in soil
- Thermal stability (TGA) of PLA after 1 month of composting has minimal change
- Degradation requires specific temperatures (55-75 °C) and anerobic conditions

Biodegradability of Biosynthetic Polymers



- Environmental factors such as aerobic vs. anerobic degradation should be considered
- Bio-based feedstock is not always the answer – PCL is more easily degradable than PLA
- Polymer molecular weights (grades) additives, copolymers play a big role

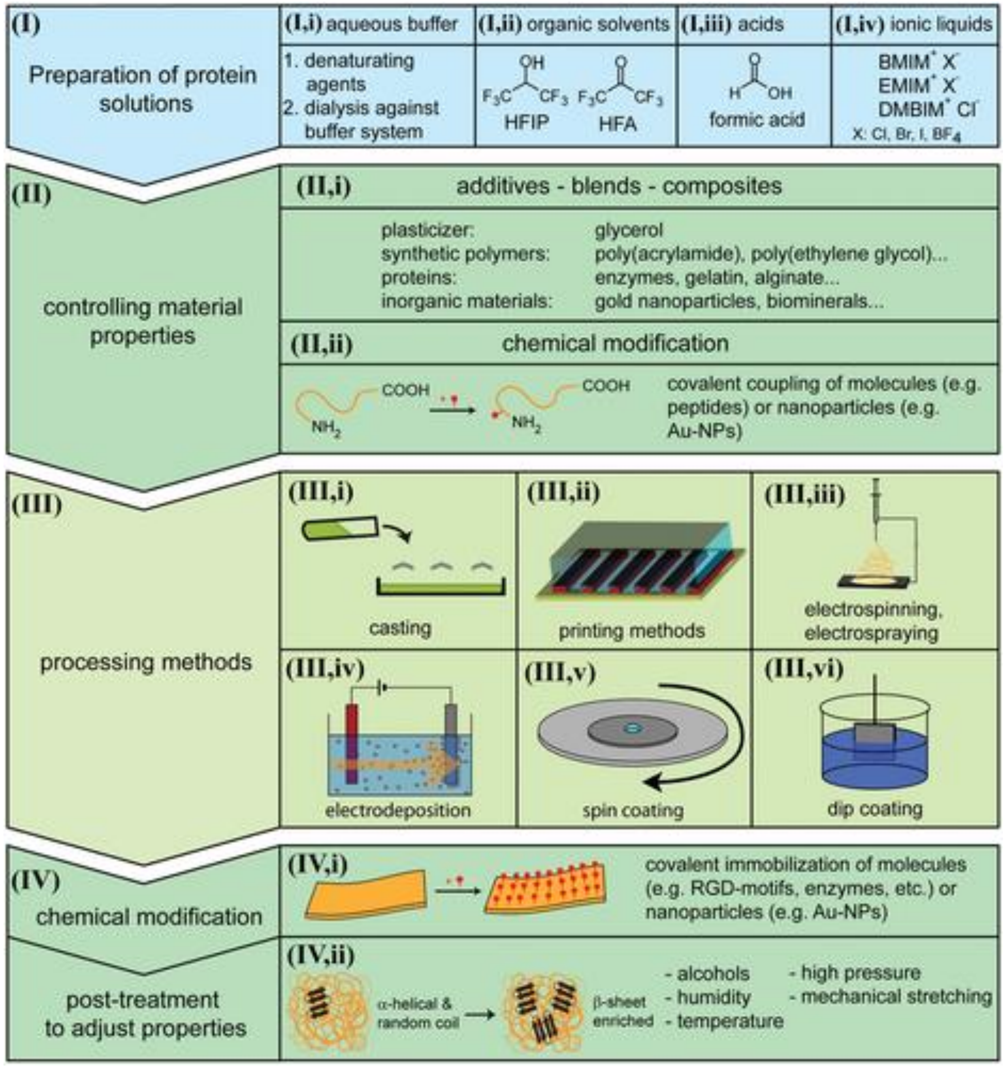
Goldstein, N. Demystifying Biopolymers and Compostable Packaing, *Biocycle*, **2020**

The Need for Biopolymer Modification Strategies

- Biopolymers are extracted from natural sources and used without depolymerization
- Biopolymers are biodegradable
- Lack of control on mechanical properties, thermal stability, aqueous stability
- Limited functionality
- Manufacturing processes and cost

Type of Modifications

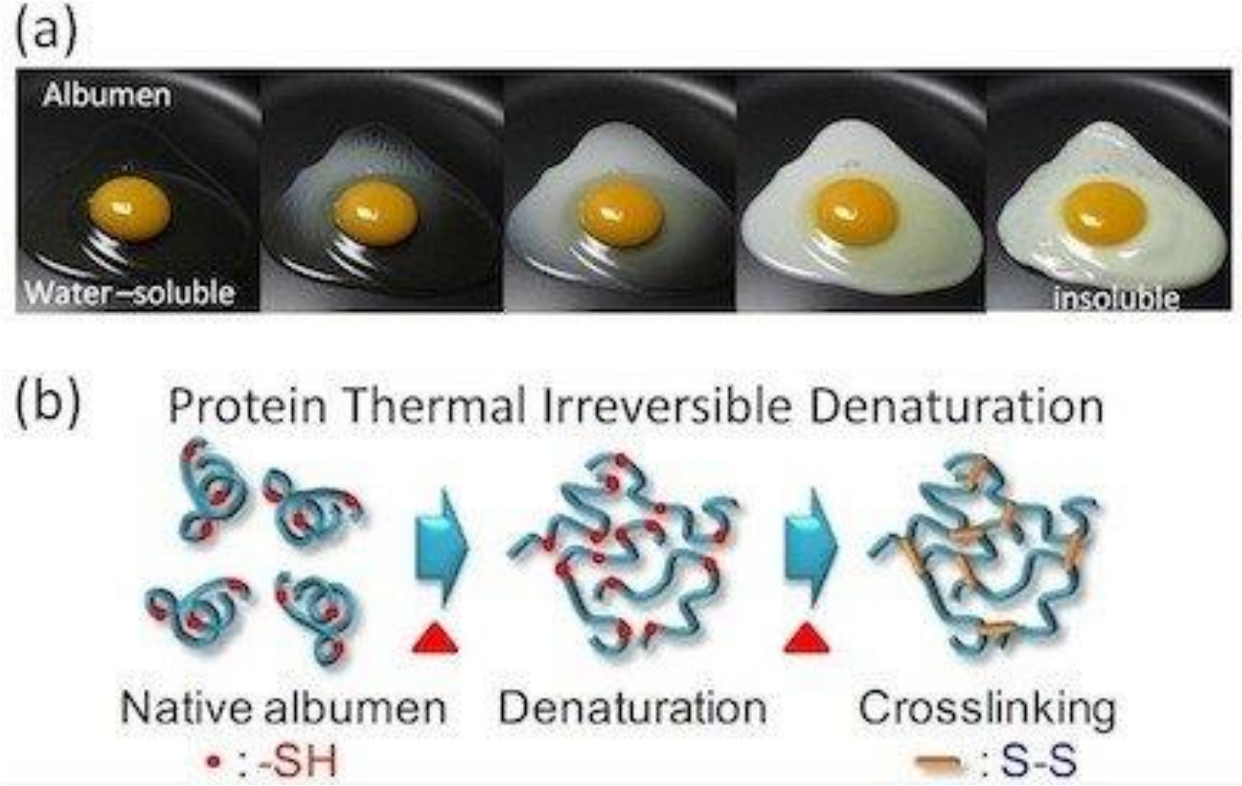
- **Physical:** Altering the secondary and tertiary structure without altering the primary structure
  - Heat, pressure, solvents, pH changes, humidity etc.
- **Chemical:** Introducing new chemical functionalities into the primary structure
  - Crosslinking, grafting
- **Composites/Additives:** Mixing one or more reagents with biopolymers to alter properties
  - Using other biopolymers or plasticizers to alter functionality



Gopalakrishnan, S. *Advanced Sustainable Systems*, **2020**

Thermal Treatment Denatures Proteins and Stabilizes Materials

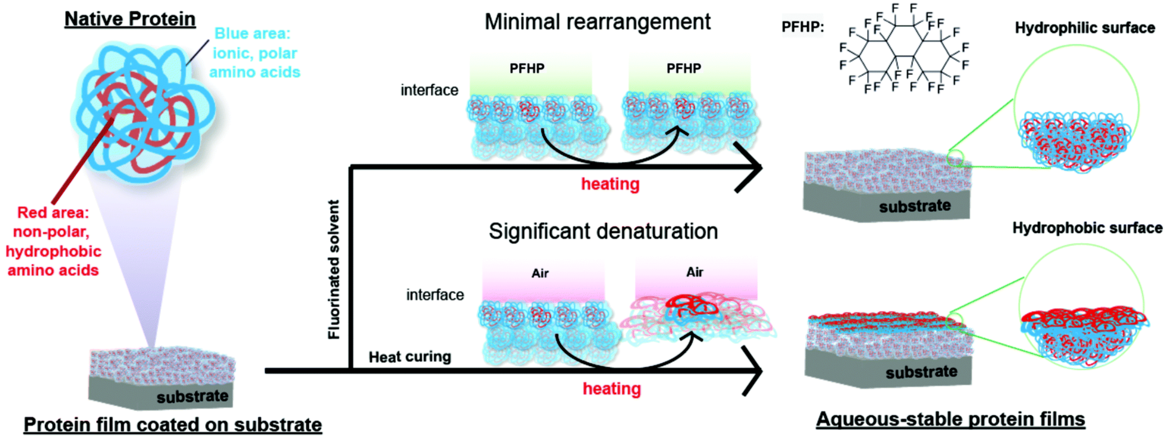
- Utilizing thermal treatment to improve water stability of proteins
- Protein secondary structure unravels and leads to insolubility
- Material is water-stable but protein structure is lost

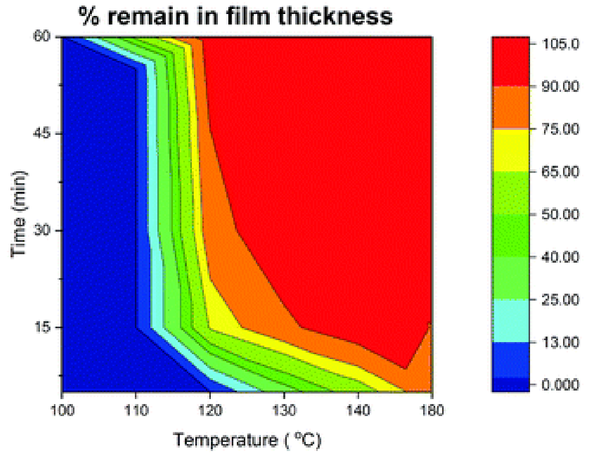


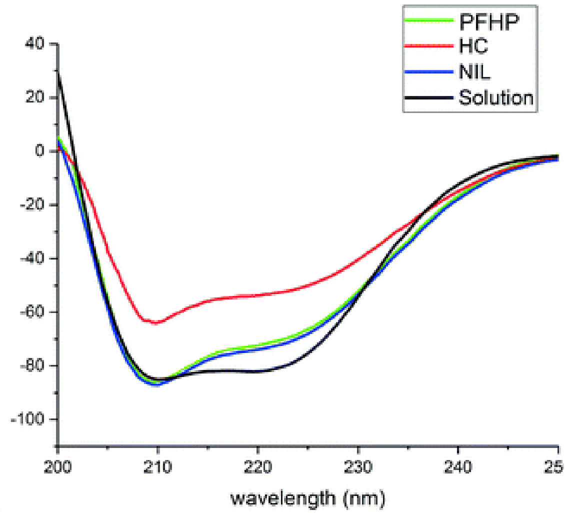
What are some issues with this approach??

Thermal Treatment in Fluorous Solvent leads to Controlled Denaturation

- Fluorous solvent reduces interaction of protein with air
- Minimizes changes in secondary structure while still stabilizing protein in water
- Since protein structure is retained, protein functionality is retained

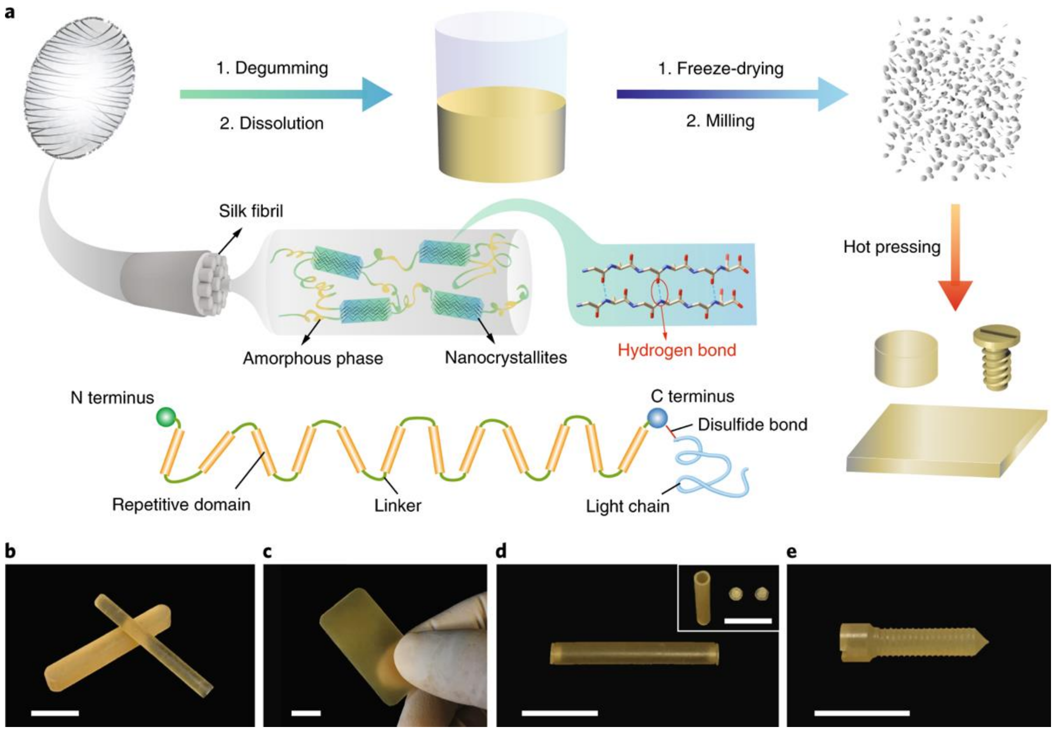


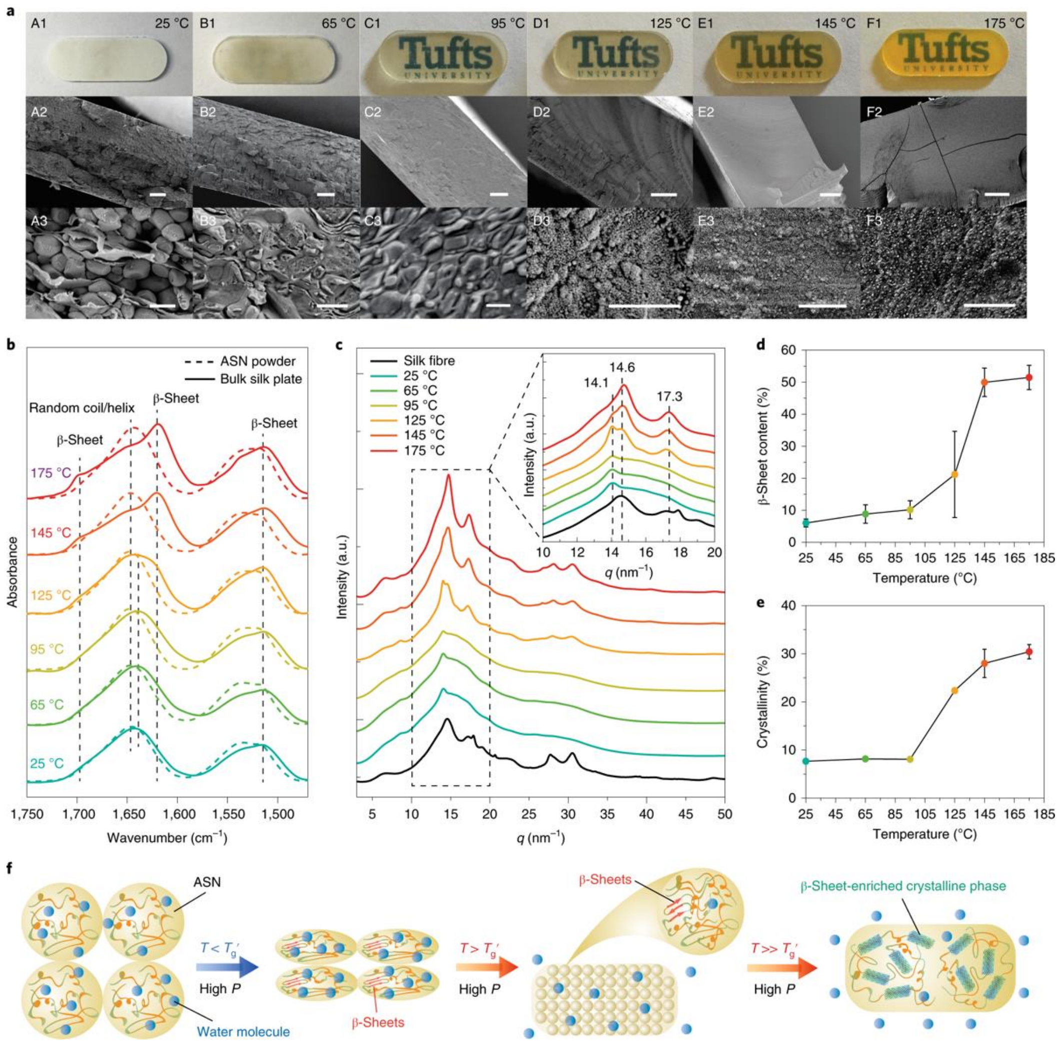




Wang, L-S., Gopalakrishnan, S. et al. *Materials Horizons*, **2018**

Thermoplastic Silk Prepared by Heat and Pressure





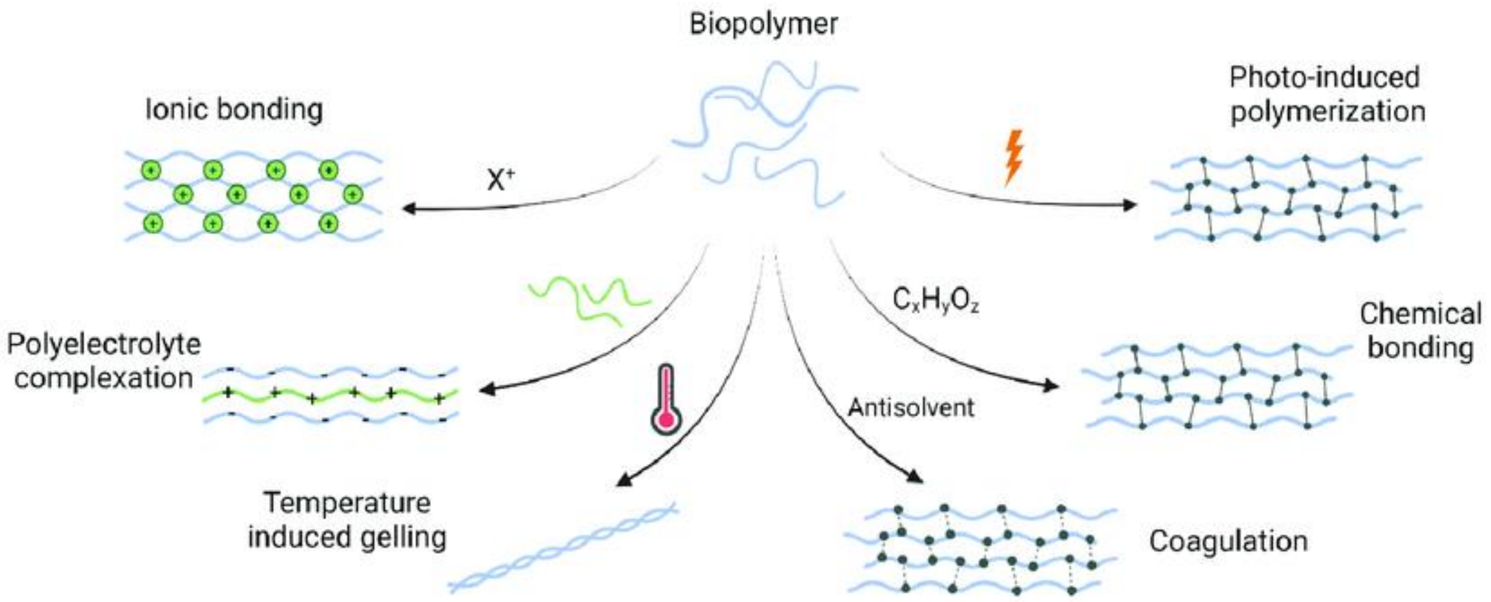
- Silk fibroin is extracted from silk cocoons and freeze-dried into powder
- Silk powder is hot-pressed in a metallic mold to prepare plastics

Guo, C. et al. *Nature Materials*, **2020**

Key Considerations:

- Lack of control on molecular structure
- Energy cost due to high heat and pressure
- Toxicity and environmental hazards of solvents

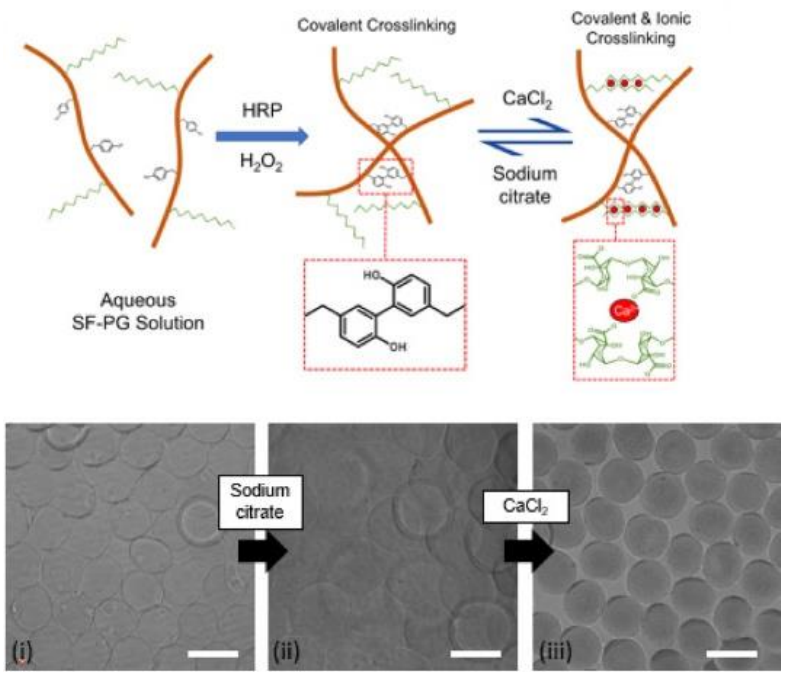
Types of Crosslinking



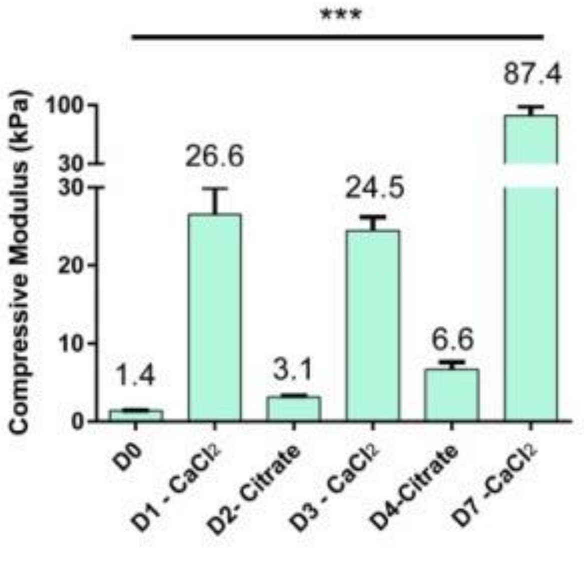
Pasqueir, E. *Bioengineering*, **2023**

- Crosslinking: Process of forming intermolecular bonds between two polymer chains
- Bonds may be covalent, ionic, or non-covalent
- Enzymes, chemical crosslinkers, ionic baths, light may be used to crosslink
- Increases molecular weight and connectivity
- Improves mechanical strength, degradability, and stability

Crosslinking Imparts Responsive Properties

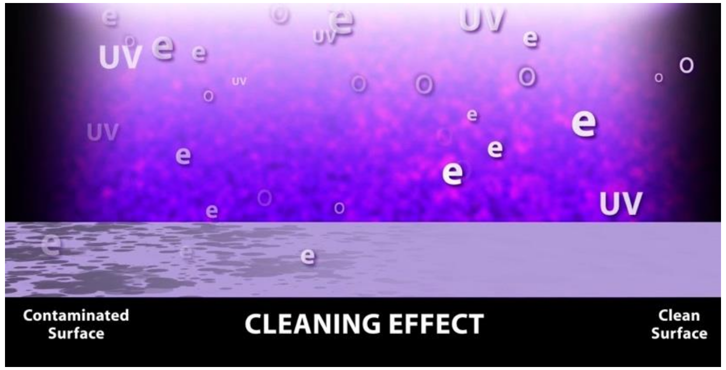


Hasturk, O. et al. *Polymers,* **2023**

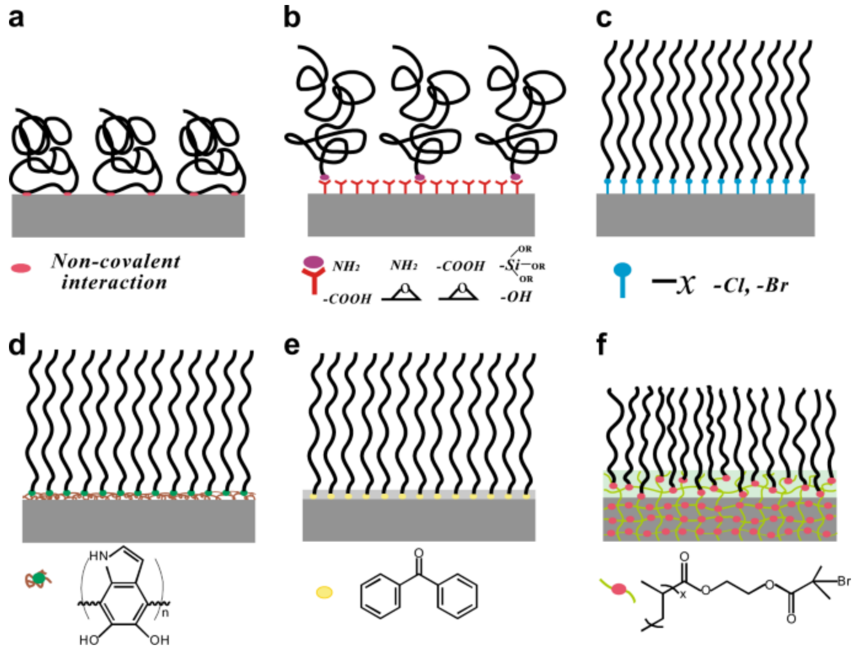


- Hydrogels prepared by crosslinking silk and polygulronate
- Dual crosslinking – Enzymatic (irreversible) and Ionic (reversible)
- External stimuli ($CaCl_2$ or citrate) reversibly stiffens and softens hydrogels

Surface Modification Imparts Specific Functionality

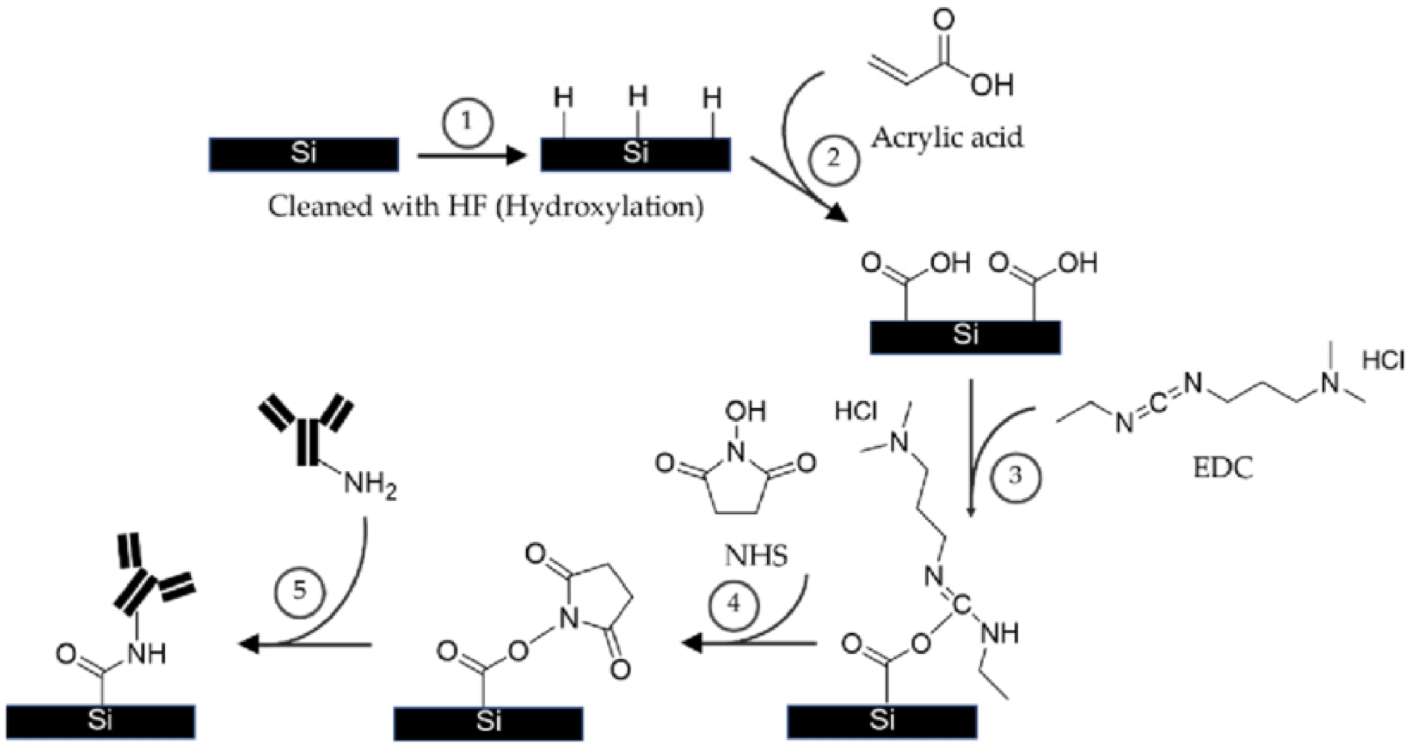


- **Plasma treatment** involves using an ionized gas to treat the surface
- Improves hydrophilicity, reactivity
- Can clean and sterilize
- Also used for specific chemical deposition (CVD)



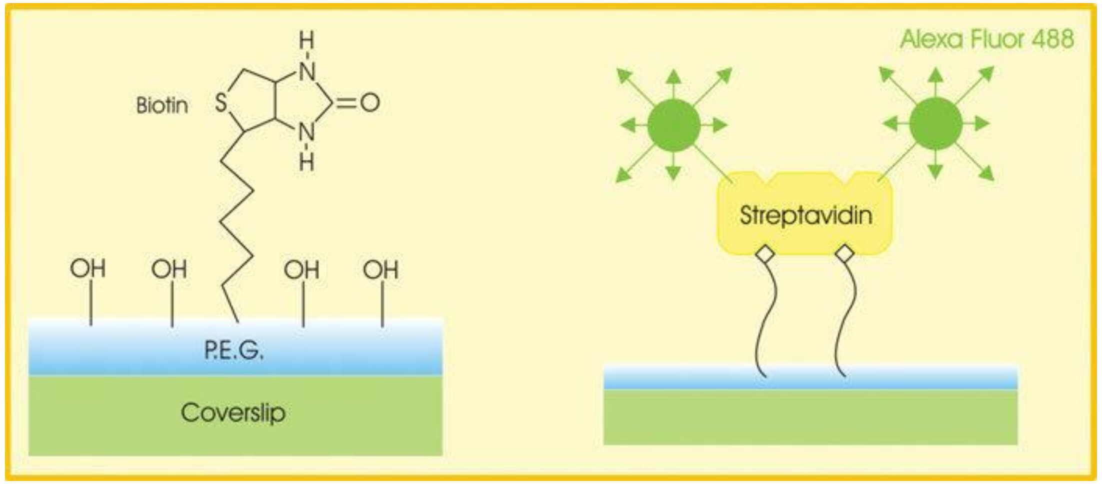
- **Surface Grafting** involves tethering molecules to the surface
- Covalent, electrostatic or non-covalent interactions
- Reversible or irreversible

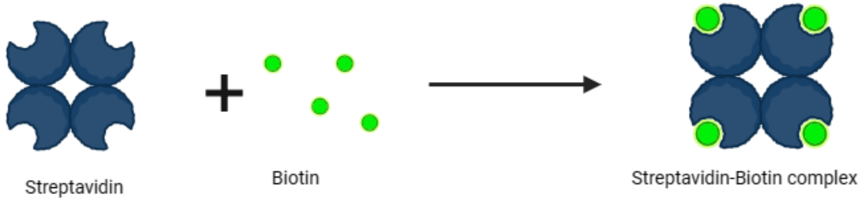
Carbodiimide Coupling for Grafting Antibodies



- Forms amide bonds between a carboxylate group and a primary amine
- Frequently utilized for functionalizing proteins
- One-pot, water-based synthesis technique
- High reaction yields
- May require carboxylation or aminolysis of materials prior to use

Biotin-Avidin-based Grafting through Non-covalent Interactions





Hallworth, R. et al. *Microscopy and Microanalysis*, **2012**

- Biotin (small molecule) and streptavidin (recepter protein) form one of the strongest non-covalent interactions in Nature
- Immobilize biotin on the surface and tether molecule of interest to streptavidin
- Non-covalent grafting of molecule of interest on biotinylated surface

Key Considerations:

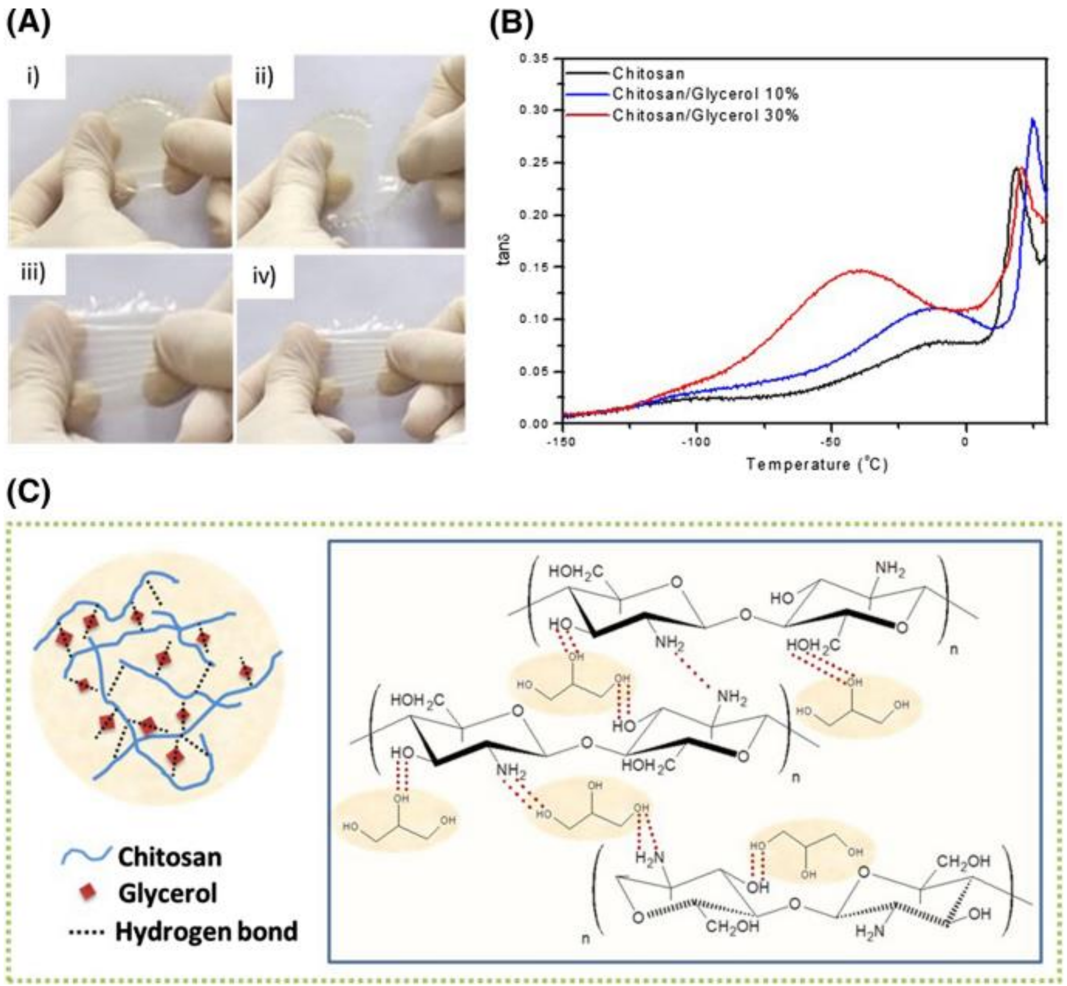
- Toxicity and environmental impact of crosslinkers
- Use of solvents, reagents during chemical processes
- Stability of chemical reactions (how likely are the grafts to peel off)
- Reversibility – depends on intended application

Types of Additives in Biopolymers

- **Small Molecule Additives:** Plasticizers, surfactants, adhesives etc
- **Biocomposites:** Biopolymers mixed with other metals, inorganic materials, synthetic polymers, or biopolymers
- **Living Material:** Microbial organisms encapsulated in a biopolymer matrix

Glycerol as a Plasticizer in Chitosan Membranes

- Glycerol is a natural food-grade molecule commonly utilized as a plasticizer for biopolymers
- Improves flexibility and ease of shaping
- Increased H-bonding between chitosan chains
- Chitosan is a polysaccharide commonly found in the outer shell of shellfish



Caroni, J.G. et al. *Polymer Bulletin*, **2021**

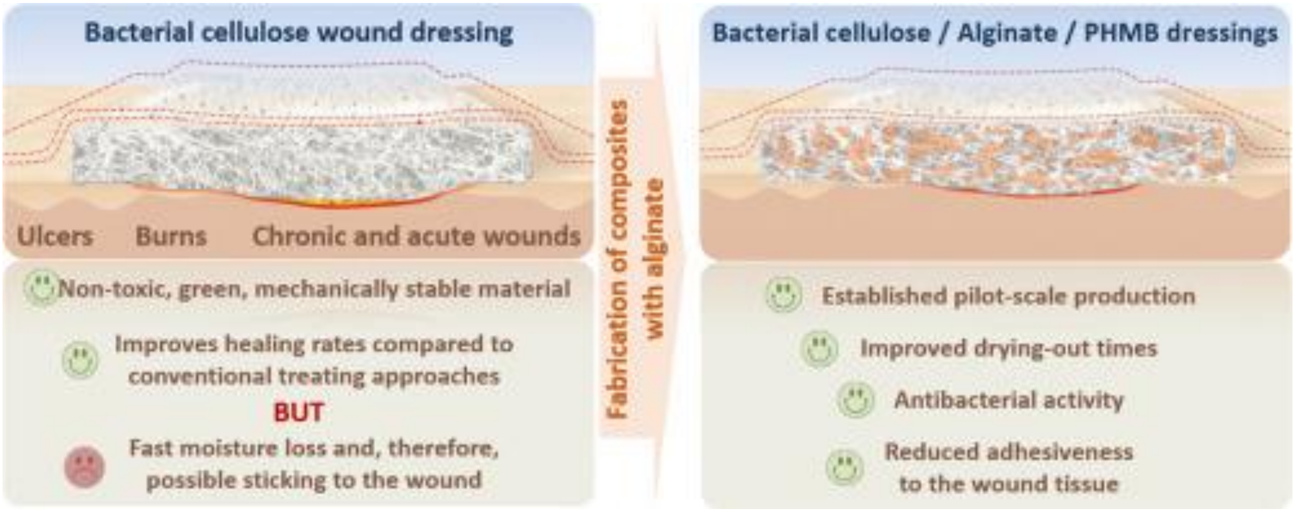
BC-Alginate Composites as Improved Wound Dressings

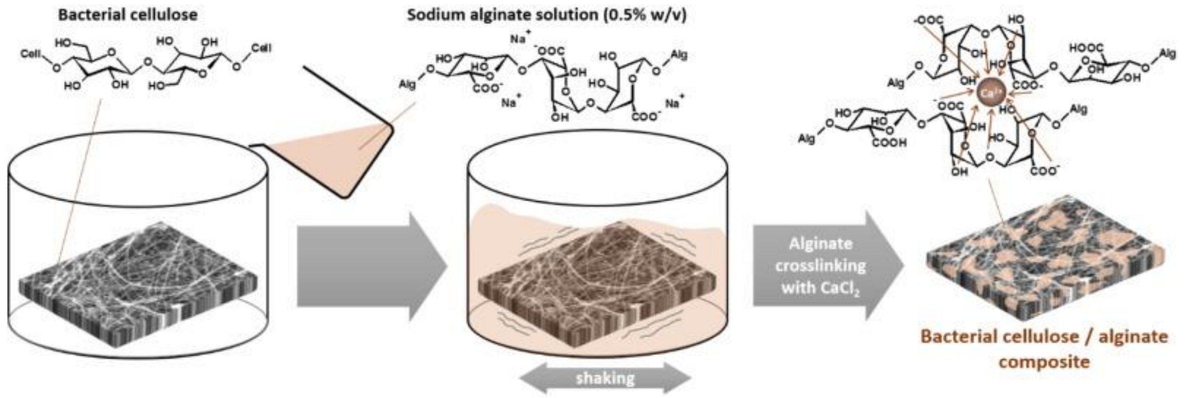
- Bacterial Cellulose was crosslinked with Alginate ionically to form BC/Alg composites

- These were loaded with antimicrobial drugs

- BC offers strength and structural stability to the dressing materials

- Alginate improves water retention





Sulaeiva, I. et al. *Material Science and Engineering: C*, **2020**

Living Materials: Mycelium Containing Self-Healing Bricks

- Mycelium a type of fungi composited with a scaffold material to make a “living” brick
- Alternative to concrete
- Has self-healing properties
- More about this to come….

Key Considerations:

- Toxicity and environmental impact of plasticizers
- Effect of additives on material properties – strength, flexibility etc
- Compatibility of materials for intended use

Final Thoughts!

- Bio-based polymers can be biosynthetic or biopolymers
- Biosynthetic polymers are similar to plastic – ease of manufacturing
- However, degradability is an issue!
- Biopolymers may be modified through various strategies to develop materials
- Choice of modification strategy depends on intended use
- Often multiple strategies are combined!

Biopolymer Metropolis: The Living Ci
Artwork made using Gemi
a Large Language Model by Goog
Generated June 4, 20

Assignment #3: for class

- For a biopolymer material of your choice, develop a modification strategy to enhance a native property, or impart a new feature

- Discuss source of biopolymer, process of extraction, modification strategy and application

- Discuss if this is a sustainable material. Why or why not?

- **Write a 2 page report**