

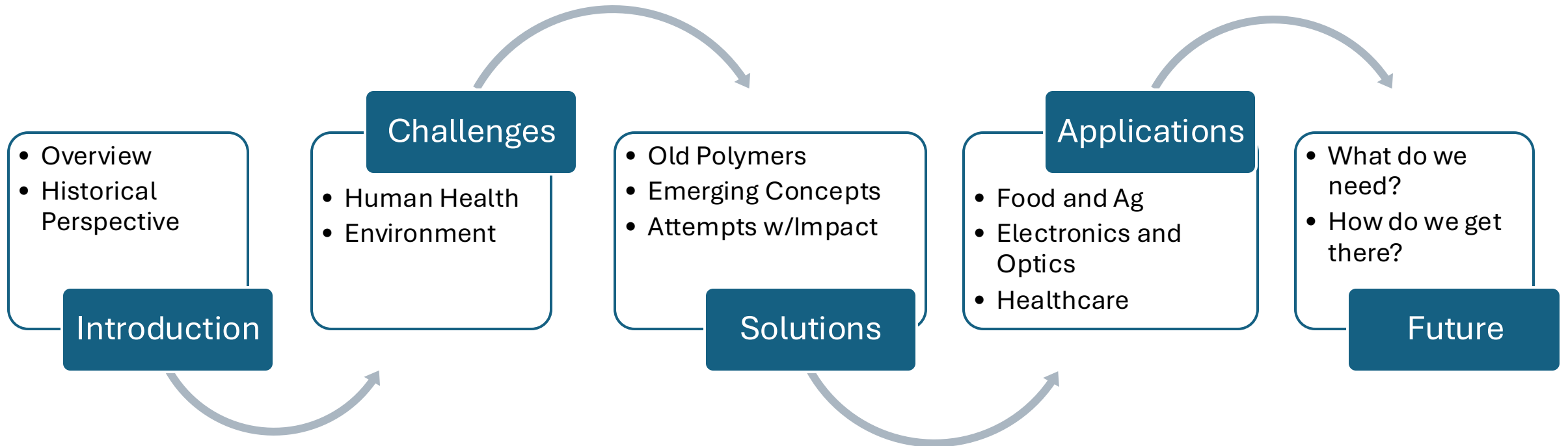


LECTURE 10: Attempts with Impact – Applications of Biopolymers

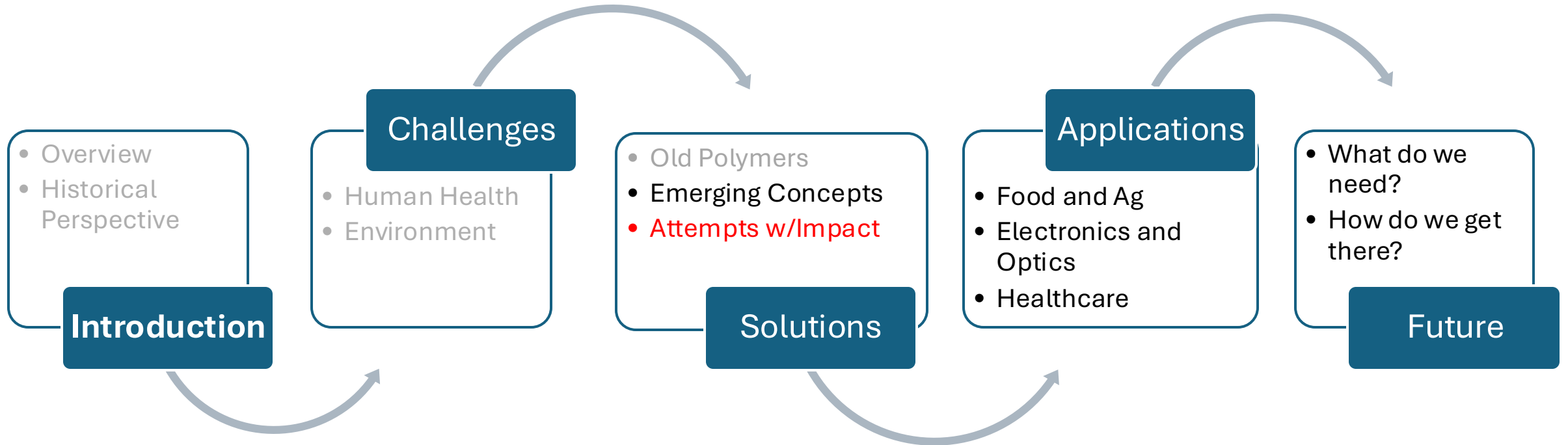
Sanjana Gopalakrishnan

Sustainable Materials, Fall 2024

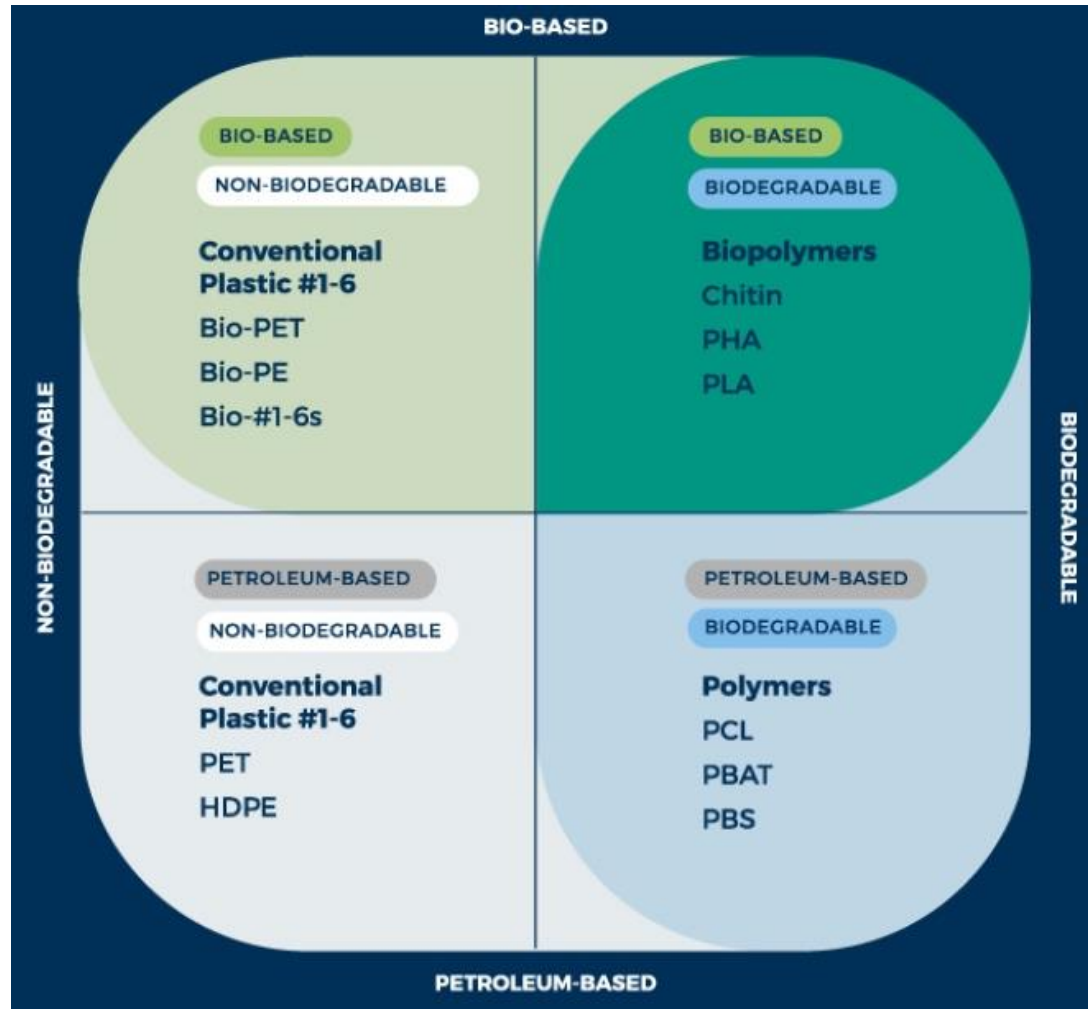
Course Overview



Lecture 9-10

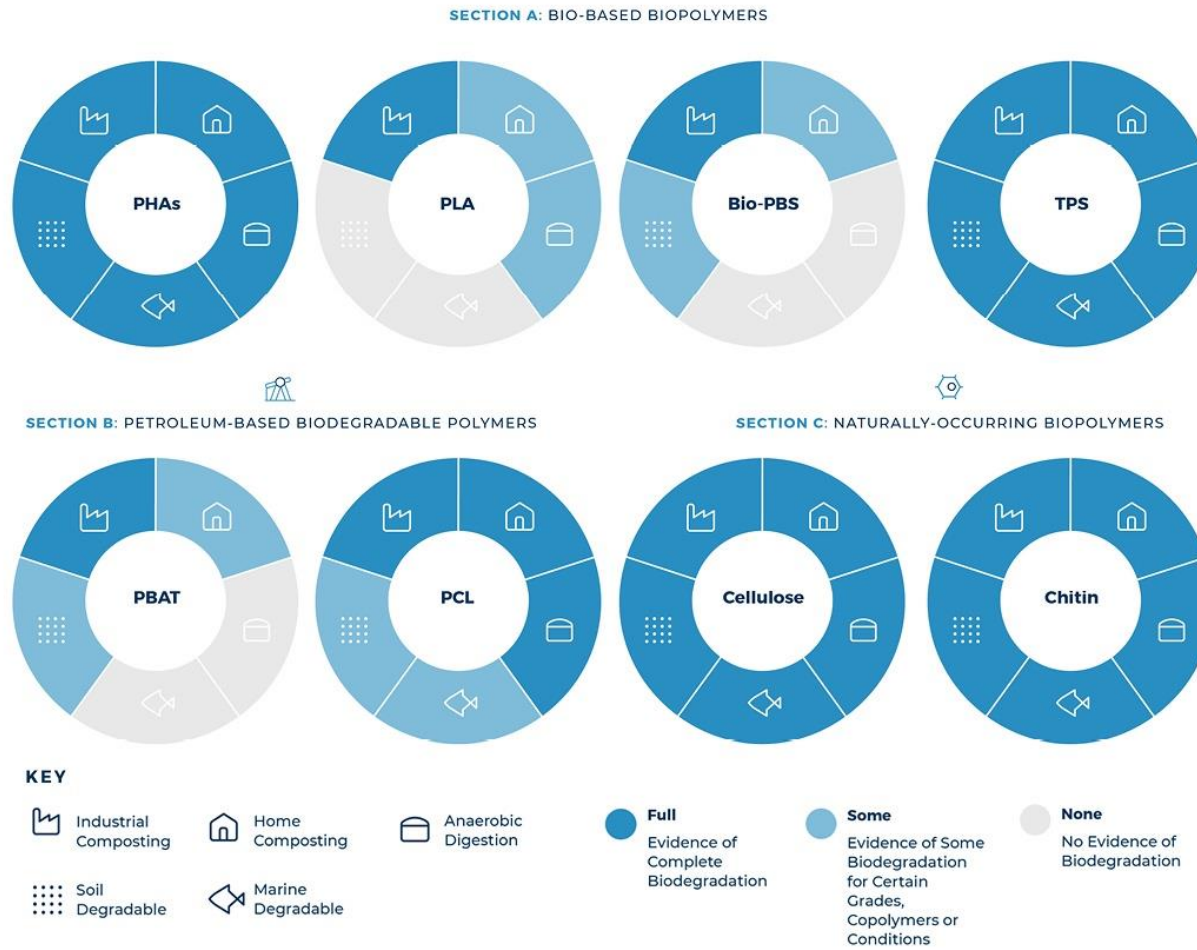


Bio-based Raw Materials as Alternative Feedstock



- 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

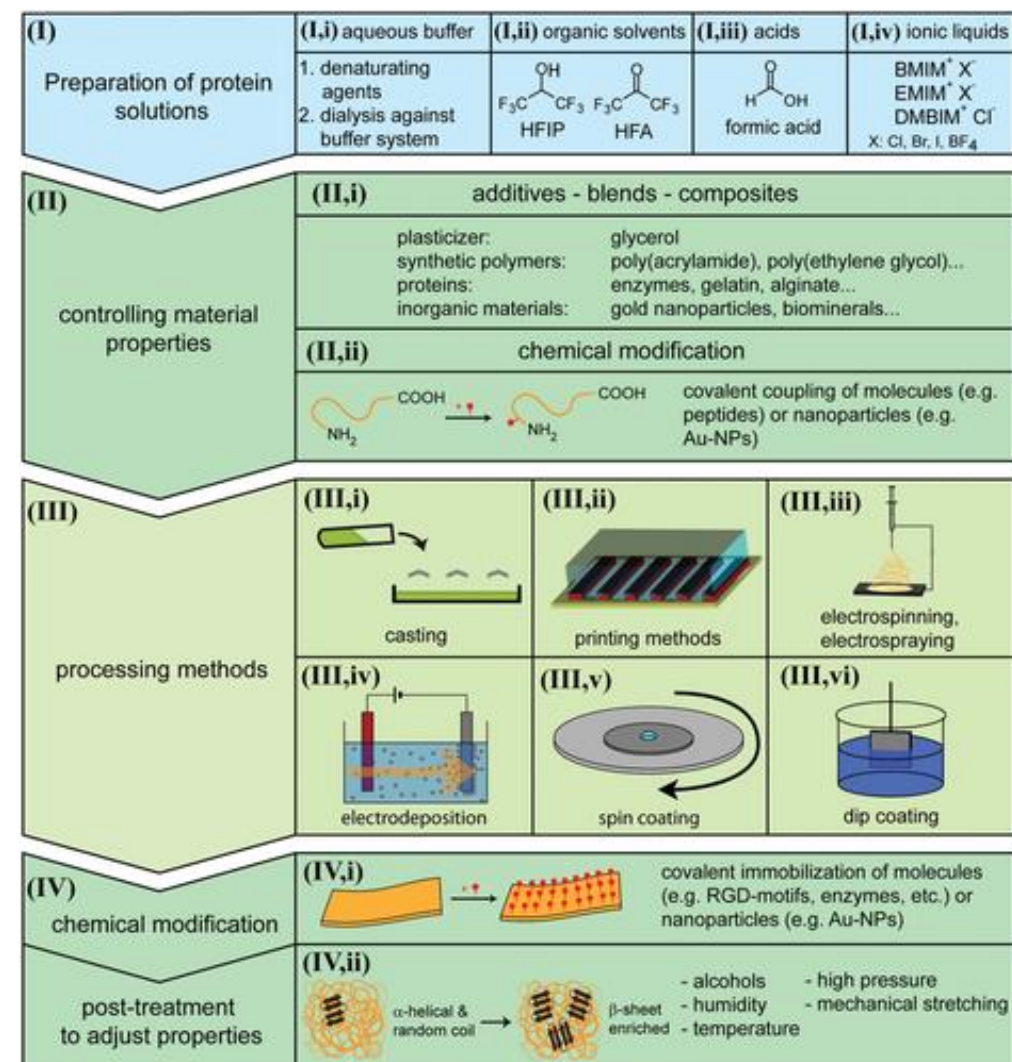
Biodegradability of Biosynthetic Polymers



- 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

Type of Modifications

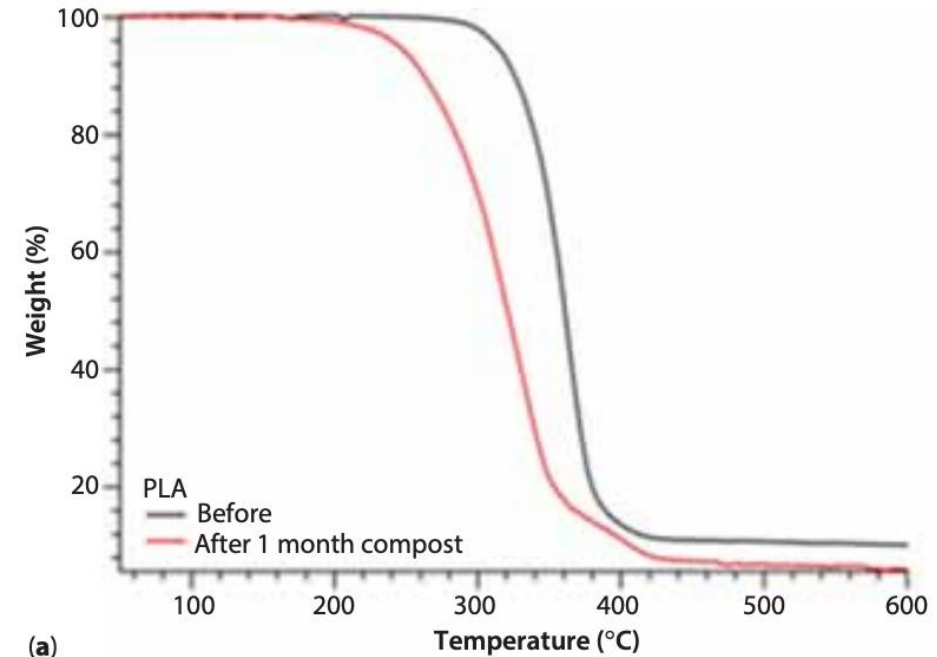
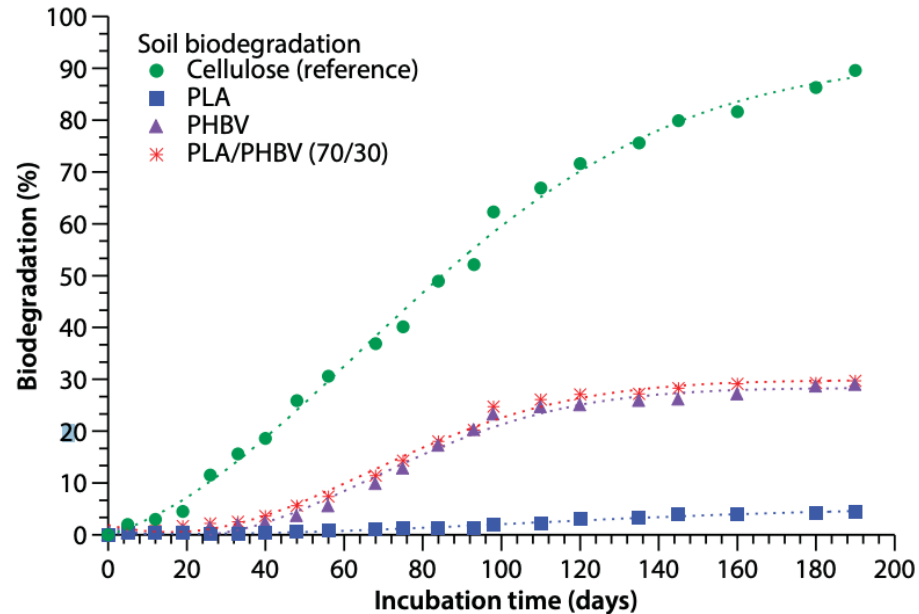
- Physical:** Altering the secondary and tertiary structure without altering the primary structure
 Heat, pressure, solvents, pH changes, humidity etc.
- Chemical:** Introducing new chemical functionalities into the primary structure
 Crosslinking, grafting
- Composites/Additives:** Mixing one or more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



Outline for Today

- Bioplastics
 - Solving the PLA problem – enzyme encapsulation
 - Flax-based elastomers
 - Silk-based thermoplastics
- Films and Coatings
 - Food packaging materials
 - Hydrophobic coatings- Alternatives to Teflon
 - Biopolymer –based filtration
- Bio-based Materials
 -
- Additives
 - Adhesives
 - Silicone Elastomer Alternatives

The PLA Problem: Not Actually Compostable



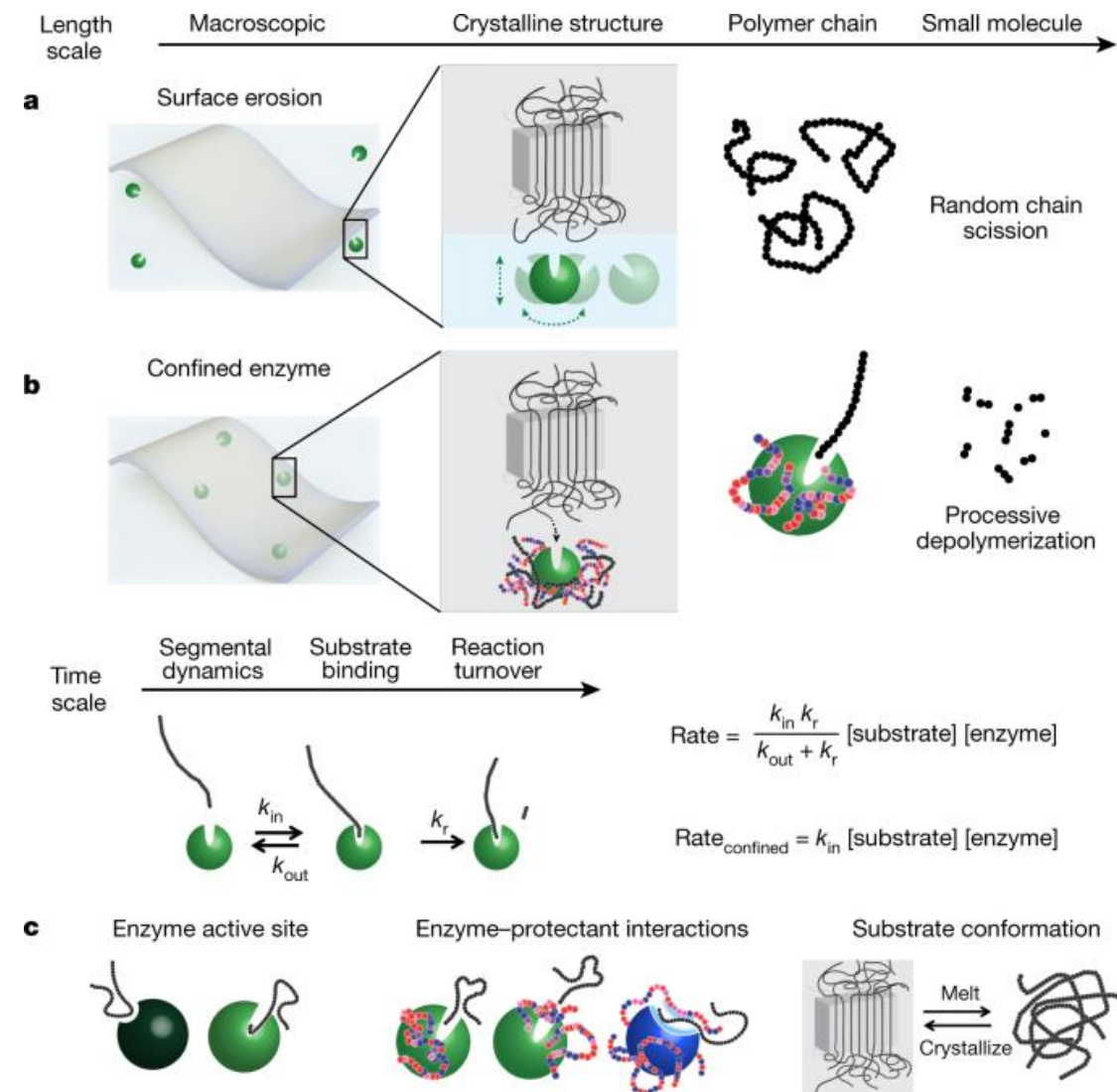
- PLA does not biodegrade in soil
- Thermal stability (TGA) of PLA after 1 month of composting has minimal change
- Degradation requires specific temperatures (55-75 °C) and anerobic conditions

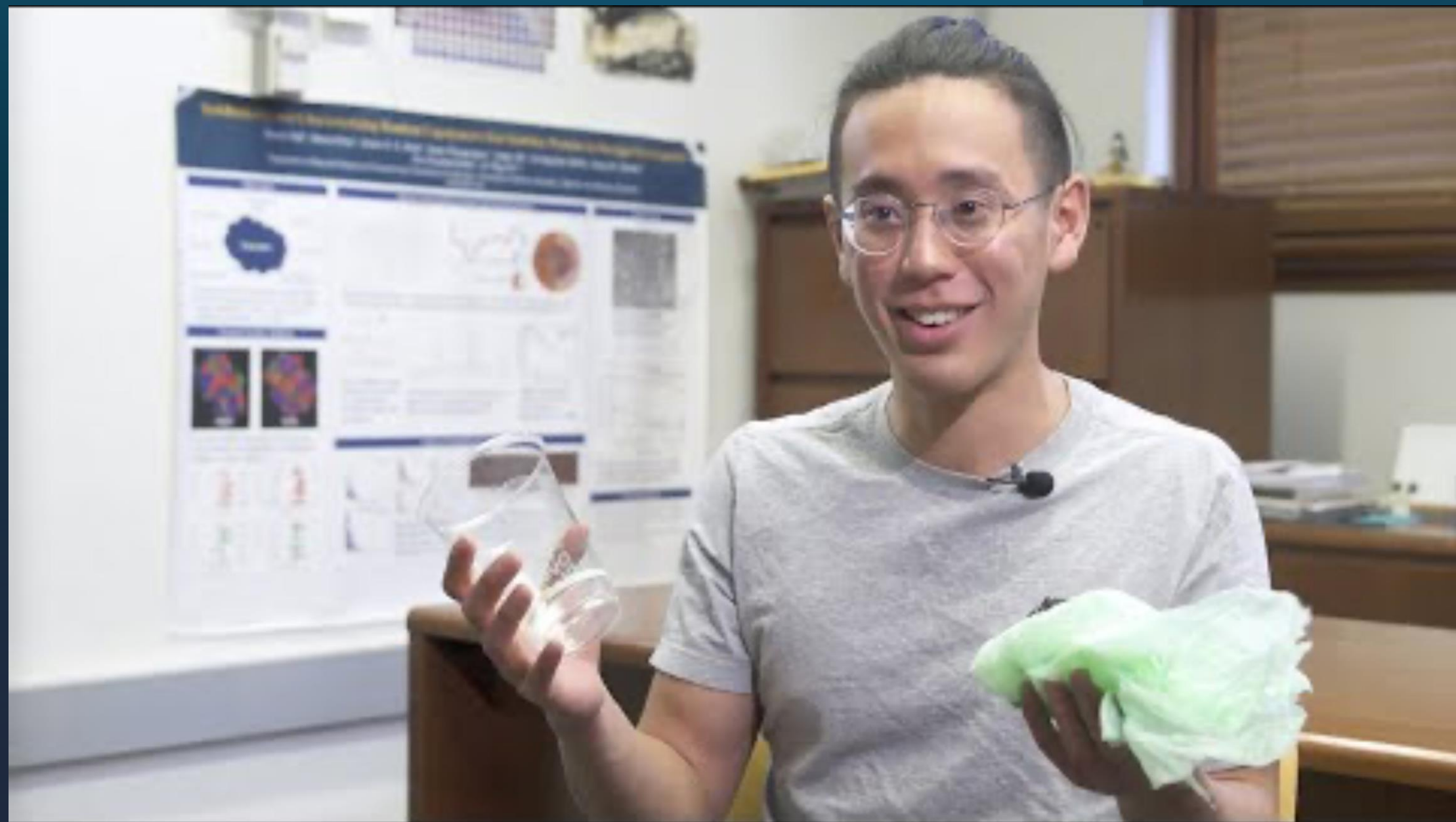
Solving the PLA Problem

- **Integration of Enzymes:** Formulating PLA plastics with embedded enzymes for improved biodegradation
- **Biopolymer Composites:** Compositing with a biopolymer to enhance breakdown during composting

Enzyme additive into Bio-synthetic Plastics

- Enzymes are confined within the bio-synthetic plastic prior to fabrication
- Enzyme is surrounded by a protectant matrix that preserves activity throughout plastic processing including in organic solvent
- Protectant-enzyme interactions facilitate processive depolymerization

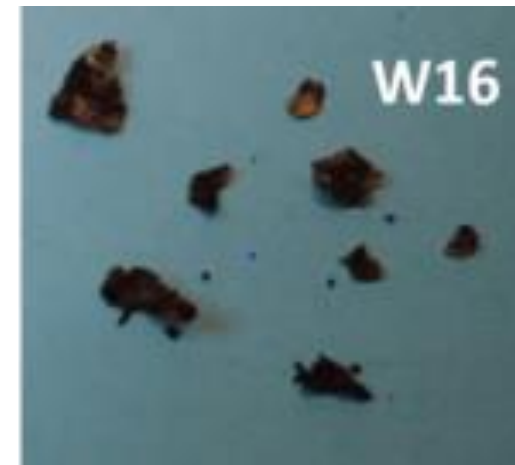




CARBIOS: Enzyme-loaded PLA Single-use Plastics



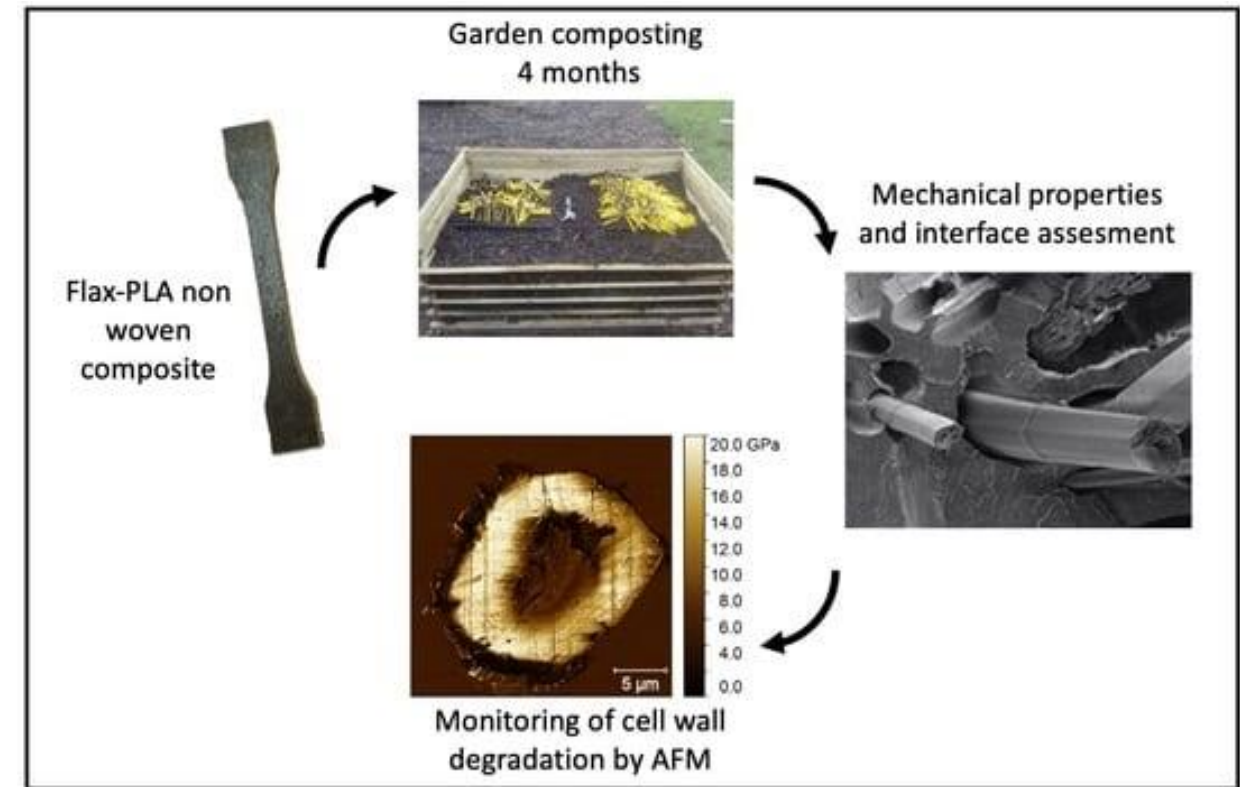
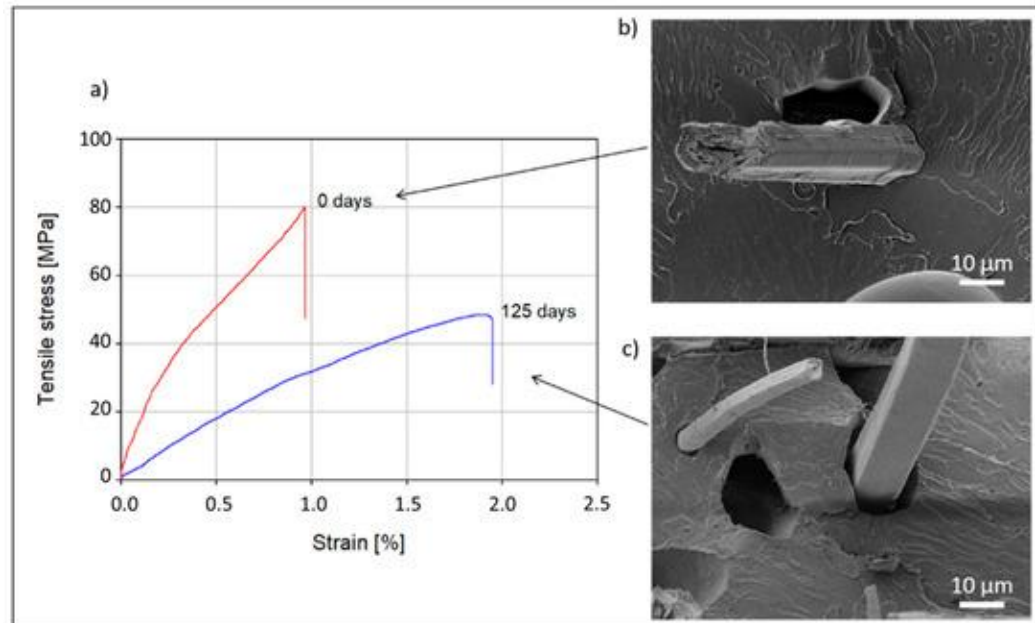
- 5% Carbios active enzyme encapsulated in PLA films for degradation testing
- Disintegration in 2-6 weeks. Total biodegradation in 120 days (microplastics)
- No toxicity observed



**What are some challenges with
using Enzymes?**

Cellulose Reinforced PLA for Improved Compostability

- Flax fibers improved strength and biodegradation in soil
- PLA imparts flexibility and transparency



Meleli, A. et al. *Polymers* 2021

The Pela Story: Flax-based Elastomers+PLA

- Biodegradable phone cases and sunglasses
- Made with 45% flax-based elastomer Flaxstic®



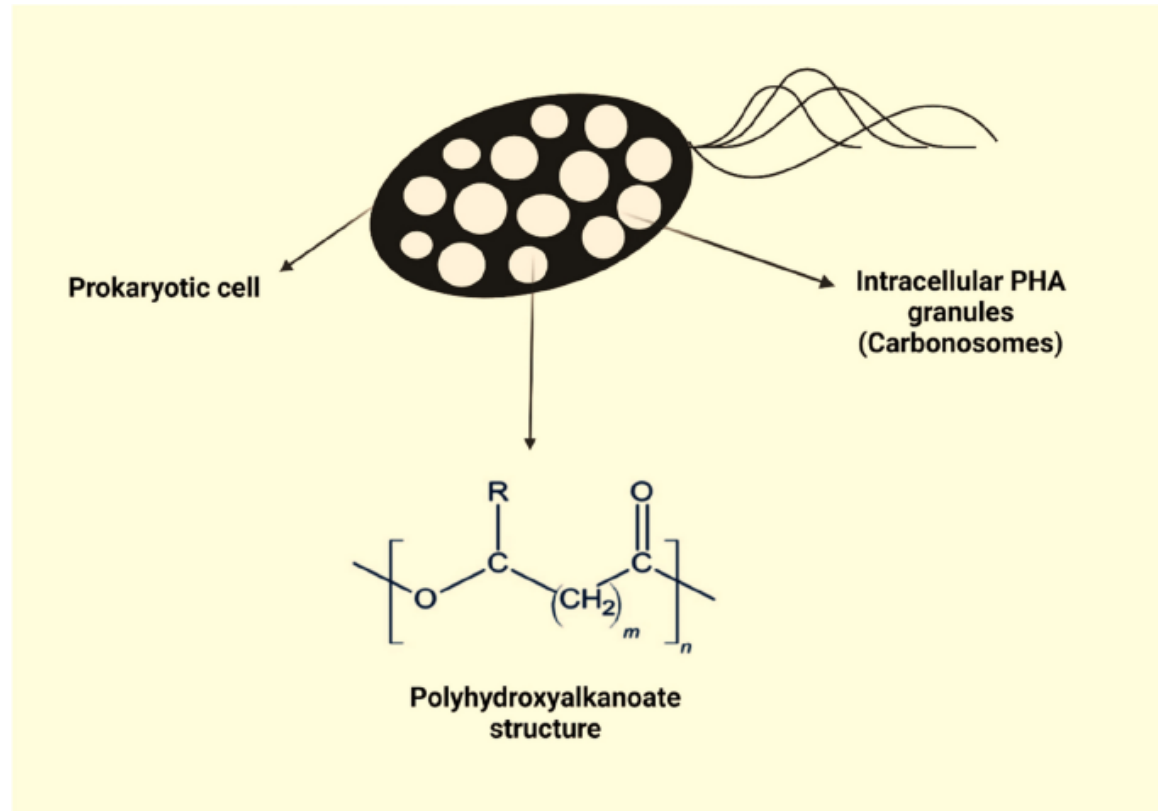
Compostable Phone Case Life Cycle Analysis

MATERIALS	EMBODIED ENERGY	WASTE & EMISSIONS
<ul style="list-style-type: none"> • Bioplastic elastomer and flax straw materials - flax fiber, flax shive • Packaging includes cardboard • Distribution involves plastic 	<ul style="list-style-type: none"> • Uses 50% less non-renewable energy than plastic • Growing flax consumes a considerable amount of diesel (approx. 4 M gal in 2014) • Machines are used to till, sow, water, harvest, bale flax straw 	<ul style="list-style-type: none"> • Zero waste- uses waste byproduct as a raw material • CO2 emissions during transportation of materials to production factory
<ul style="list-style-type: none"> • The bioplastic elastomer is melted in an extruder at approximately 300° F. 	<ul style="list-style-type: none"> • Heating the bioplastic elastomer consumes energy • Injection mold facility & engraving facility operate on electricity 	<ul style="list-style-type: none"> • GHG emissions electrically powered machinery
<ul style="list-style-type: none"> • Bioresin is packaged in a plastic-lined 250 pound fiber drum and shipped to company • Individual cases are distributed in cardboard packaging 	<ul style="list-style-type: none"> • Trucks transport flax straw from the field to factory/manufacturer (Pela) • Amazon transportation i.e trucks, warehouses • Pela ships directly to consumers worldwide 	<ul style="list-style-type: none"> • Cardboard packaging used for shipping • CO2 emissions from shipping
<ul style="list-style-type: none"> • No maintenance necessary for product usage • The product is reused in soil when composted 	<ul style="list-style-type: none"> • Reusing involves shipping the case to Pela • Pela then must ship the functioning case to a new customer 	<ul style="list-style-type: none"> • Can be composted and reused as nutrient rich soil • No emissions during use
<ul style="list-style-type: none"> • The material is not recycled as it degrades and needs to be composted 	<ul style="list-style-type: none"> • No energy required to compost the case • Energy is required to recycle the packaging 	<ul style="list-style-type: none"> • Cardboard packaging should be recycled • Broken/old Pela cases can be recycled into a new case
<ul style="list-style-type: none"> • The product is compostable when properly disposed 	<ul style="list-style-type: none"> • Cases returned to Pela require shipping energy • Pela claims that the case can be composted in a backyard, no energy required 	<ul style="list-style-type: none"> • Zero waste- Can be composted or returned to Pela for recycling when broken • Methane and other GHG emissions during composting

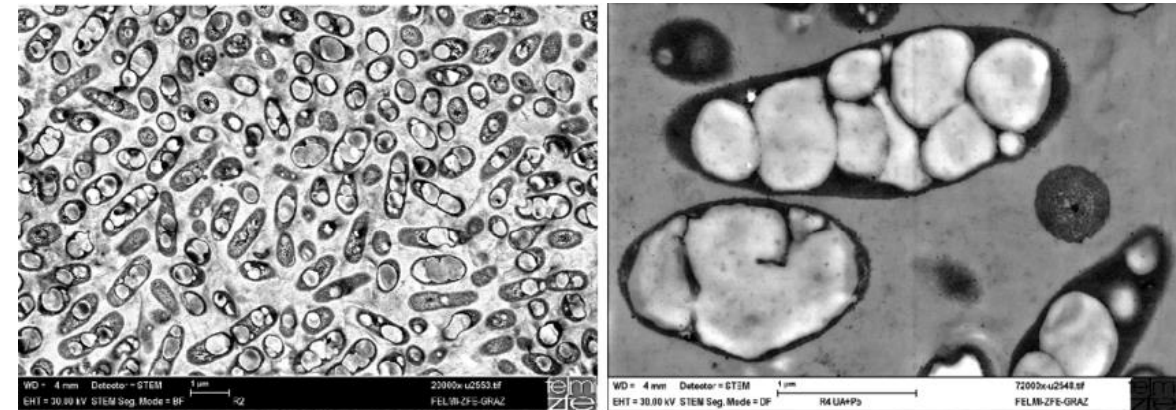
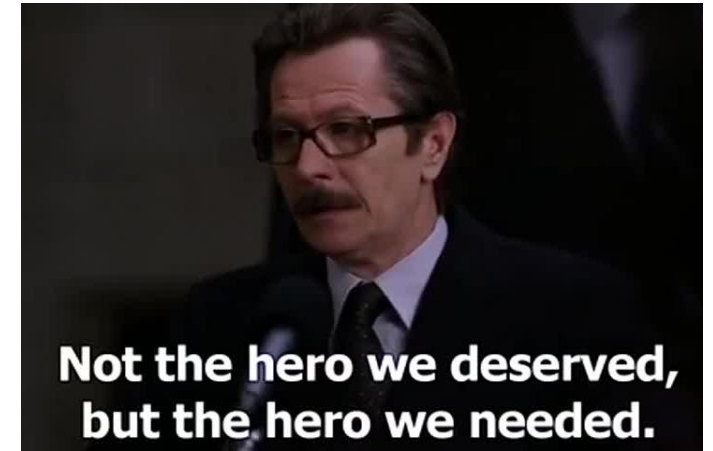
pela

COMPOSTABLE PHONE CASE LIFE CYCLE
FALL 2019
DES 40A
Malia Helms
Maria Vargas
Zhanna Kravtsova

PHAs: The Hero We Need?

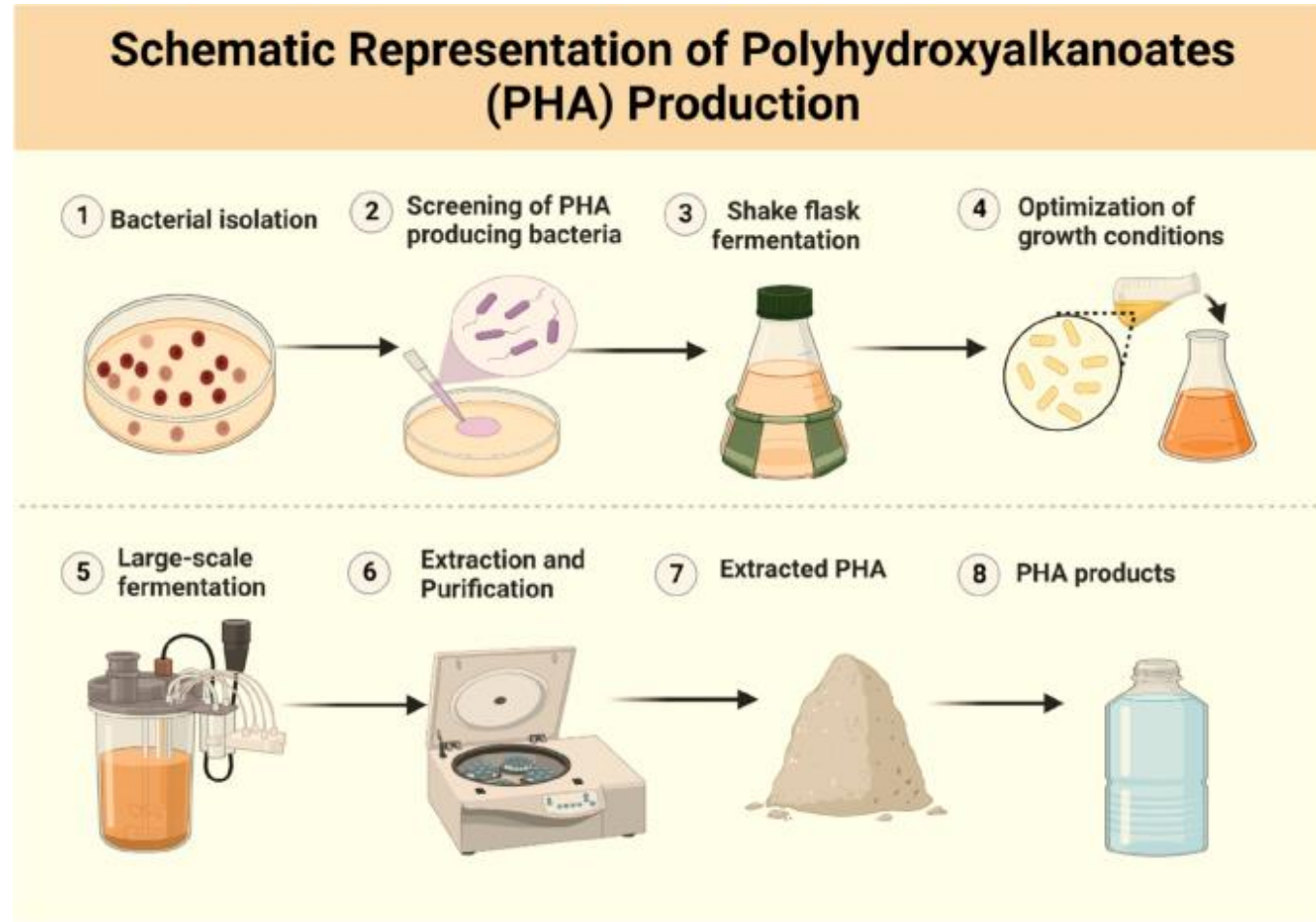


Mahato, R. P. et al. *Archives of Microbiology*, 2023



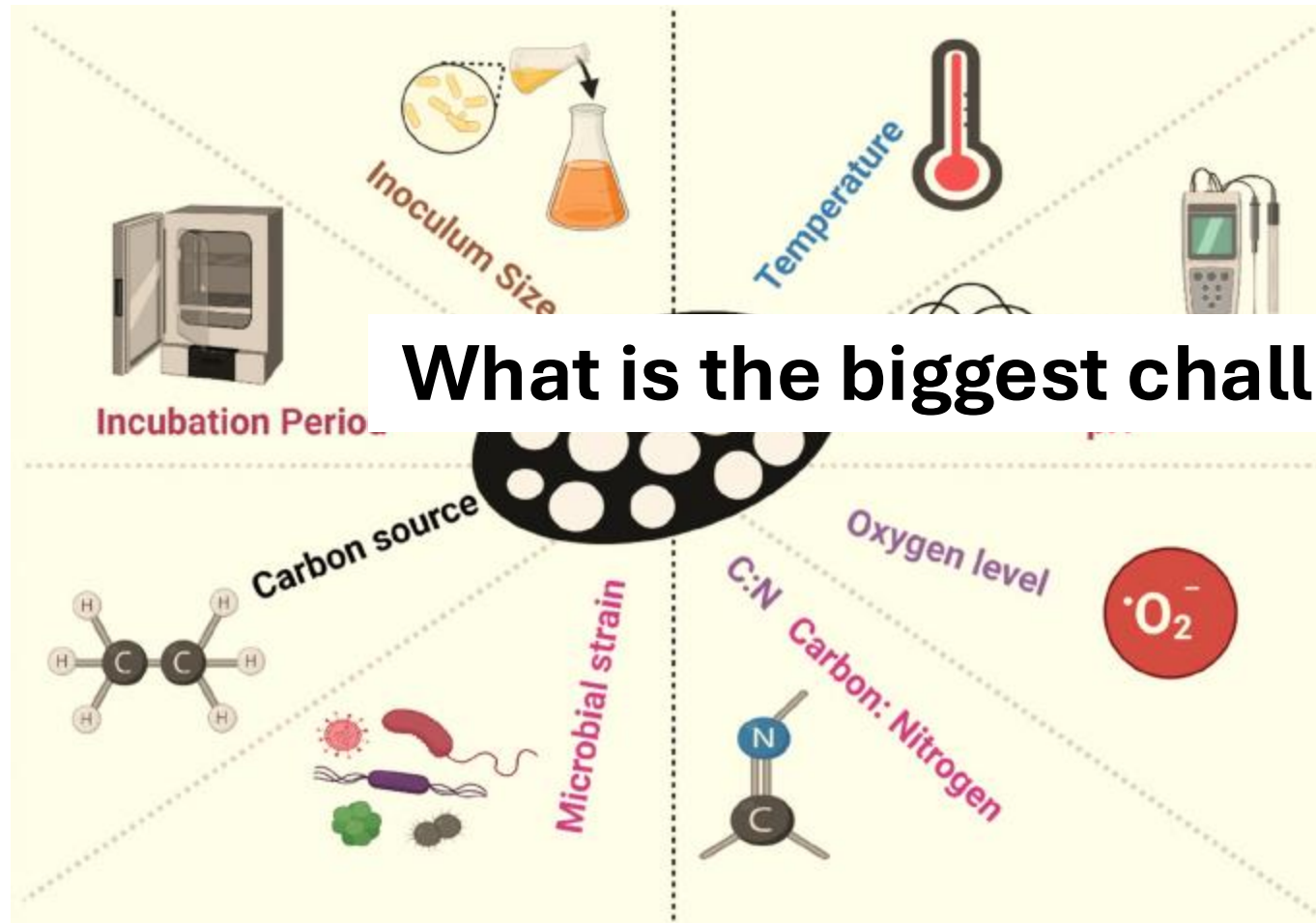
- PHAs or Polyhydroxyalkanoates are naturally produced in some bacteria and archaea species
- Naturally-occurring biodegradable polyesters

PHAs are Produced via Biofermentation



- Microbes are isolated and screened for identifying PHA producing strains
- Microbes may be fermented on small or large scales
- PHA must be extracted and purified prior to use
- PHA is used for application ranging from tissue engineering to consumables

Cost and Efficiency must be Optimized for Large-Scale Production



- Optimize-
 - Biofermentation conditions
 - E.g. pH, temperature and time

E.g. microbial strain, multiple strains

- Carbon source
- E.g. nutrition source for growing microbes

Renewable Carbon Sources Bring Down Costs



Lignocellulose:

- Agriculture waste
- Abundant resource
- Needs Pre-treatment



Plant Oil Waste:

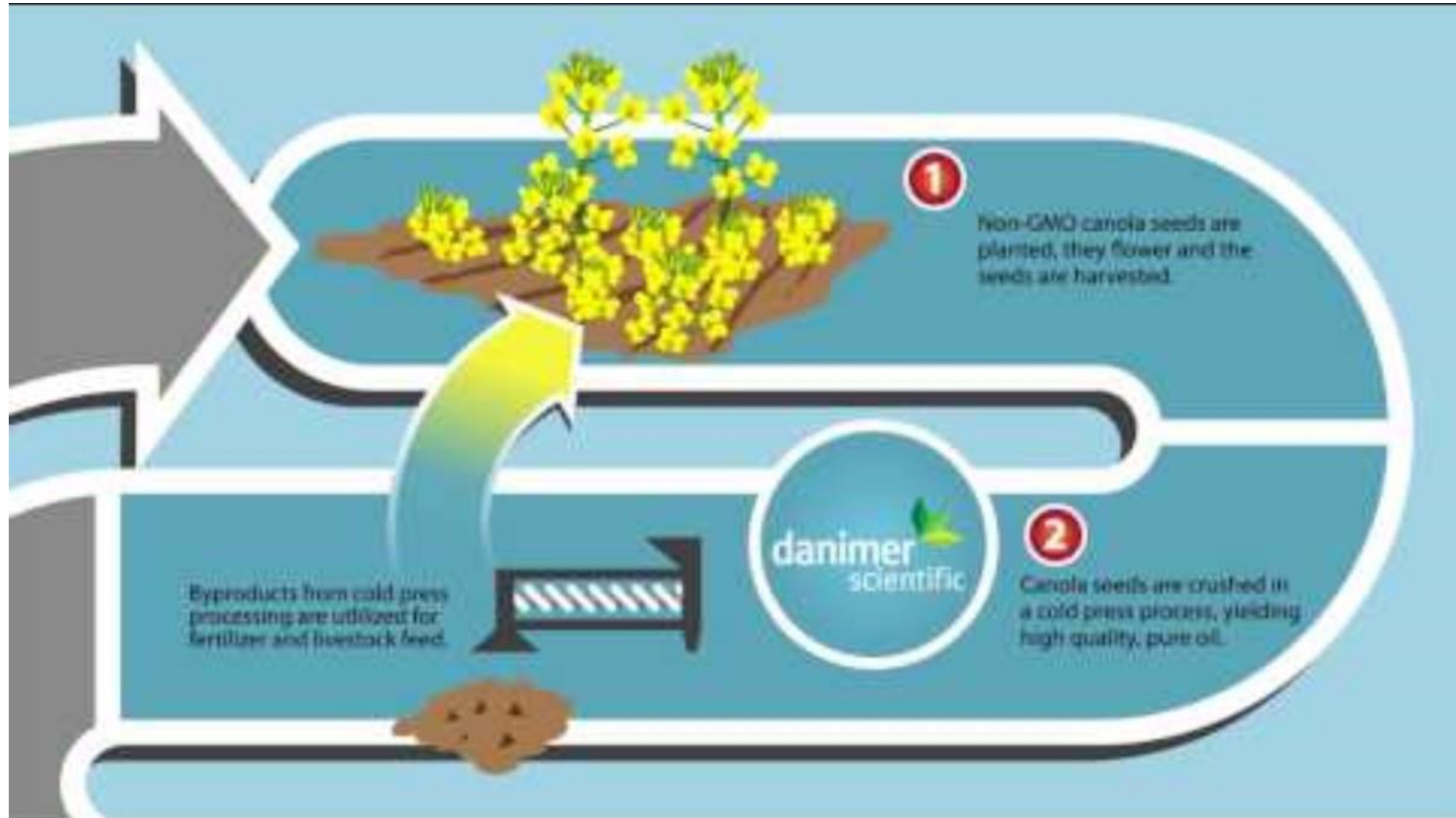
- Byproduct of cold-pressed oils
- High efficiency
- Fatty acid- impacts structure



Cheese Whey:

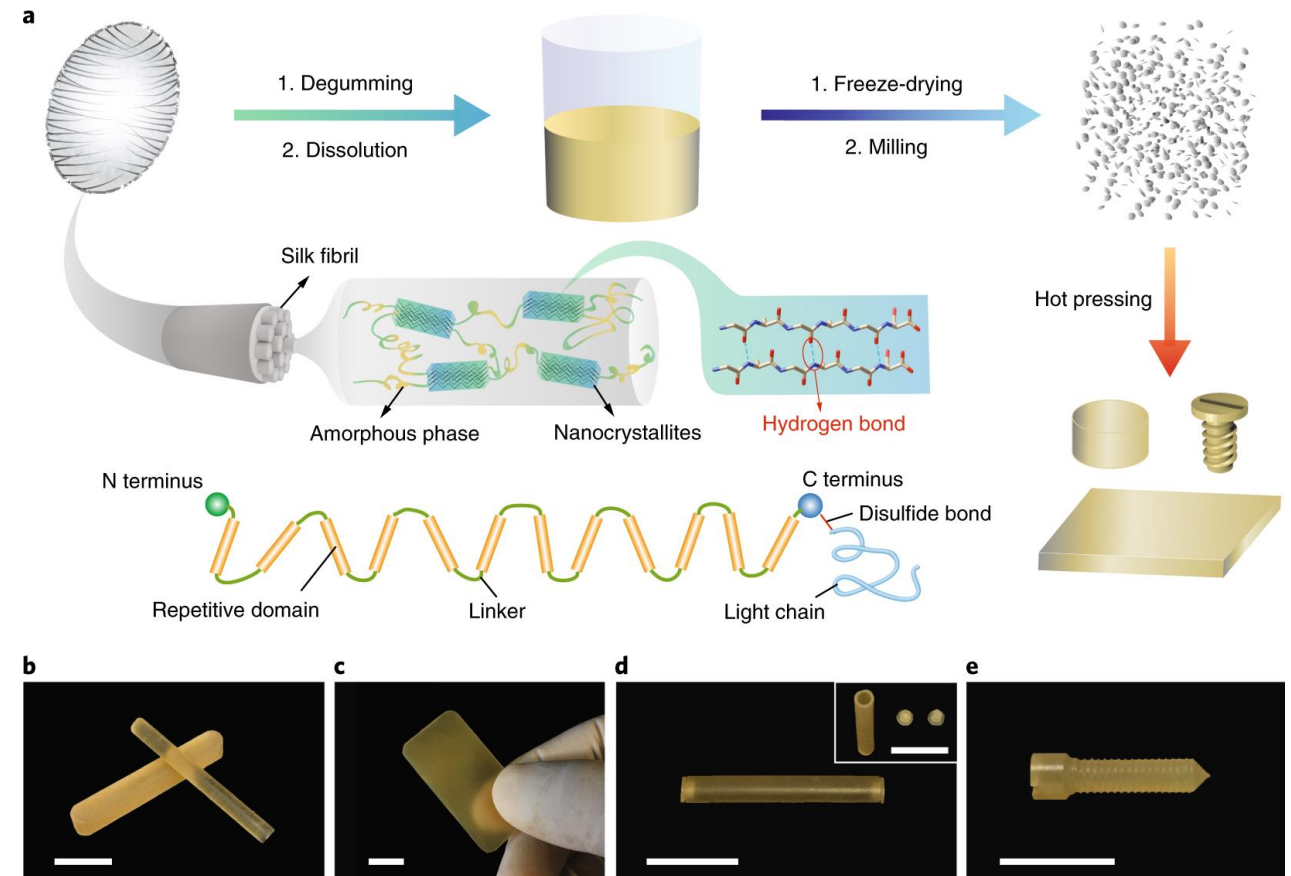
- High in glucose and sugars
- No pre-treatment
- Strain optimization needed

Applications of PHAs



Silk Thermoplastics are Prepared from Silk Fibroin Powder

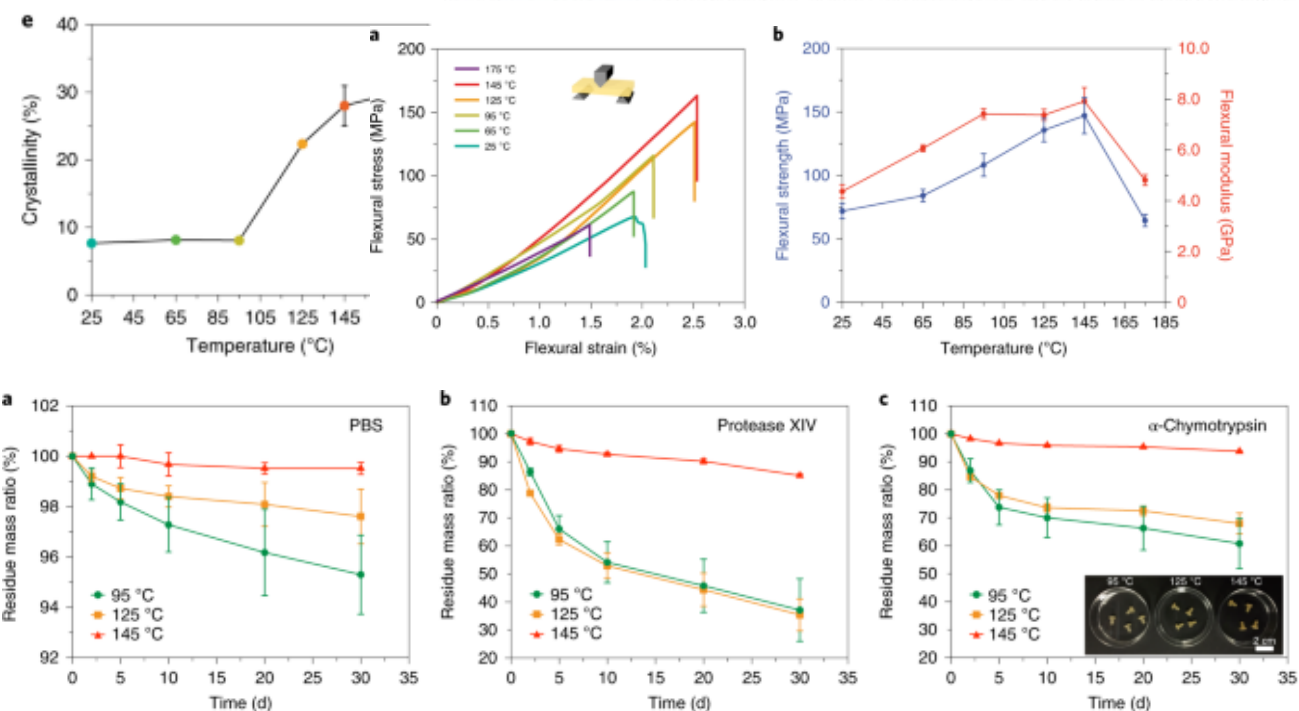
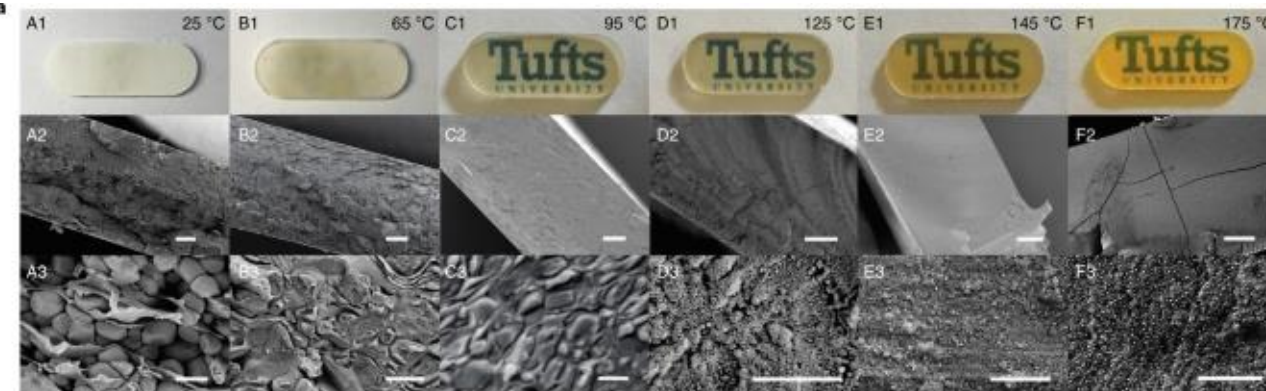
- Silk fibroin is extracted from silk cocoons and freeze-dried into powder
- Silk powder is hot-pressed in a metallic mold to prepare plastics
- Plastics are rigid and strong. May also be machined



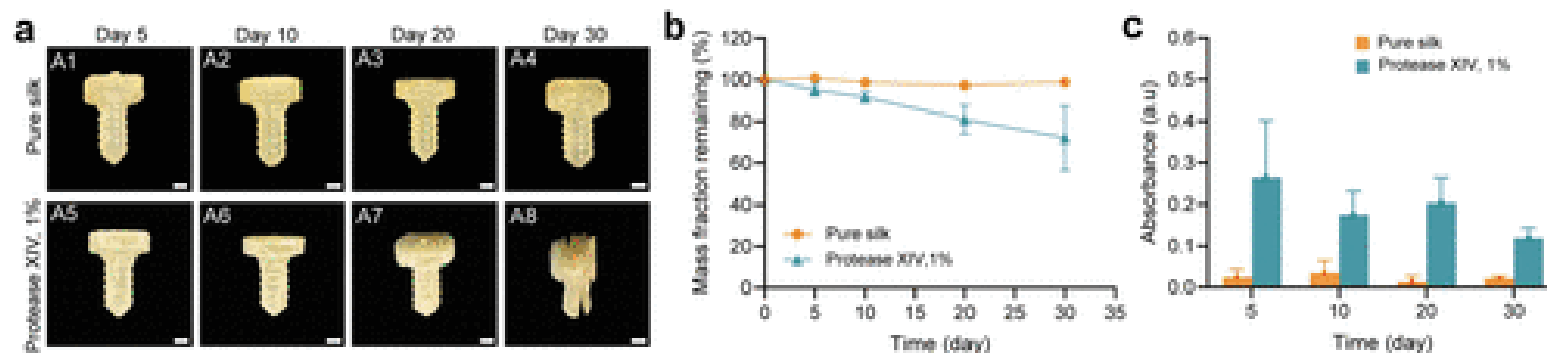
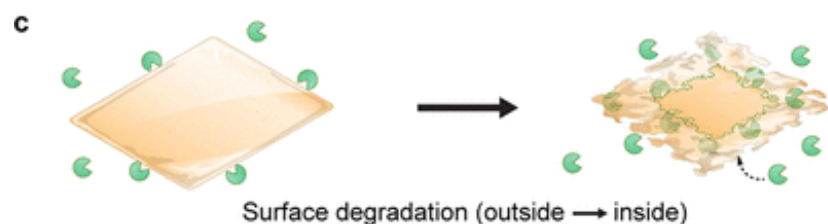
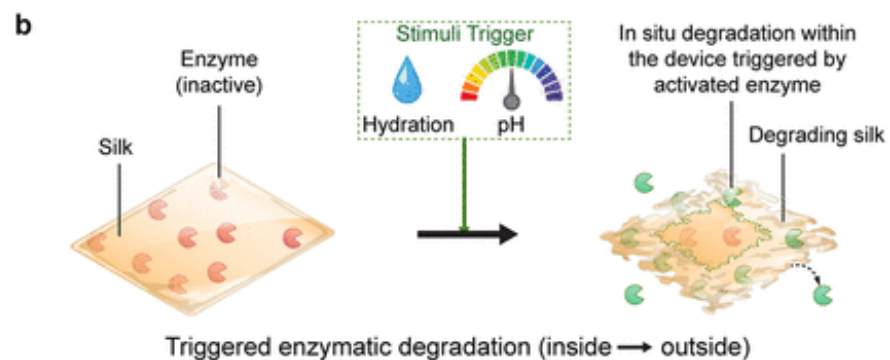
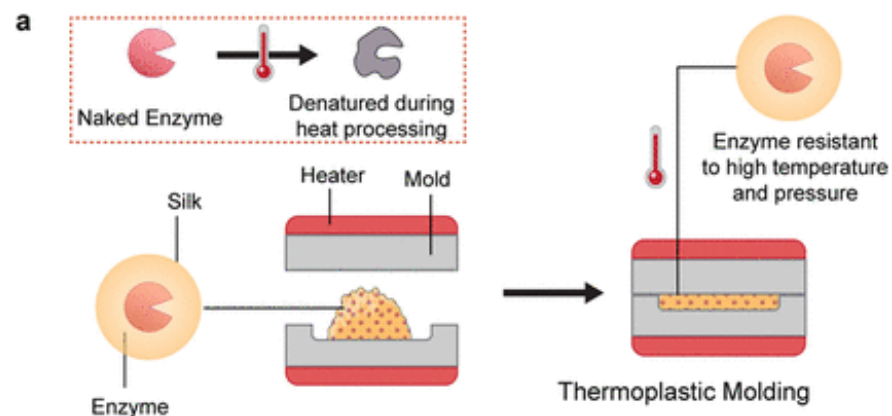
Guo, C. et al. *Nature Materials* 2020

Varying Temperature and Pressure Modulates Plastic Properties

- Increased Optical transparency and crystallinity at higher temperatures
- Changes in mechanical properties based on treatment temperatures
- Changes in enzymatic degradation rate due to treatment temperatures



Silk Plastics Loaded with Enzymes to Facilitate Degradation



- Silk acts as protectant during thermopressing
- Enzyme activity is preserved
- Facilitates inside to outside degradation

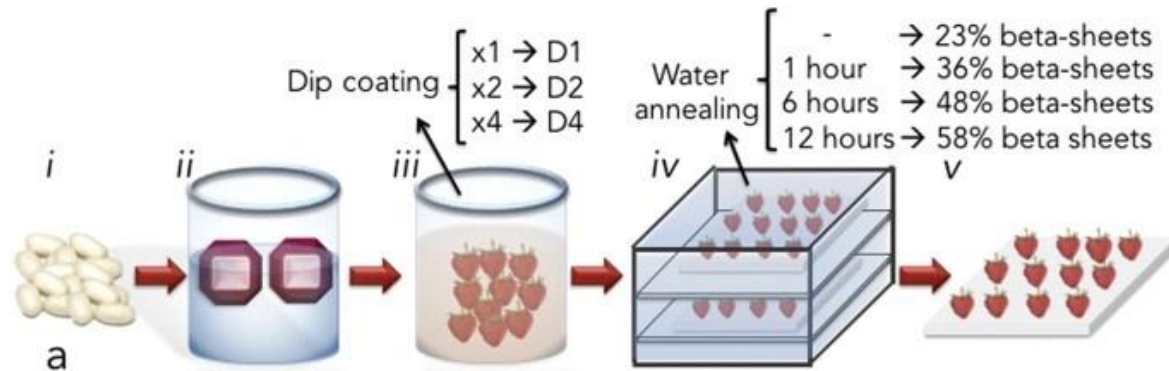
Biopolymer Coatings Impart Surface Functionality to Materials

- Surface properties such as charge, roughness and hydrophilicity may be modified using biopolymer coatings
- Biodegradable and green surface modification techniques for all materials and devices



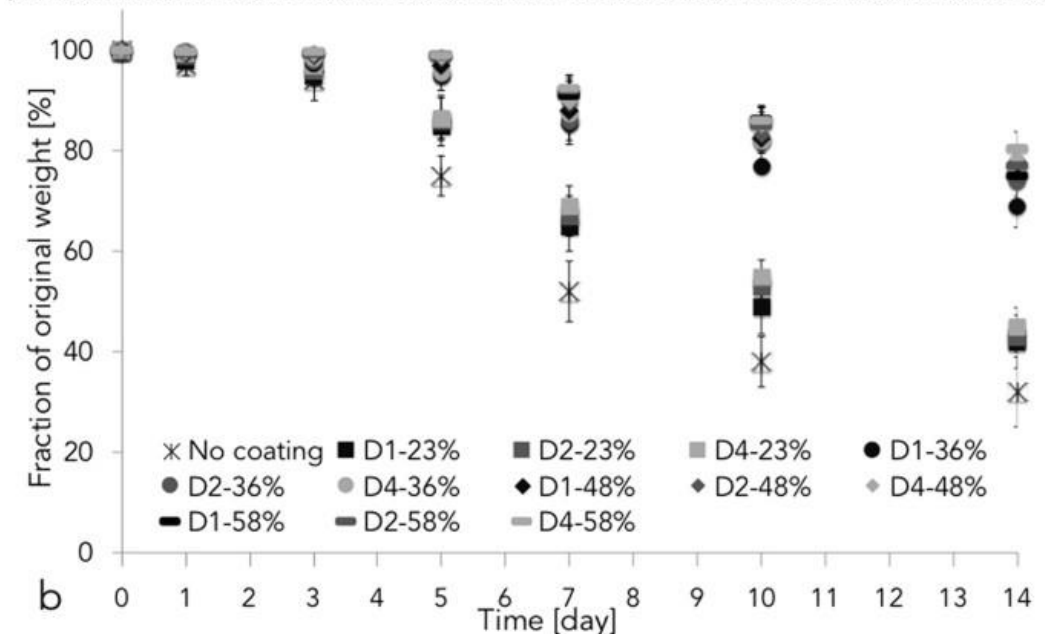
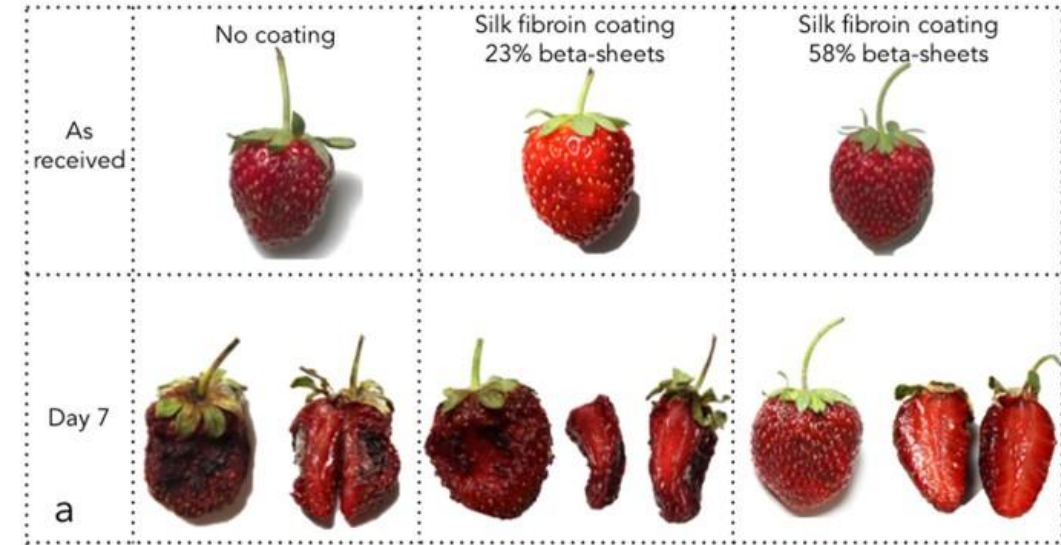
Nouri, A. et al. *Smart Materials in Manufacturing*, 2023

Silk-based Edible Coating for Improved Food Storage



Marelli, B. et al. *Scientific Reports*, 2016

- Silk fibroin is dip-coated onto food and water annealed to induce beta-sheeting
- Coating improved moisture retention, prevent weight loss and decay of food
- Edible, food-grade coating



Mori: Edible Silk Coating for Food Storage and Preservation



Hit your numbers.

All-natural protection sustainably keeps food from going to waste. Driving efficiency and flexibility in your distribution system.



Reduce plastic use.

Mori makes food more sustainable; it increases shelf-life without the need for single-use plastic.



Limit food waste.

By naturally preserving food, Mori reduces the financial impact of shrink.



Go the distance.

Mori lets you reach new markets and develop new product categories, Mori keeps food naturally fresher for longer.



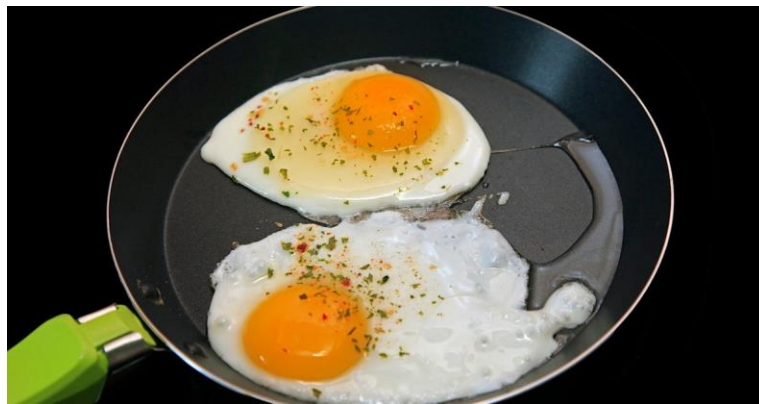
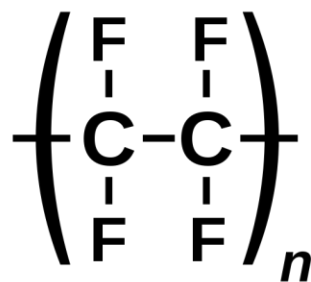
With Mori

Without

- Silk coating prevents –
 - Moisture loss
 - Air contact
 - Bacteria/ mold growth

mori

Hydrophobic Biopolymers: Teflon Alternatives



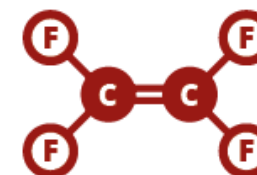
- Hydrophobic coatings like Teflon are prepared from fossil fuels
- PFAS exposure and release is an environmental concern

TODAY IN CHEMISTRY HISTORY

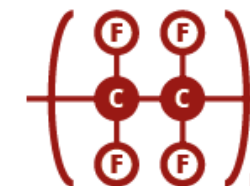
4TH FEBRUARY – PATENT ISSUED FOR TEFLON (1941)



TEFLON PAN



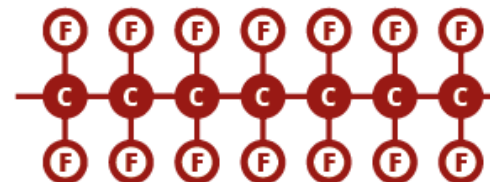
TETRAFLUOROETHENE



POLYTETRAFLUOROETHENE

Teflon is the brand name for polytetrafluoroethene (PTFE). It's a white, waxy substance, and was actually created by accident by Roy Plunkett in 1938. During research on new refrigerants, the tetrafluoroethene Plunkett was using was accidentally polymerised.

HOW DOES IT WORK?



Teflon's non-stick properties are in part due to the strength of its carbon-fluorine bonds, which are chemically inert. Additionally, due to the fluorine atoms, the intermolecular forces between PTFE and other molecules are very weak.

IS TEFLON SAFE?

327°C

MELTING POINT

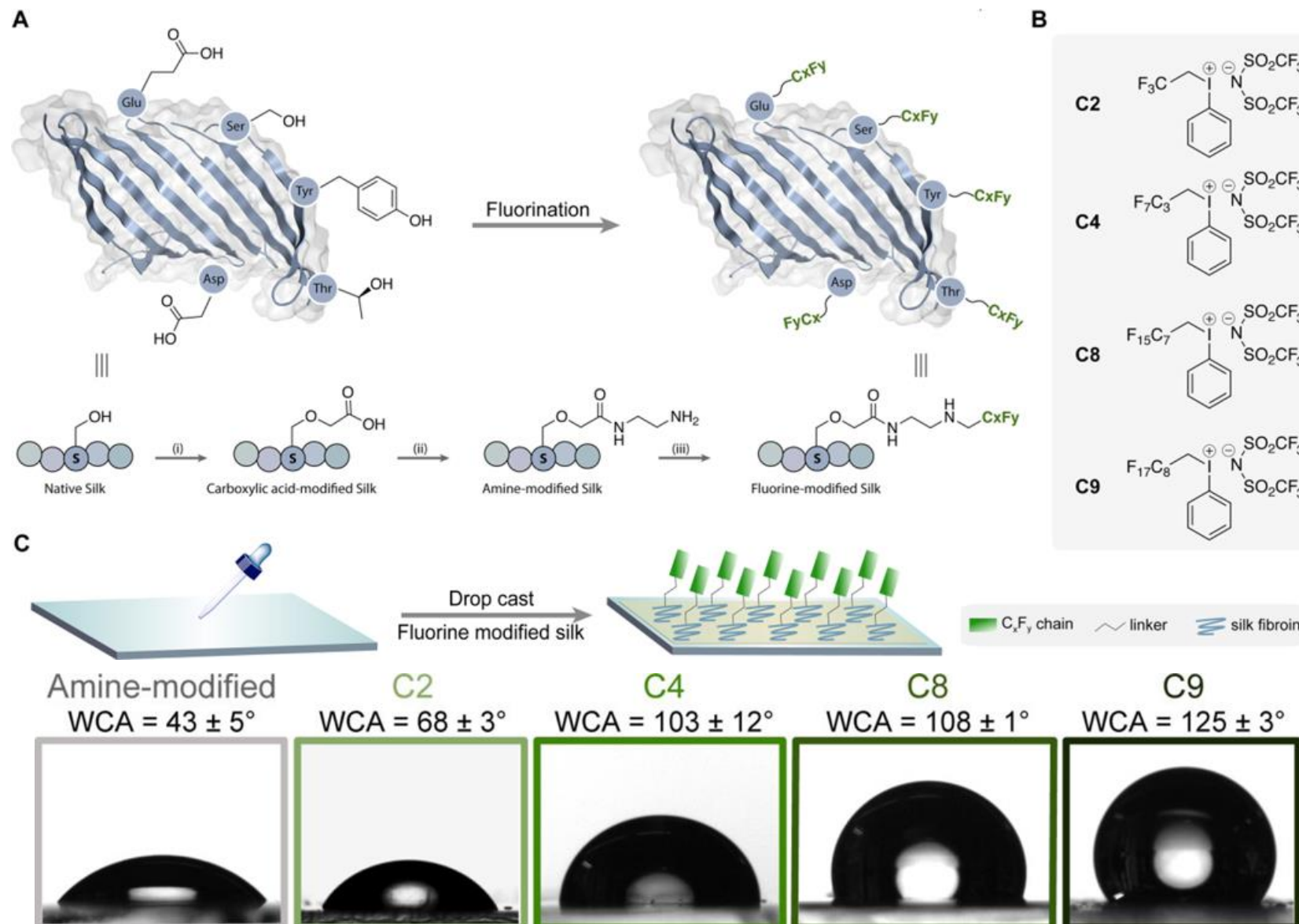
260°C

RECOMMENDED MAX SAFE USE TEMPERATURE

During appropriate use, Teflon does not reach the temperatures required for it to degrade. However, if the coating is overheated the polymer can begin breaking down, and the fumes produced can cause flu-like symptoms. At present, the long term effects of human exposure to these fumes are still largely unknown.

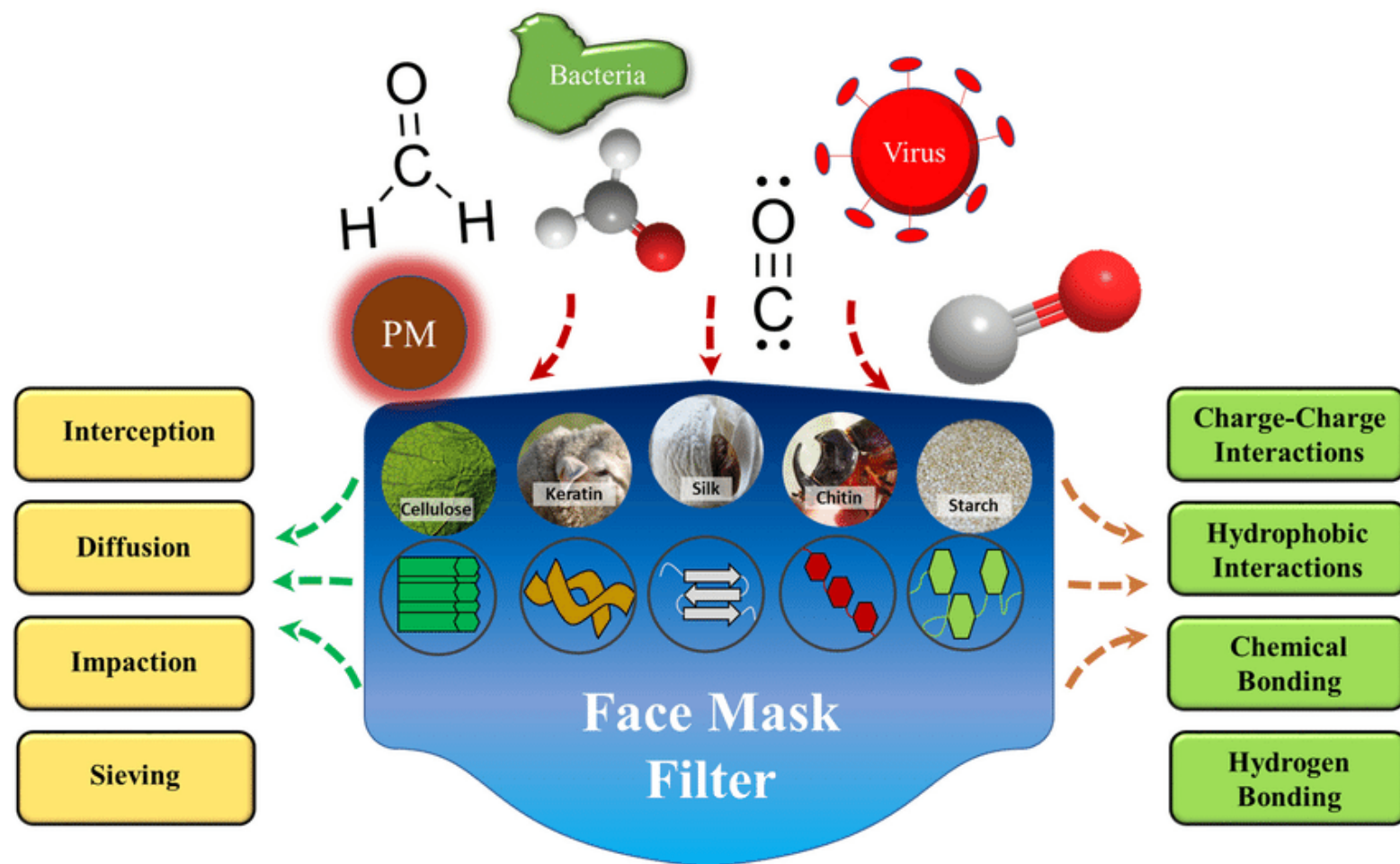


Fluorinated Silk as Biodegradable Alternative for Teflon



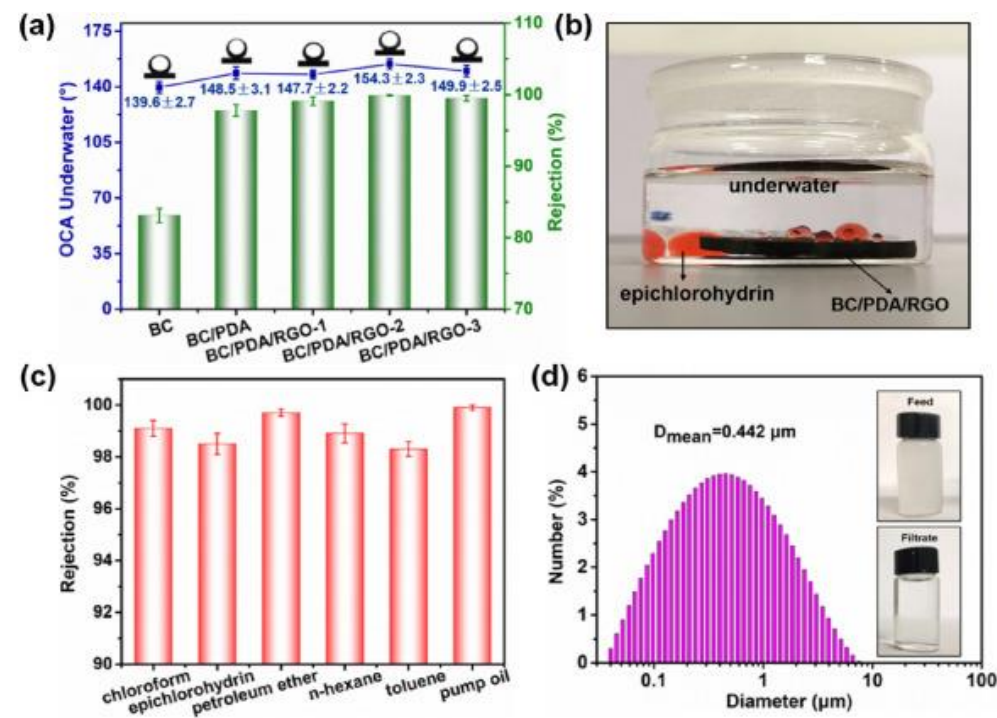
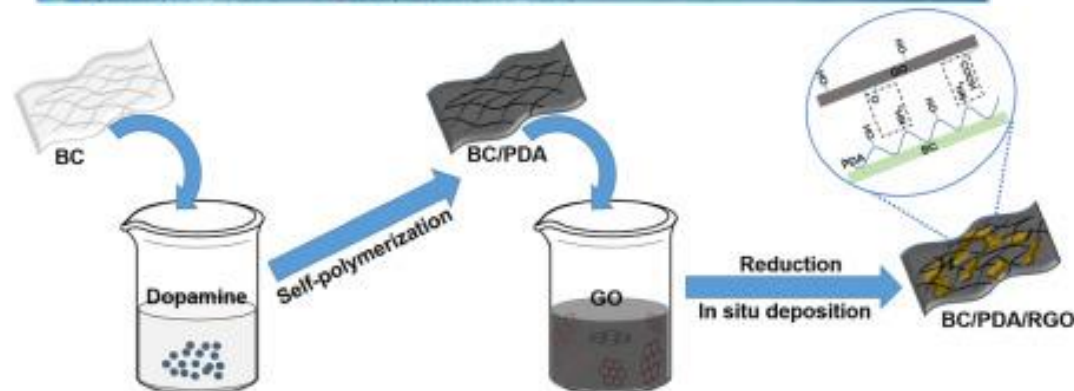
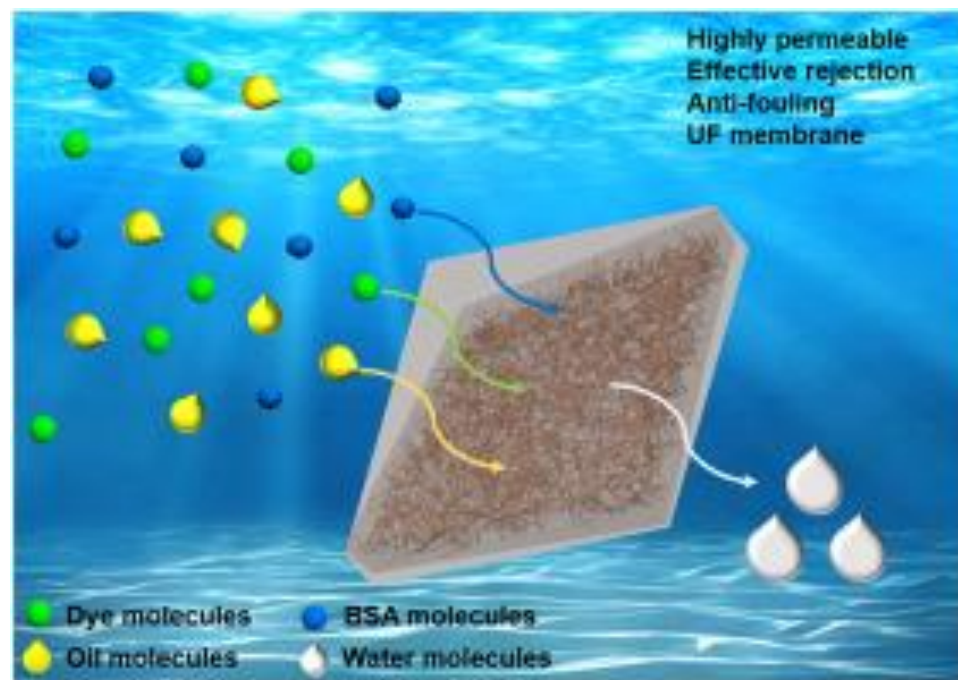
- Biodegradable Alternative
- High water contact angles
- Still using perfluorocarbons

Biopolymers as Filtration Membranes



- Modifiable with green chemistry and fabrication techniques
- Biodegradable – ideal for single use
- Non-toxic and safe

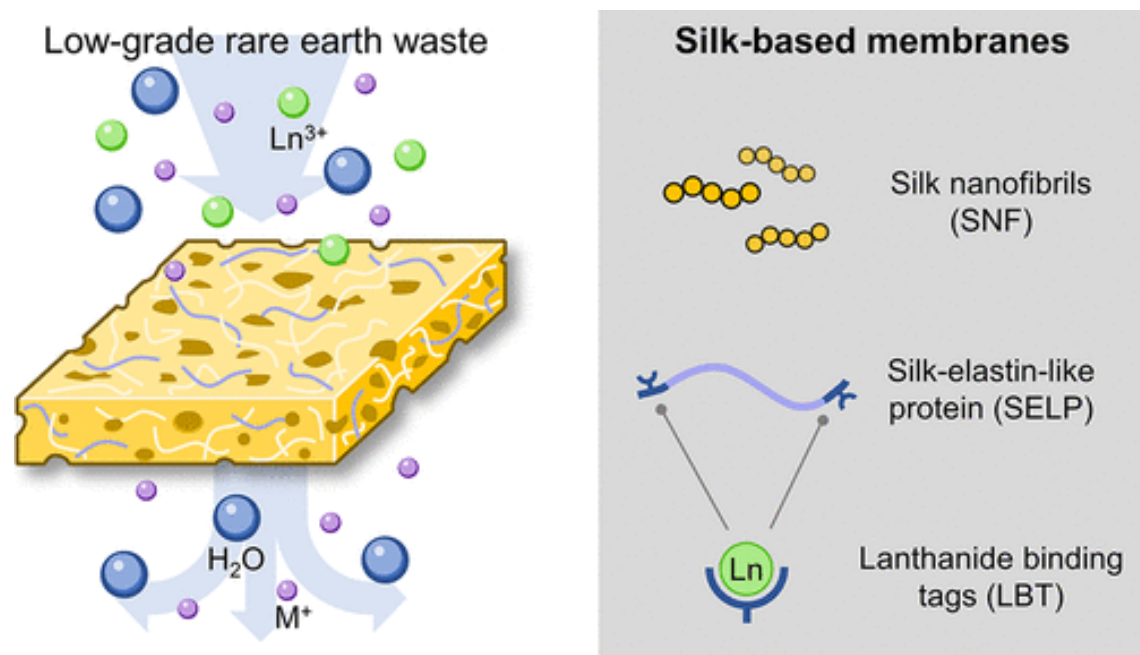
Bacterial Cellulose Filtration Systems for Wastewater



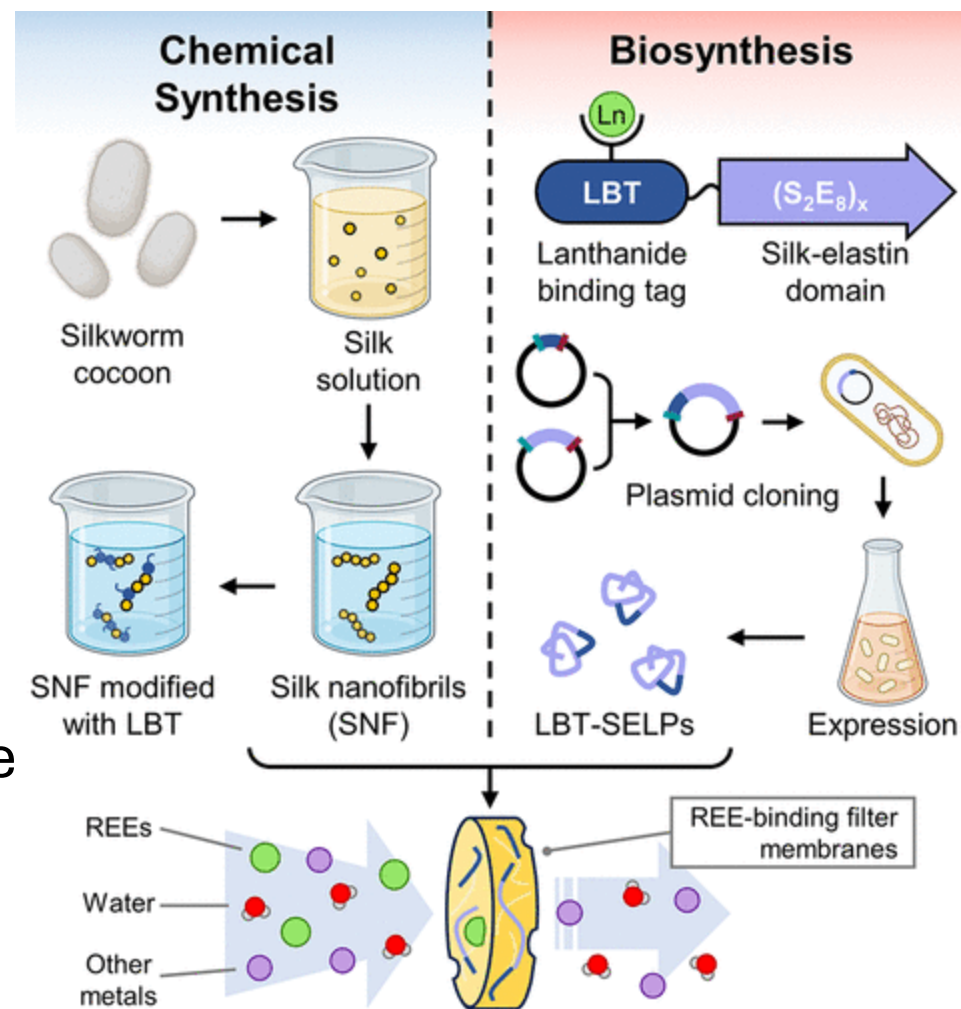
Hu, Y. et al. *Journal of Membrane Science*, 2021

- Polydopamine coated BC membranes show good affinity for most oils and dyes
- Wastewater treatment strategy

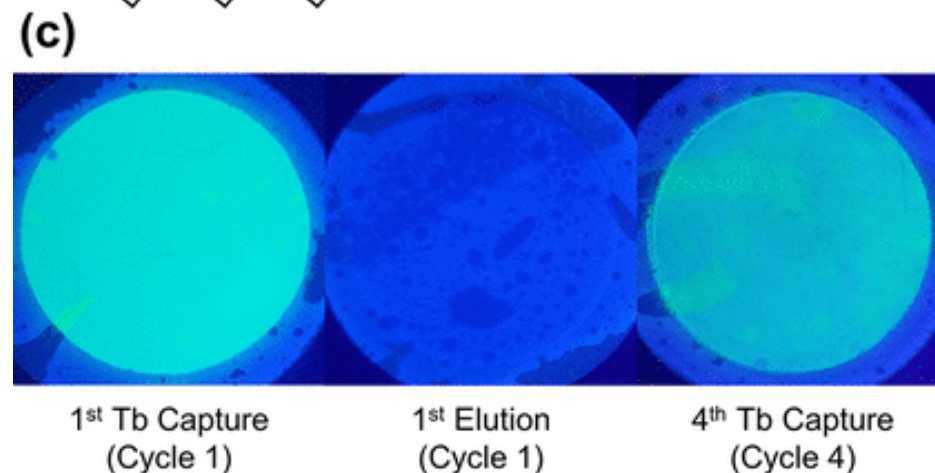
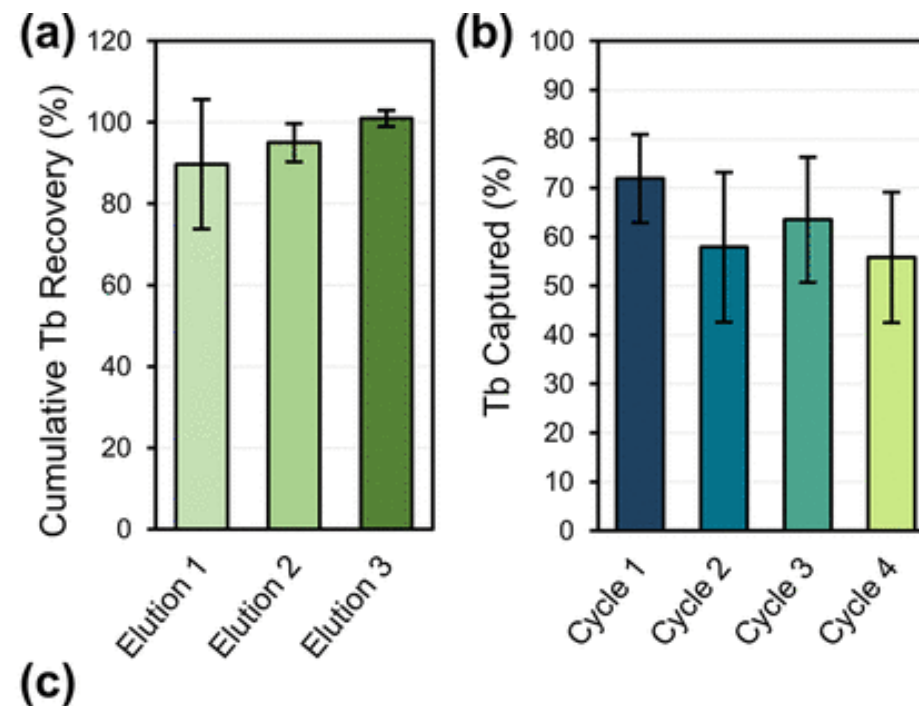
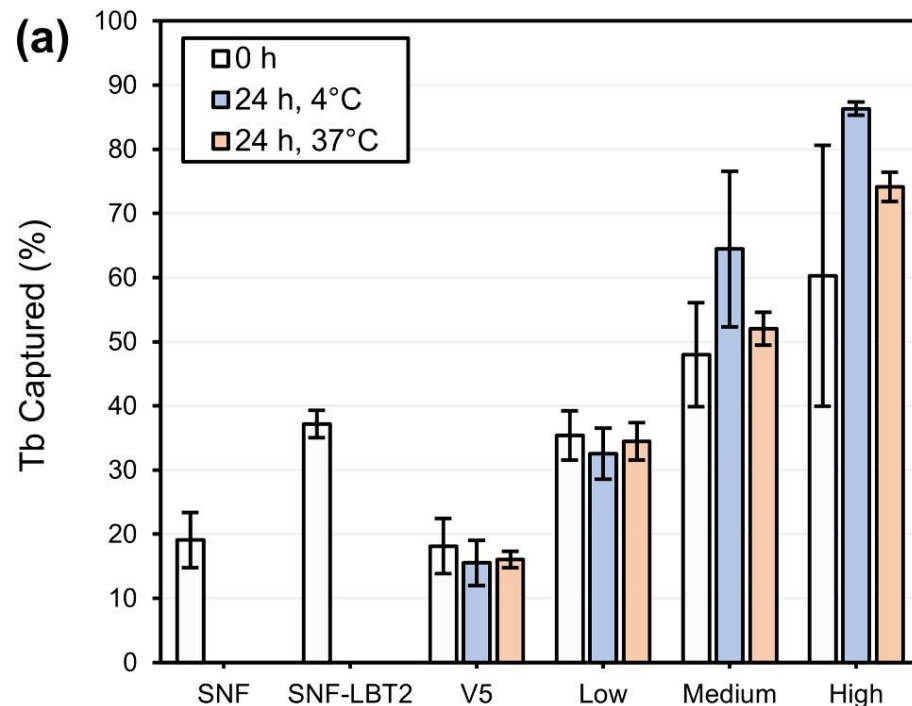
Silk Membranes utilized for Recovering REEs



- Silk membranes modified to include a Lanthanide binding moiety
- Can purify and recover rare-earth elements from waste streams
- Reduce mining of rare-earth elements

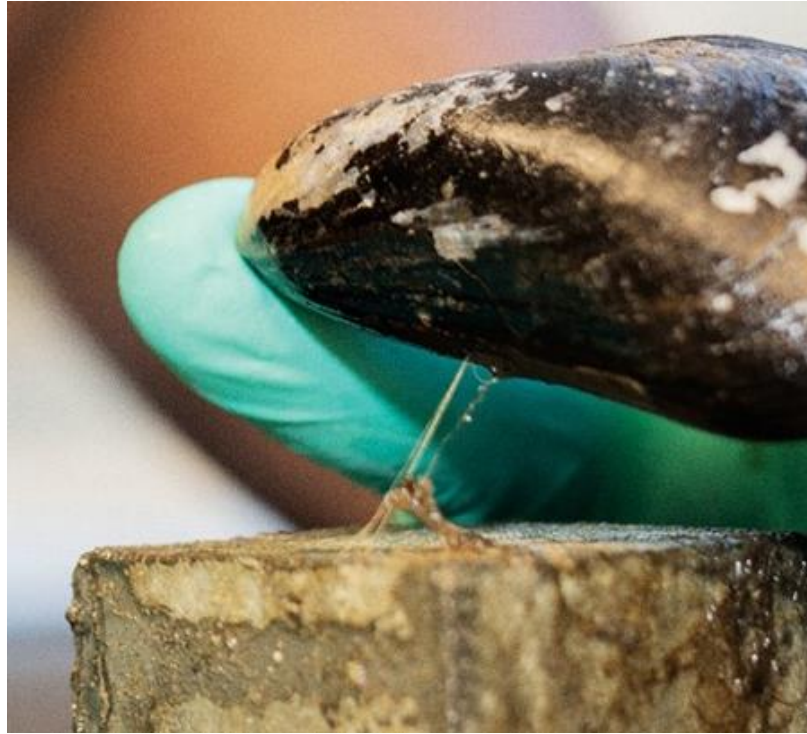


Silk Membranes utilized for Recovering REEs

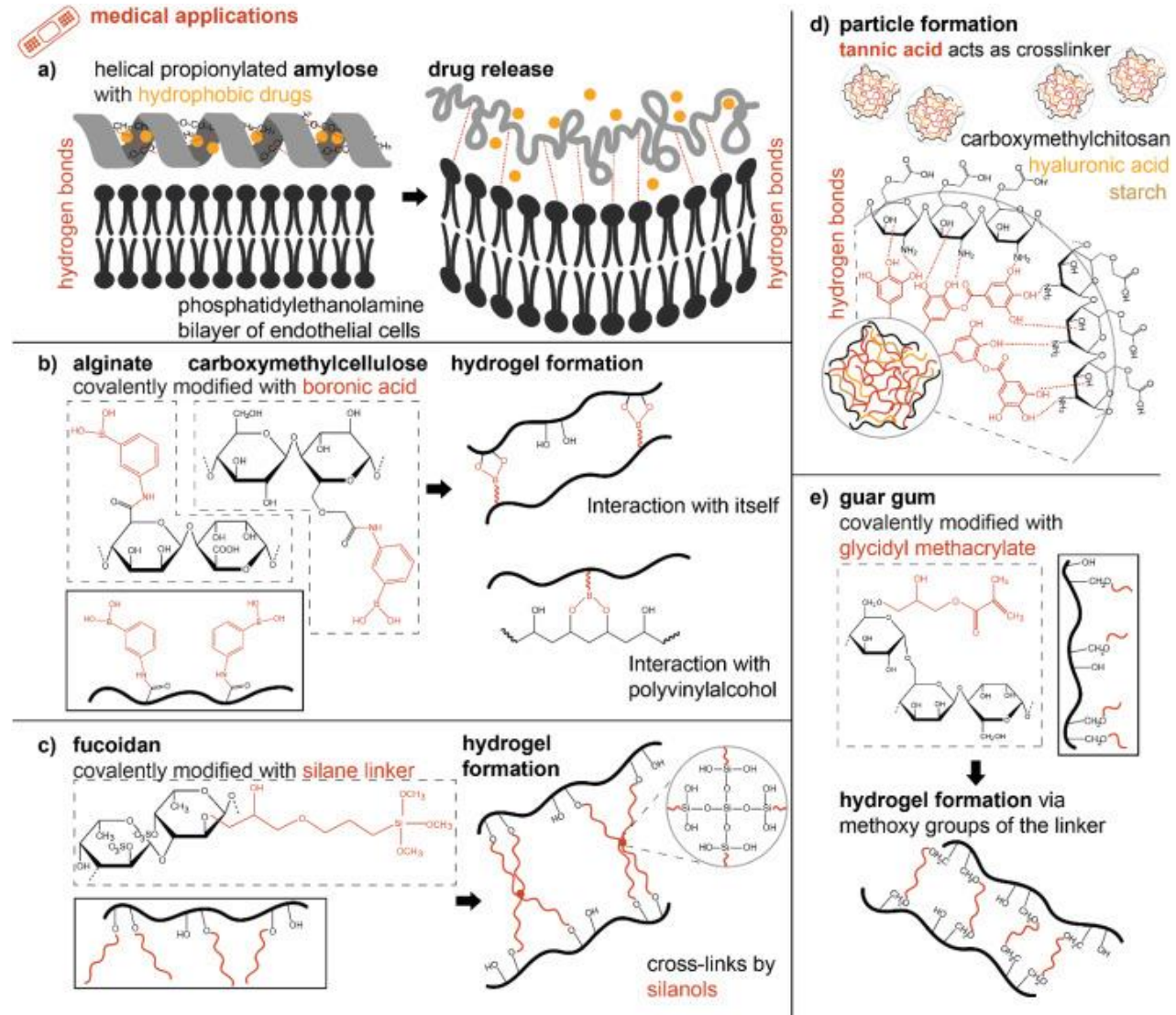


- Upto 80% Terbium captured from solution
- Terbium recovered by eluting membrane with acidic solution
- Membrane is reusable

Biopolymer-based Adhesives



- Adhesives made from biopolymers inspired by adhesive materials in nature



Biopolymer-based Elastomer Alternative to Silicones



B-SILK™ VALUE PROPOSITION

B-silk™ is result of **13+ years of deep R&D**. Now, this patented and proprietary polypeptide is ready to effectively meet the market demand **to replace silicone elastomers across Beauty & Personal Care**—

BIOBASED & BIODEGRADABLE

Unlike silicone elastomers, b-silk™ is biodegradable

B-silk™ is USDA Certified Biobased product

Vegan Verified by Eurofins Chem-MAP

Microbiome friendly

FORMULATOR FRIENDLY

B-silk™ is highly versatile — it is stable, robust, and does not negatively react with other ingredients found in skincare, suncare, color cosmetics, or haircare.

CLINICALLY PROVEN CONSUMER BENEFITS

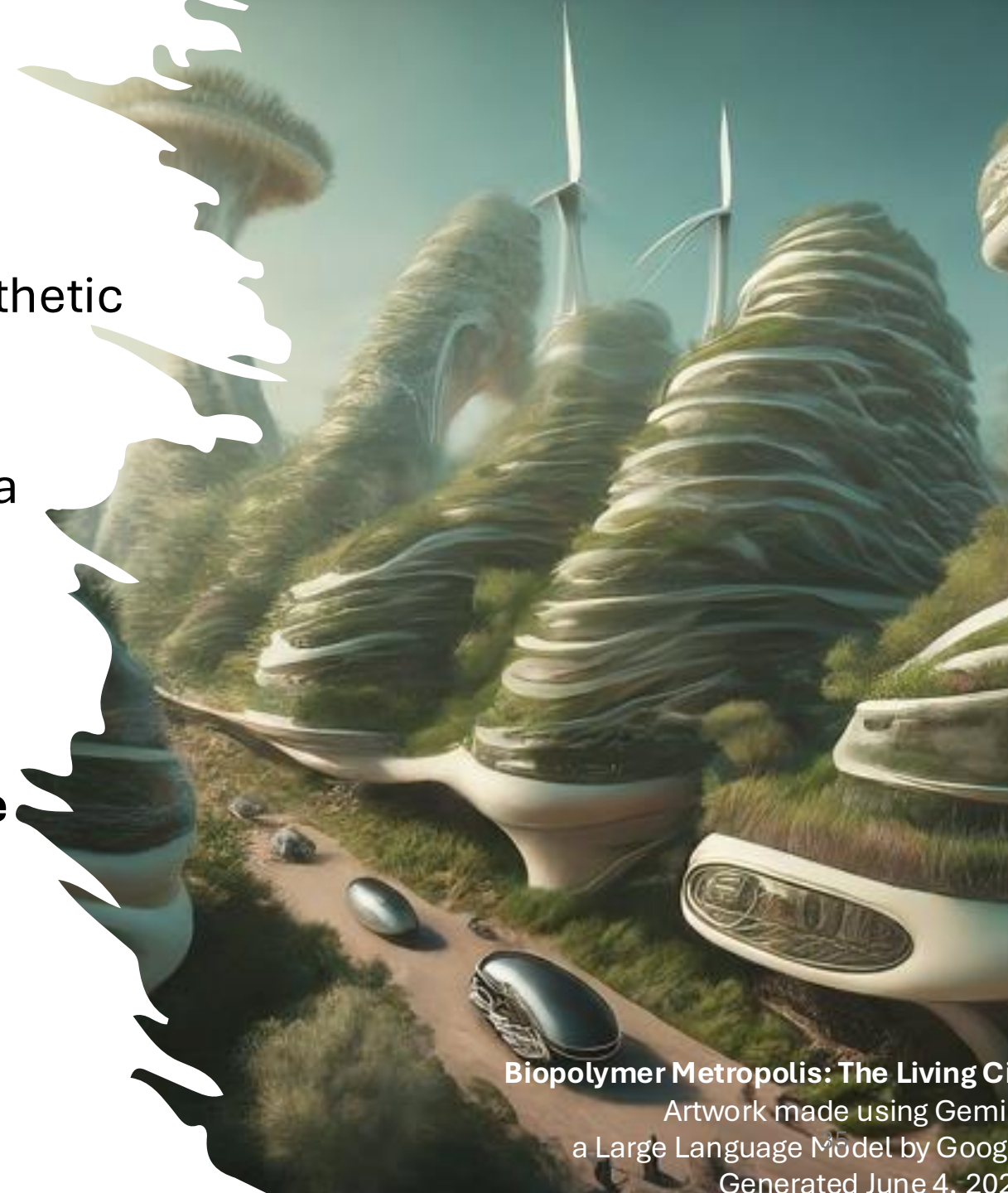
B-silk™ has been on the shelf in hair care products since 2020 and boasts 20+ established benefits, including giving the appearance of firmer and more elastic skin, making the cosmetic signs of aging less noticeable, increased pollution cleansing, hair curl retention, and more.

B-silk™ Value Proposition & Market Differentiators — 35

- Silicones provide the slip and smoothness in many cosmetic and medical products
- Fossil fuel generated, many health and concerns
- Recombinant spider silk-based alternative produced from bioengineered yeast

Final Thoughts!

- Biopolymer replacements for traditional synthetic polymers have several applications
- Cost of manufacturing, cost of goods is still a concern
- **Is scale-up feasible?**
- **Can existing manufacturing techniques be translated for biopolymers?**



Biopolymer Metropolis: The Living C

Artwork made using Gemini

a Large Language Model by Google

Generated June 4, 2023