What are Plastics? Envisioning the Next 100 Years of Polymers

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Taking inspiration from the Phoenix Public Works

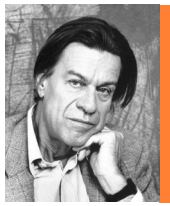
The world will produce 57M pounds of plastic during the next 30 minutes!

Presentation Outline

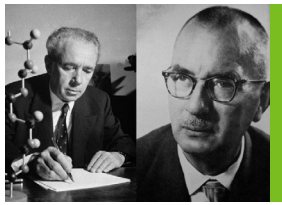
- **Plastics *versus* polymers**: Defining the landscape
- Polymer **structure-viscoelastic properties-processing-performance** relationships
- Topology and morphology influencing **recycling decisions**
- **Bio**polymers, **bio**plastics, **bio**based, **bio**sourced, and **bio**degradation

Nobel Laureates Leading the Path for Innovation

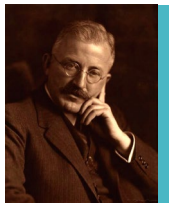
Robert Grubbs
Air stable metallic compounds for metathesis



Pierre-Gilles de Gennes
Order-disorder transitions



Ziegler-Natta
Catalyst for synthesis of polyethylene/polypropylene



Hermann Staudinger
Macromolecular Chemistry

We are approaching one trillion pounds of global plastic per year!

However, have we considered the larger polymer industry?

Reckoning with the U.S. Role in Global Ocean Plastic Waste; National Academies Press: Washington, D.C., 2022. https://doi.org/10.17226/26132.

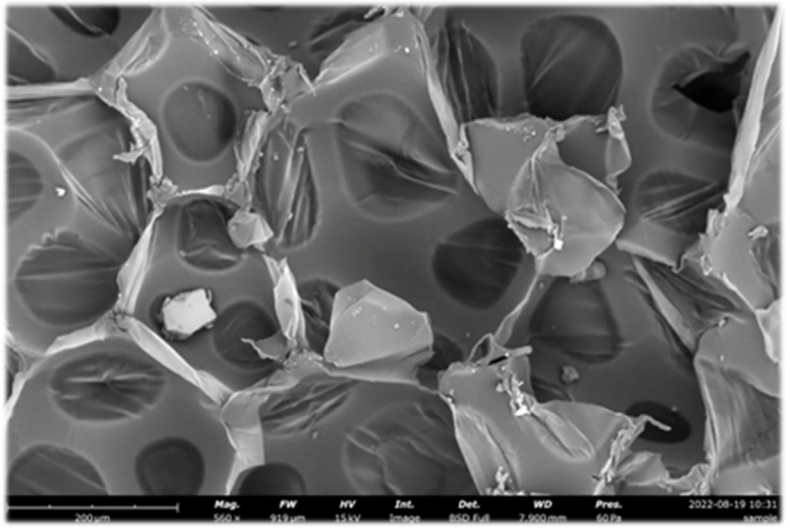
Plastic *versus* Polymer

Plastic (*noun*): a synthetic thermoplastic material that is **moldable with heat** and has a glass transition temperature **above room temperature**

e.g., plastic utensils, bags, hair clips, milk jugs, pipes, toys

Polymer (*noun*): any **macromolecular structure** with a repeating unit

e.g., DNA, proteins, rubber tires, mattress foams, adhesives and glues, paint, laminate flooring



Annual US Plastic Production

MMT = million metric tons // US Recycling Rates

1 Poly(ethylene terephthalate)

2 High density polyethylene

3 Poly(vinyl chloride)

4 Low density polyethylene

5 Polypropylene

6 Polystyrene

7 **Other: Polyurethane, Polycarbonate, Polyamides**

2015 US Plastic Production https://cen.acs.org/environment/recycling // 2019 US Recycling Rates, *Resources, Conservation and Recycling*, **2022**, *183*, 106363

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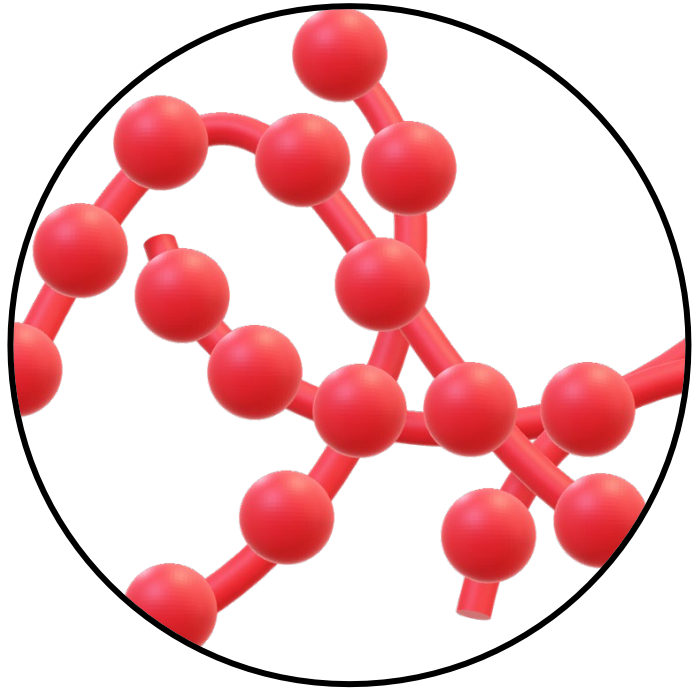
Polymers: Ubiquitous beyond “simple” plastics

*All numbers represent global market shares

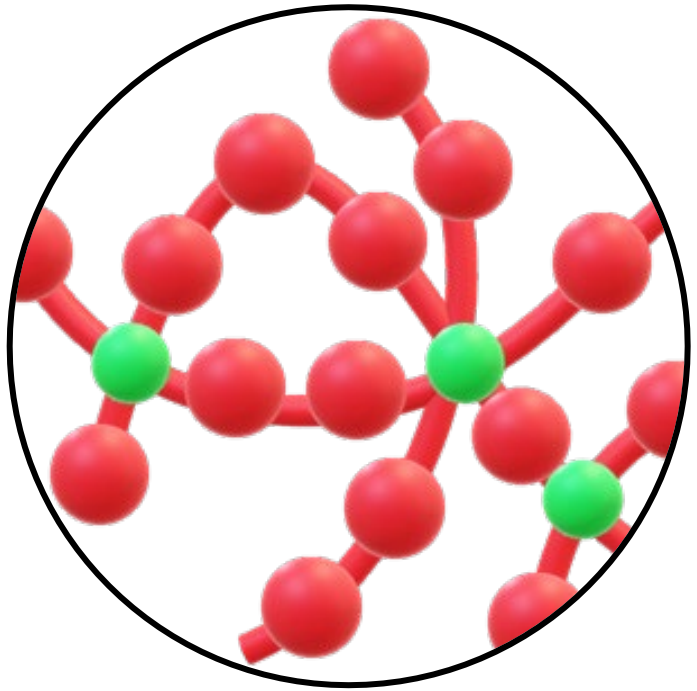
Thermal Behavior Dictates Application and Re-processability

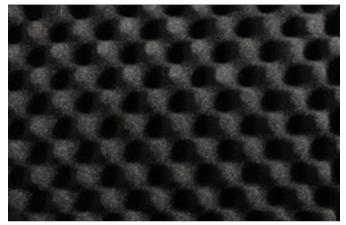
Thermoplastics



- **Thermally re-processible** with concern for molecular weight change
- Common for **consumer products**

Thermosets

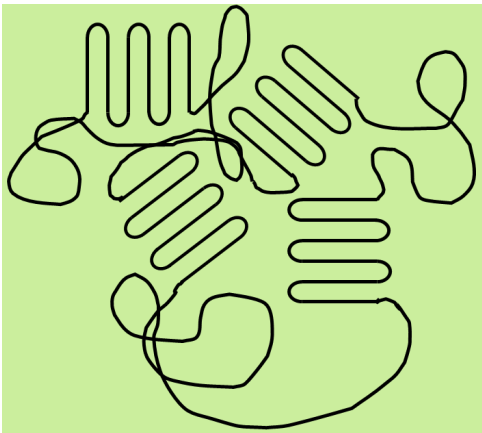




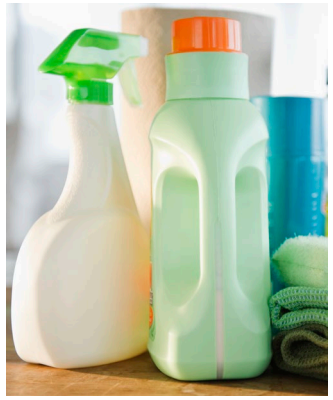
- **Chemically crosslinked** not thermally re-processible
- Common for **structural and higher temperature applications**

Morphology provides insight into polymer properties and performance

Semi-crystalline



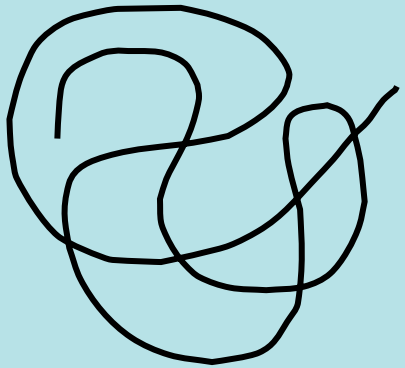
Contains **crystalline (T_m)** and **amorphous (T_g)** phases



Optically **Clear** or **Opaque (depends on crystal size)**

Fatigue and **Chemical Resistance**

Amorphous



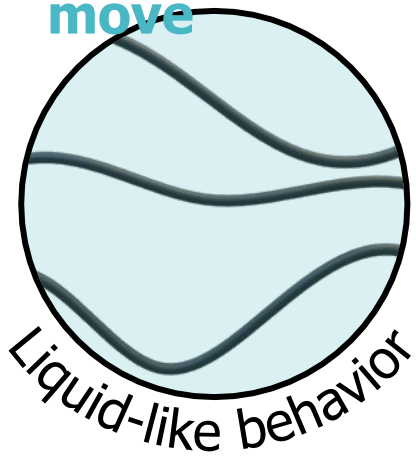
Relatively **disordered** structure where **entanglement** plays a critical role

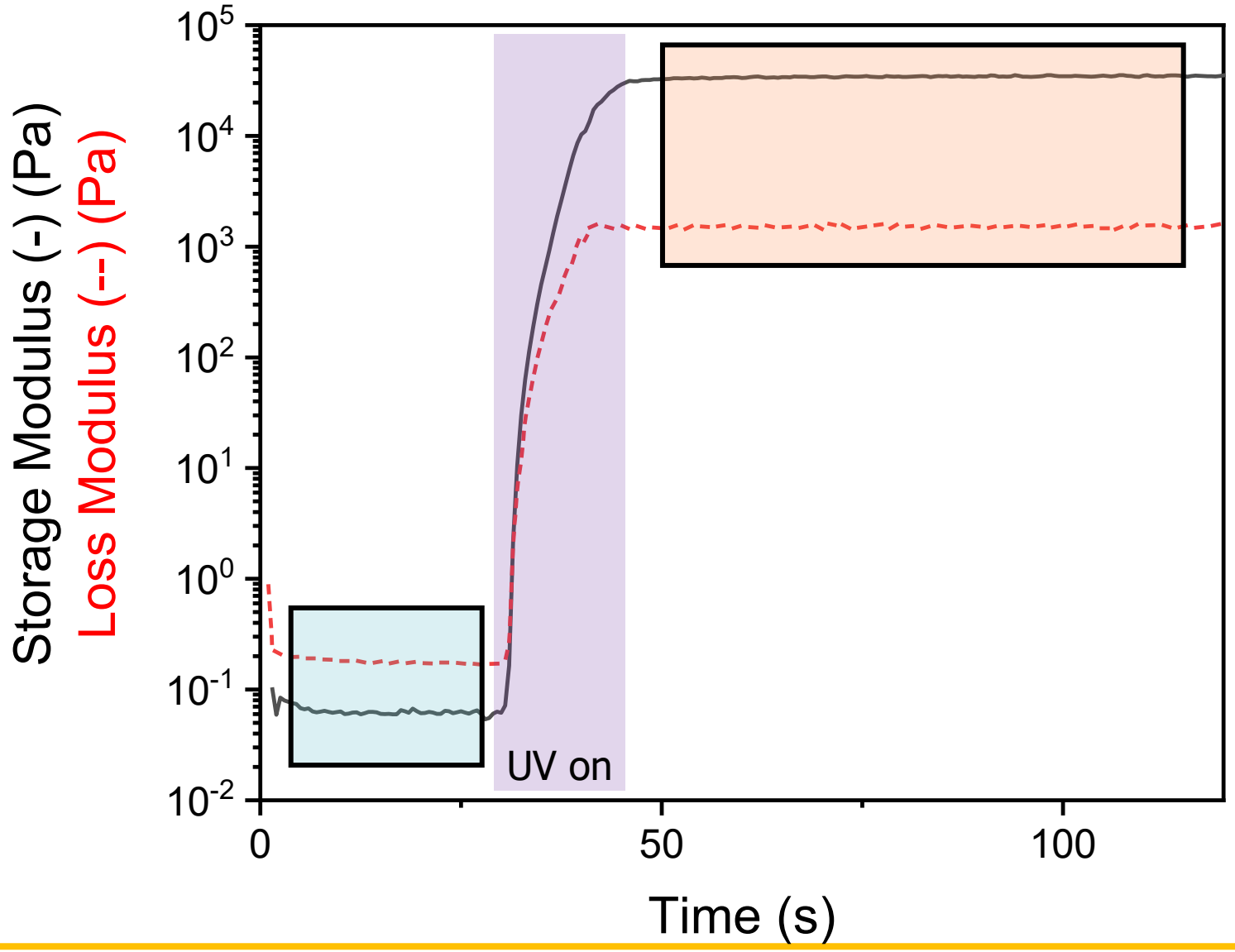
Optically **Transparent**

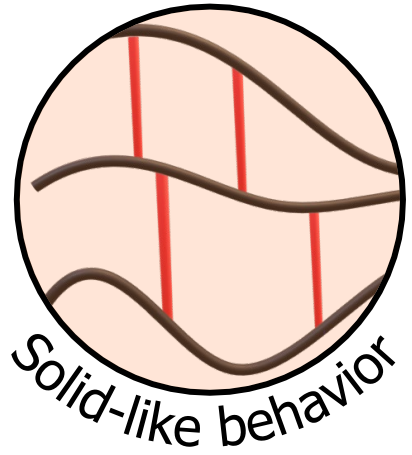
High **Compressibility** and **Low Moisture** Sensitivity

UV-initiated crosslinking transitions viscoelastic polymer behavior from liquid-like to solid-like

- **Liquid-like** behavior
- **Un-crosslinked** linear polymer chains
- Polymer chains are **free to move**

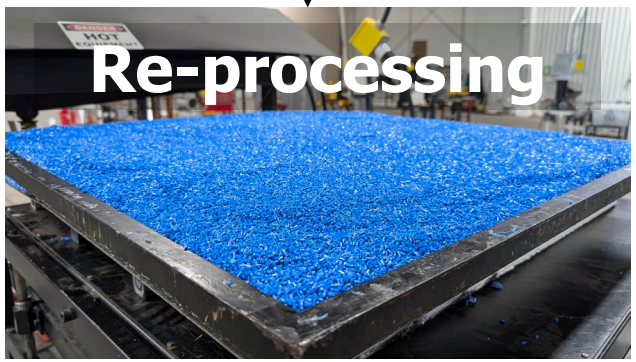




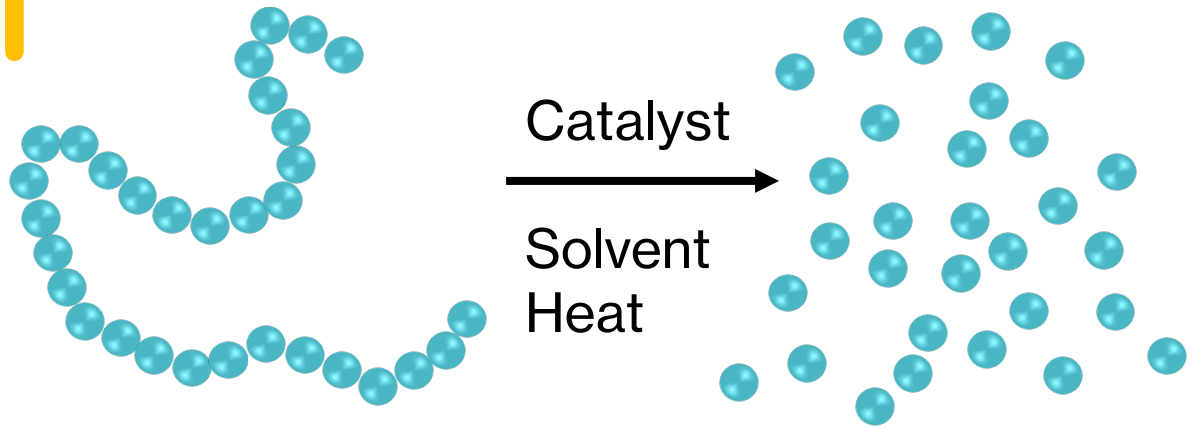


- **Solid-like** behavior
- **Crosslinked** topology
- Polymer chains are **irreversibly crosslinked**

Goodwill microfactory launching mechanical recycling efforts of thermoplastics



Chemical recycling returns polymers to monomers



1 Poly(ethylene terephthalate)

Chemical Recycling Steps

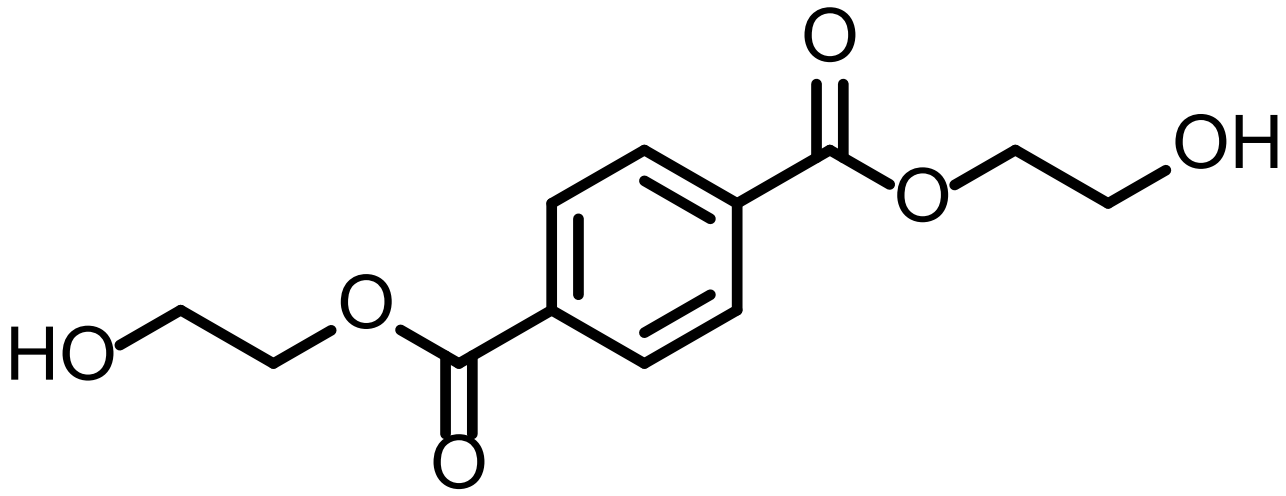
1. Collection
2. Washing
3. Grinding
4. Depolymerization
5. **Monomer isolation**
6. Synthesis into new polymers

Valorizing waste streams from chemically recycled plastics such as poly(ethylene terephthalate) (PET)

Poly(ethylene terephthalate)

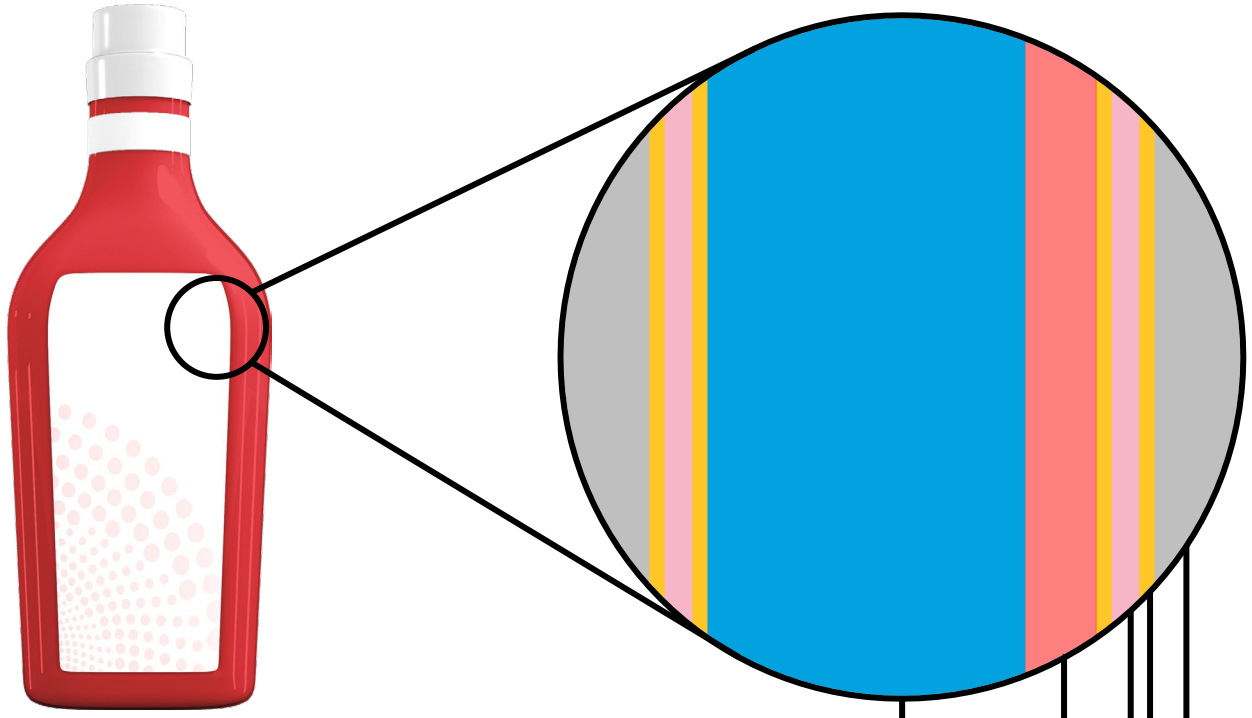
- Over **82 MMT** produced each year[1]
- Global market is estimated at over **$39 Billion**[2]
- **3rd most** common polymer used in the packaging industry[3]
- Market for recycled PET rapidly rising

Bis-(2-hydroxyethyl)terephthalate (**BHET**) is the monomeric glycolysis product of PET



1. https://**www.nrel.gov**/news/program/2021/researchers-engineer-microorganisms-to-tackle-pet-plastic-pollution.html
2. https://www.**thebusinessresearchcompany**.com/report/polyethylene-terephthalate-global-market-report
3. https://www.**plasteurope**.com/news/PLASTICS_PACKAGING_t209101/

What comprises multilayered plastic containers we enjoy?



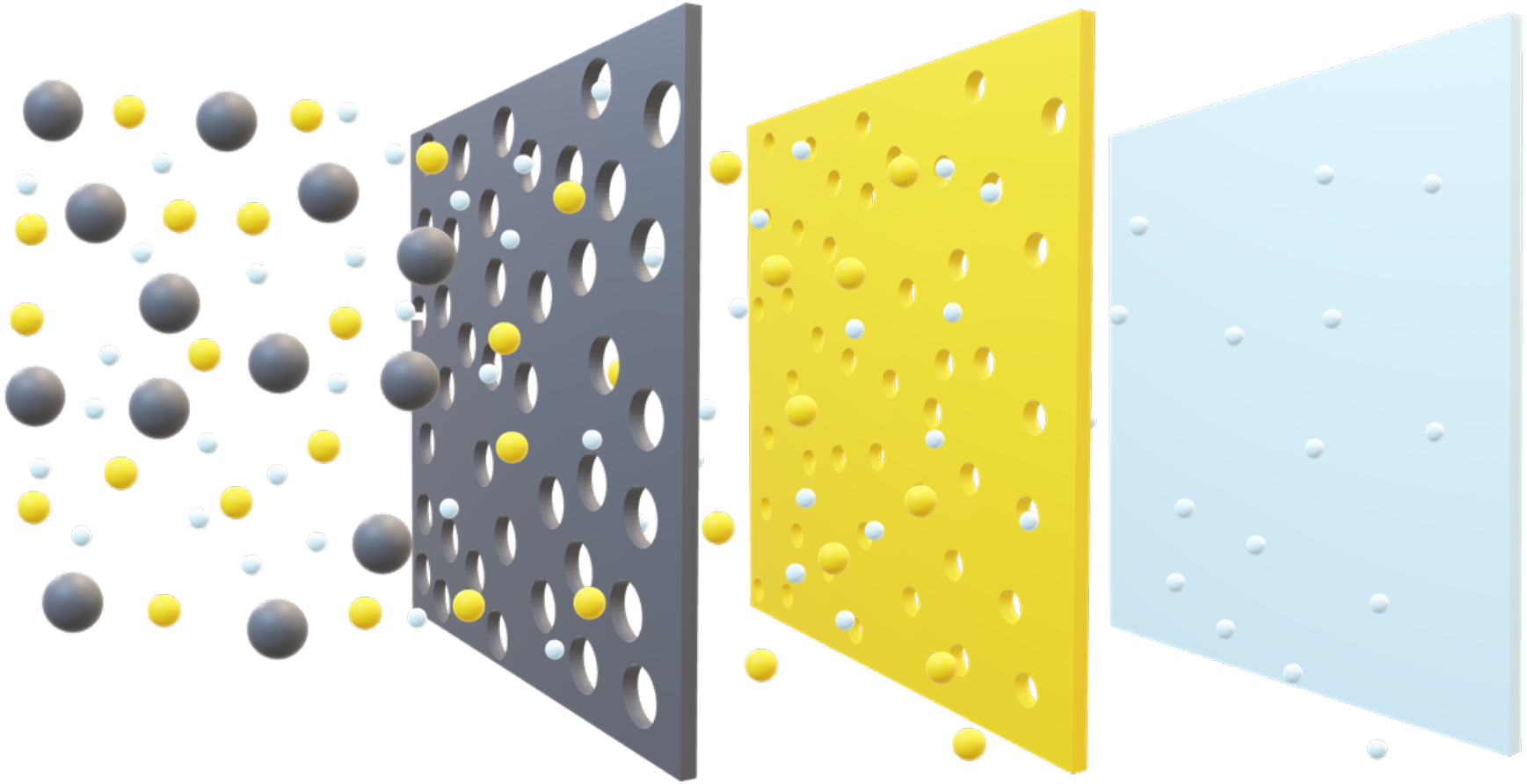
Polyethylene + Regrind Layer
Oxygen Absorbing/Tie-Layer
EVOH Oxygen Barrier Layer
Oxygen Barrier Layer/Tie Layer
Polyethylene Layer

- Different plastics for different applications have more complex compositions
- Complex compositions makes end-of-life processing difficult

Mebius-pkg.co.jp. https://www.mebius-pkg.co.jp/en/technical/technology

Multi-layered membranes for emerging separation and purification technologies

- **Membranes** are **critical** component for **purification** processes
- **Multi-layered** membranes find use in a **variety of applications**
- **Limited end-of-life** strategies provide **opportunity** for **sustainability** research

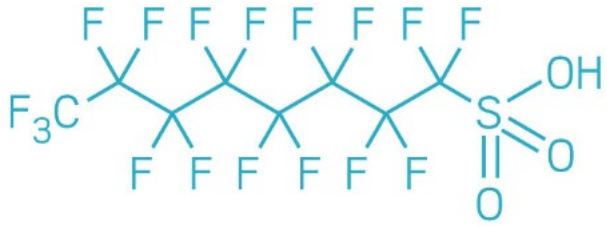


Multi-layer membrane to separate particles or molecular compounds with varying diameters

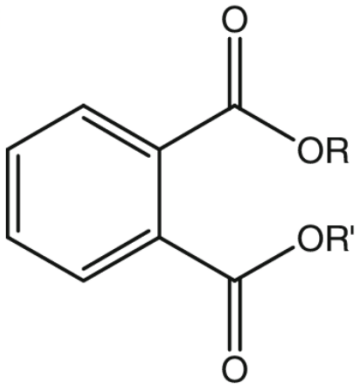
Additives Galore: Complicating the Polymer Waste Stream

Additives are designed to enhance performance, improve processibility, increase mechanical durability, and facilitate polymerization processes

- **Plasticizers**
- Anti-plasticizers
- Anti-oxidants
- UV absorbers
- Glass fiber
- Nucleators
- Carbon fiber
- Calcium carbonate
- Flame retardants
- Pigments
- Dyes
- Release agents



PFOS



PHTHALATES

Critical issues

Minimal amounts

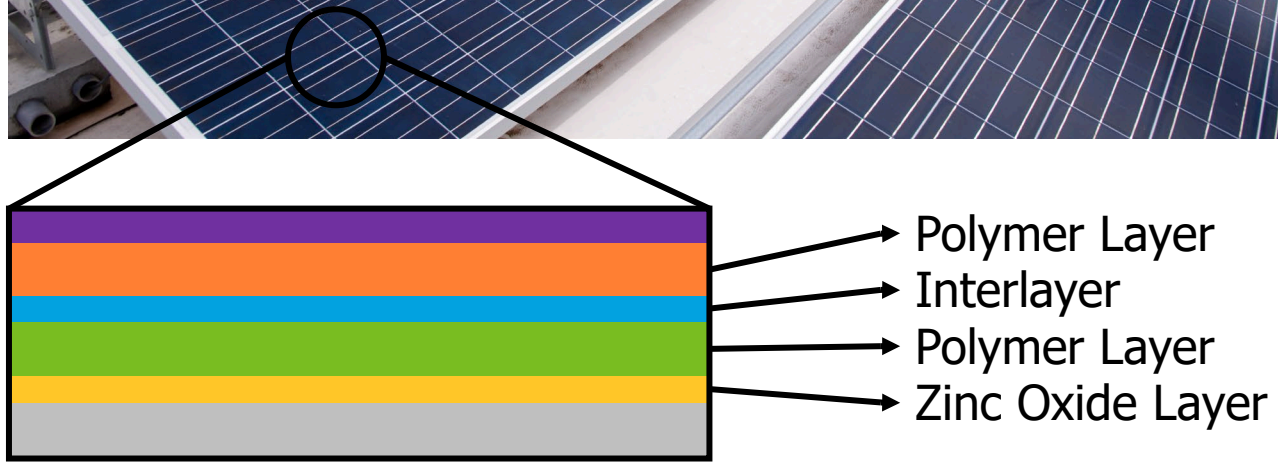
Miscibility/Dispersibility

Migration prevention

Toxicity

- Anti-microbial agents
- Impact modifiers
- Anti-static agents
- Blowing agents
- **Surfactants**
- **Processing aids**
- Anti-scratch coatings
- Anti-glare coatings
- Smoke suppressants
- Char formers
- Odors
- Reheat agents

Composites complicate reprocessing and end-of-life strategies

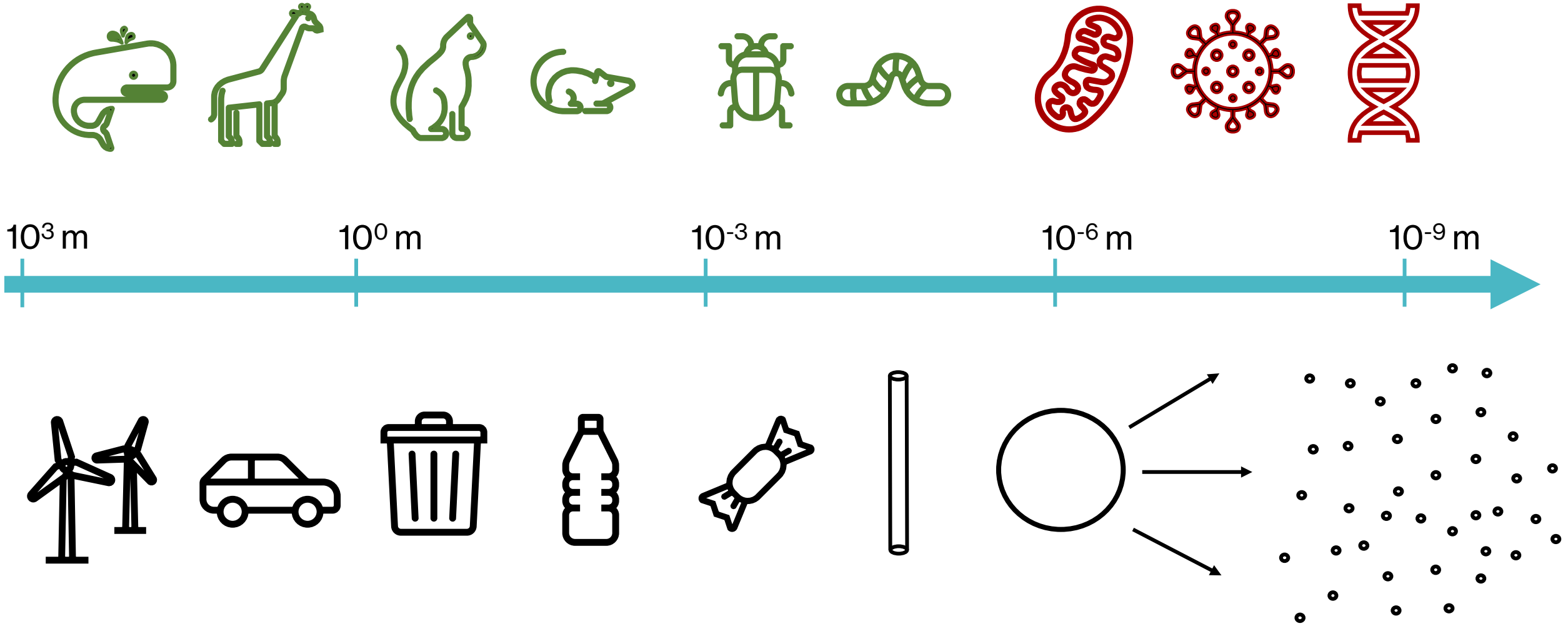


- **Perfluorinated alkyl substances (PFAS)** are **commonly used** in solar panels
- Fluorinated polymers provide **numerous advantages**:
  - Improved **efficiency**
  - Enhanced **durability**
  - **Low maintenance**
  - **Chemical resistance**
  - **Low surface energies**
- Federal initiatives to **minimize PFAS** in **manufacturing** and **disposal** making **end-of-life** for solar panels difficult

US EPA, O. Key EPA Actions to Address PFAS. www.epa.gov.

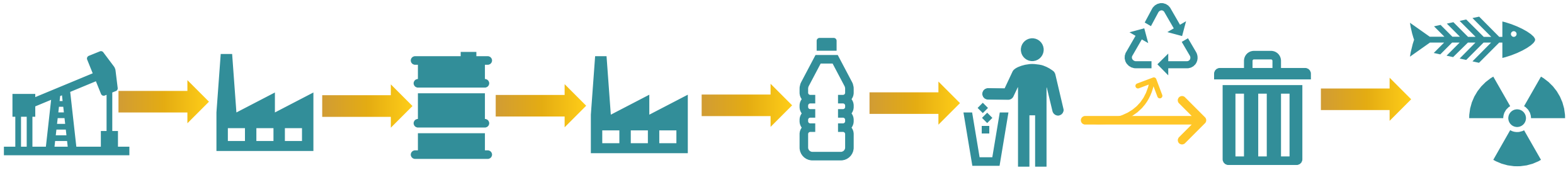
Kromhout, W. W.; Angeles, U. of C.-L. Tandem polymer solar cells that set record for energy-conversion. phys.org. https://phys.org/news/2012-02-tandem-polymer-solar-cells-energy-conversion.html.

Micro- and nanoplastics and the human environment

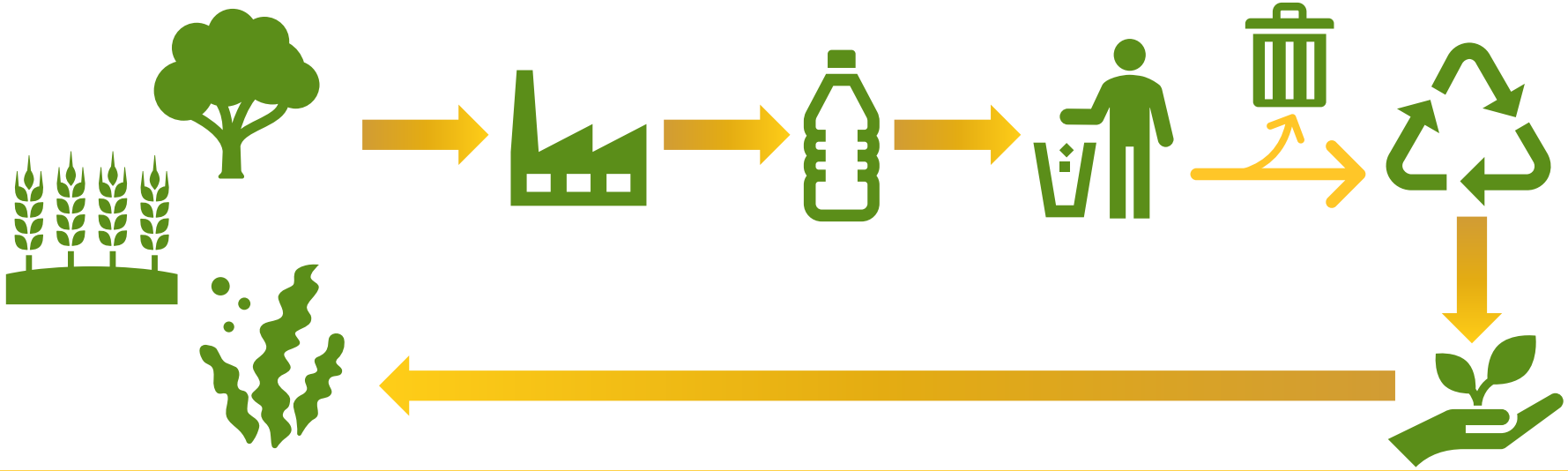


Envisioning a circular approach for the plastic factory of the future

Traditional Manufacturing Process



Environmentally Focused Approach



- ✓ **Renewable monomers**
- ✓ **Recycled feedstocks**
- ✓ Green chemistry
- ✓ Increase recyclability
- ✓ **Direct path to add value back to environment**
- ✓ Economically equal

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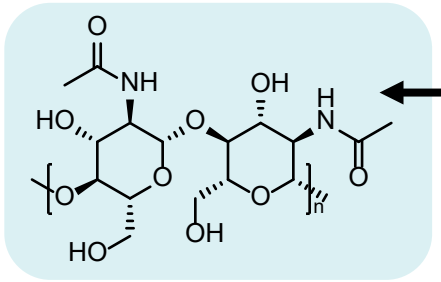
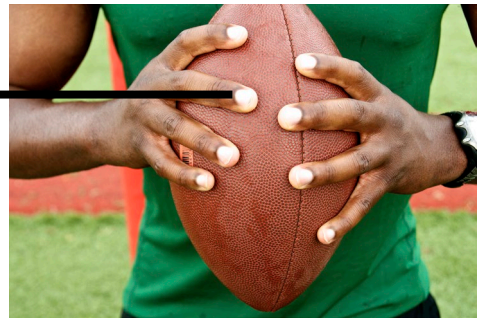
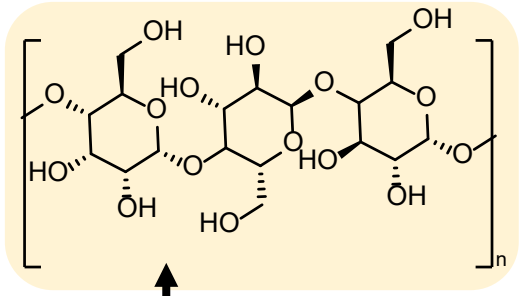
Nature's biopolymers provide additional platforms for sustainable production

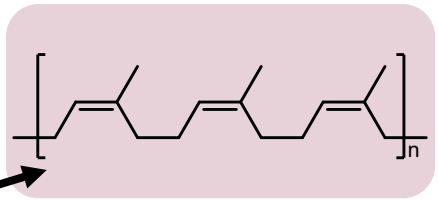




Chitin
Fingernails



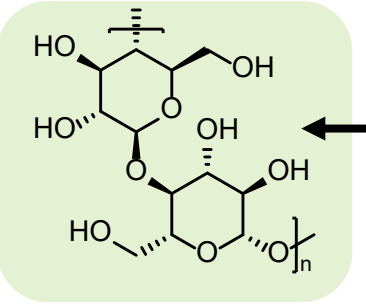
Polysaccharides
Starches and sugars



Natural rubber
Tree sap

Lignin
Hardwood

Cellulose



Proteins and DNA

Functionalization of biopolymers have found use in

- Medicine
- Construction
- Clothing
- Single-use food packaging
- Food additives
- ...and more

Bioderived and biodegradable terminology

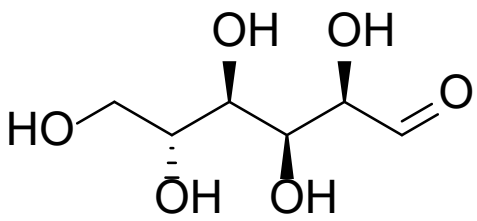
Bioderived

Monomers sourced from plant, animal or other natural resources

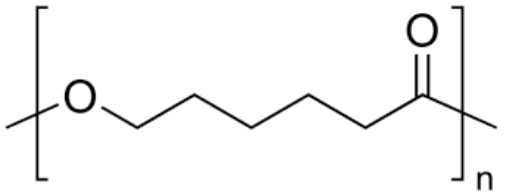
versus

Biodegradable

Polymers can be broken down into non-toxic components under ambient conditions



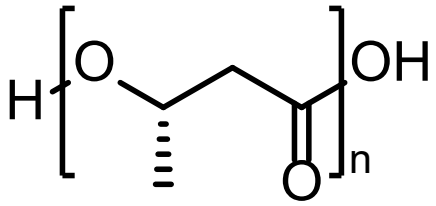
Glucose is a bioderived monomer that can be used to produce poly(hydroxyalkanoates), rapidly emerging polyesters



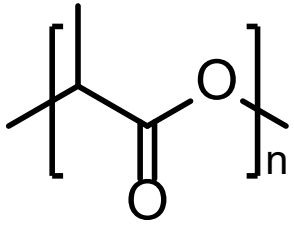
Poly(caprolactone), a biodegradable polyester produced through ring-opening of ε-caprolactone and stannous octoate

Multi-pathway degradation leads to non-toxic or beneficial products in composting

Compostable Polymers



Polyhydroxyalkanoates



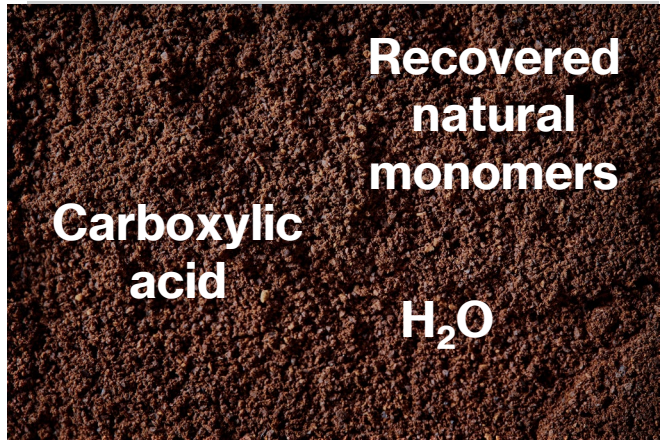
Poly(lactic acid)

UV

Enzymatic

Hydrolysis

CO_2, CH_4



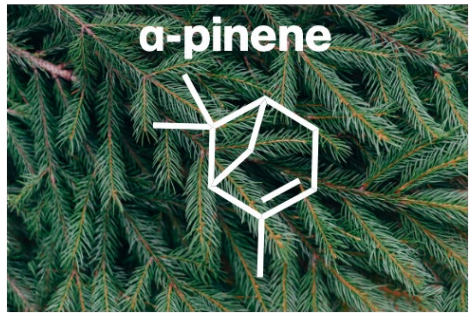
In the marketplace

Food packaging

(100% of food containers at ASU are compostable)

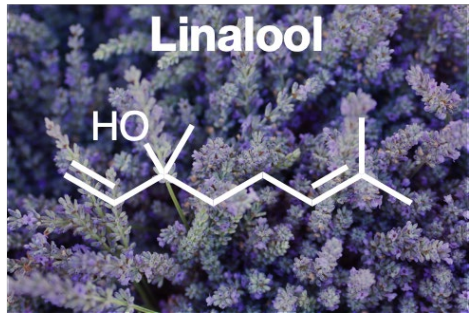
Laundry detergent can be loaded onto water-soluble and biodegradable sheets

Biomass-derived monomers to polymer products



Primary ingredient of turpentine

Antimicrobial properties from citrus



Anti-inflammatory from lavender

Reactants and catalysts

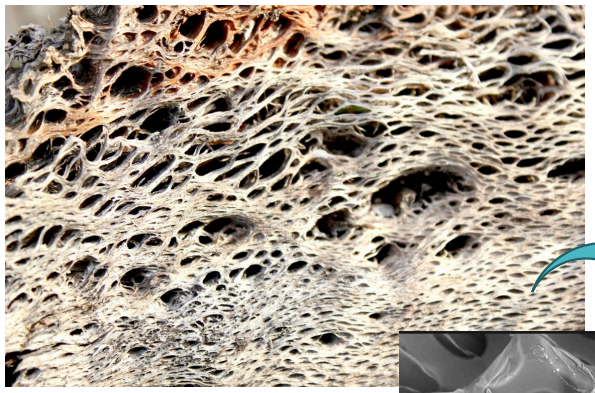
Fuel additives

Food packaging

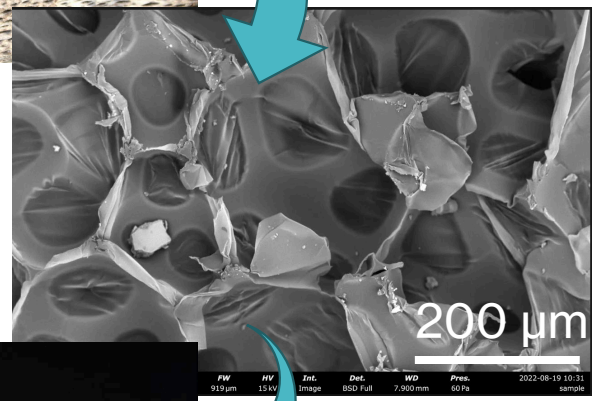
Foam

Hydrogels and skin care

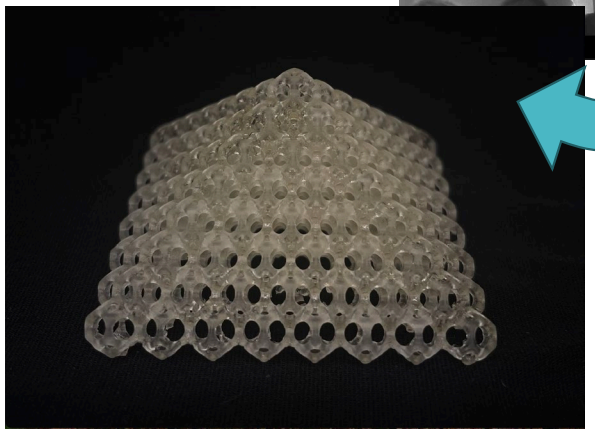
Nature-inspired dematerialization: mimicking both form and function



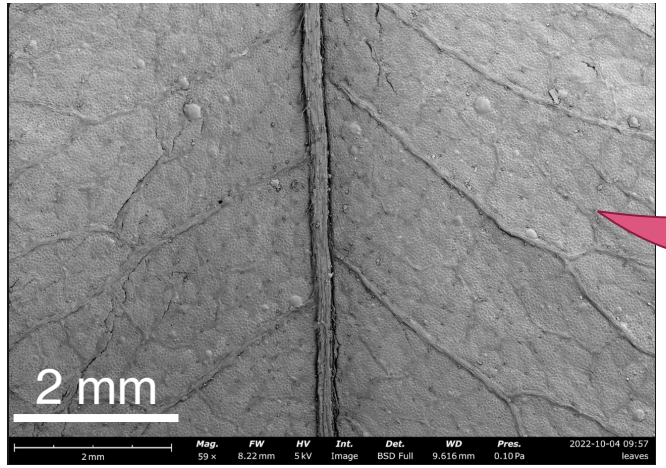
Internal structure of a saguaro cactus



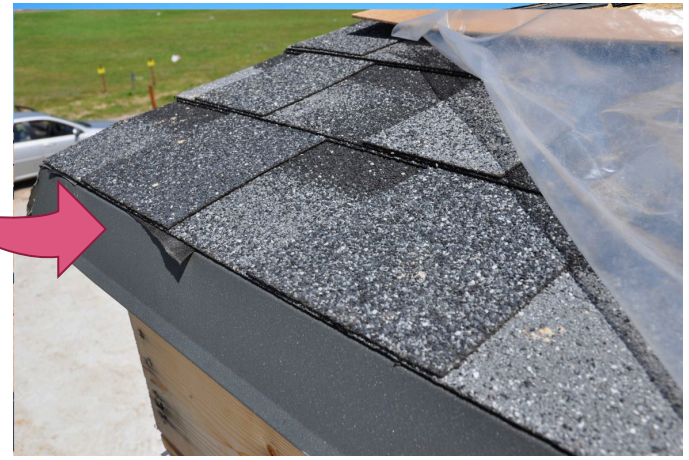
Polyurethane foam pore structure



Lattice architecture for structural materials



Plant transport mechanisms



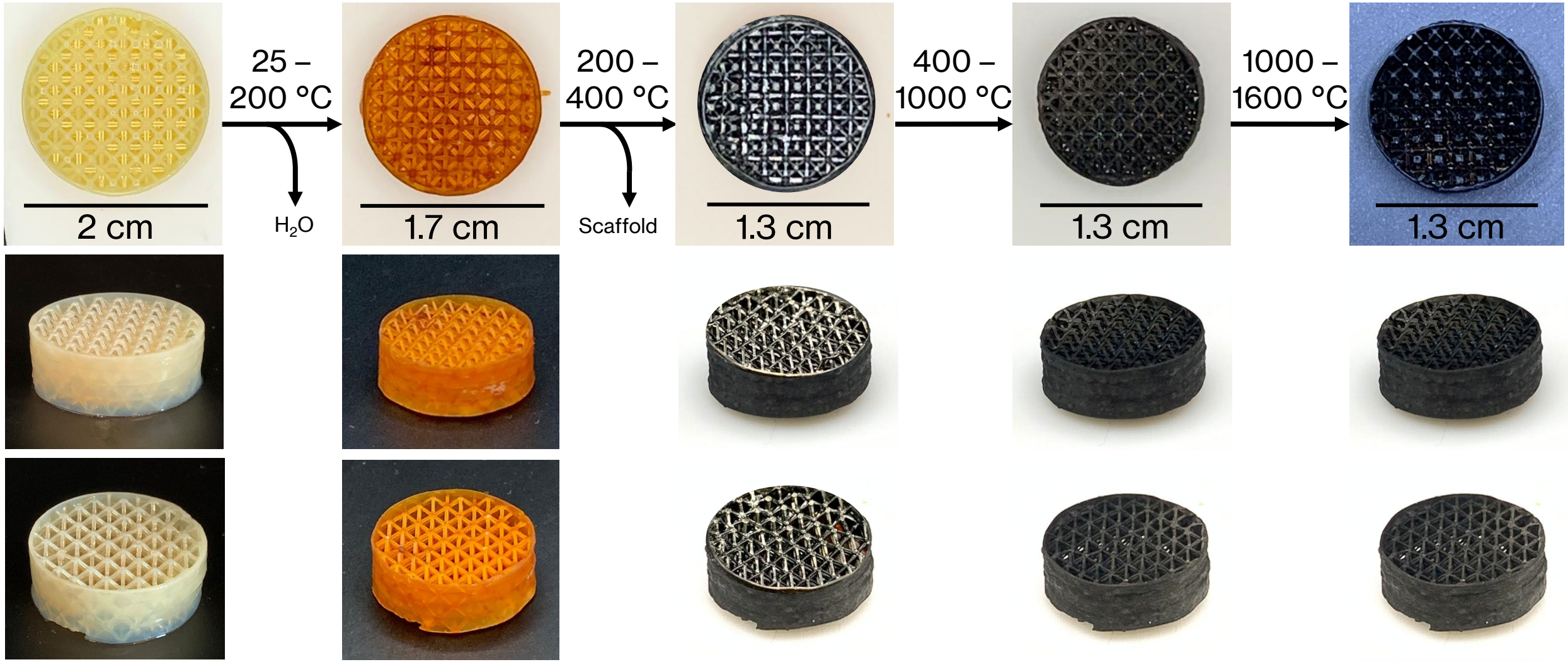
Membranes

Bee hives

Honeycomb structural lattices

Additive manufacturing enables dematerialization

Simply stated, *consume less*



Thank you..

"Innovation is the ability to see change as an opportunity – not a threat"

- Steve Jobs