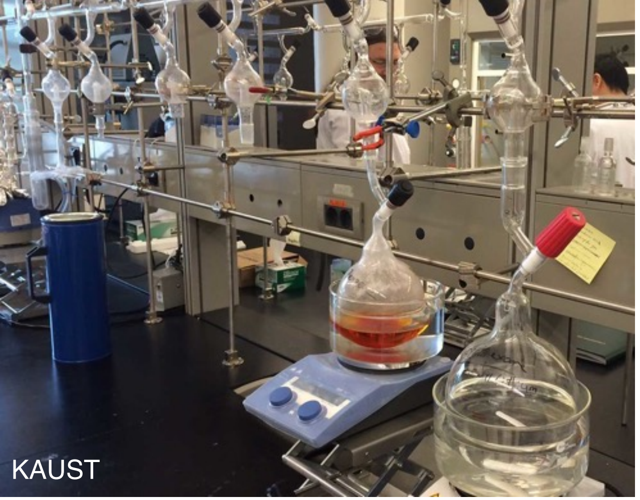
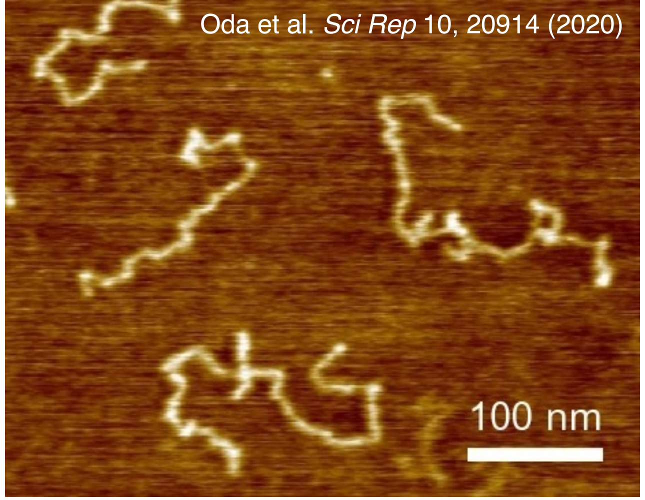





Materials Engineering I (MSE 214)

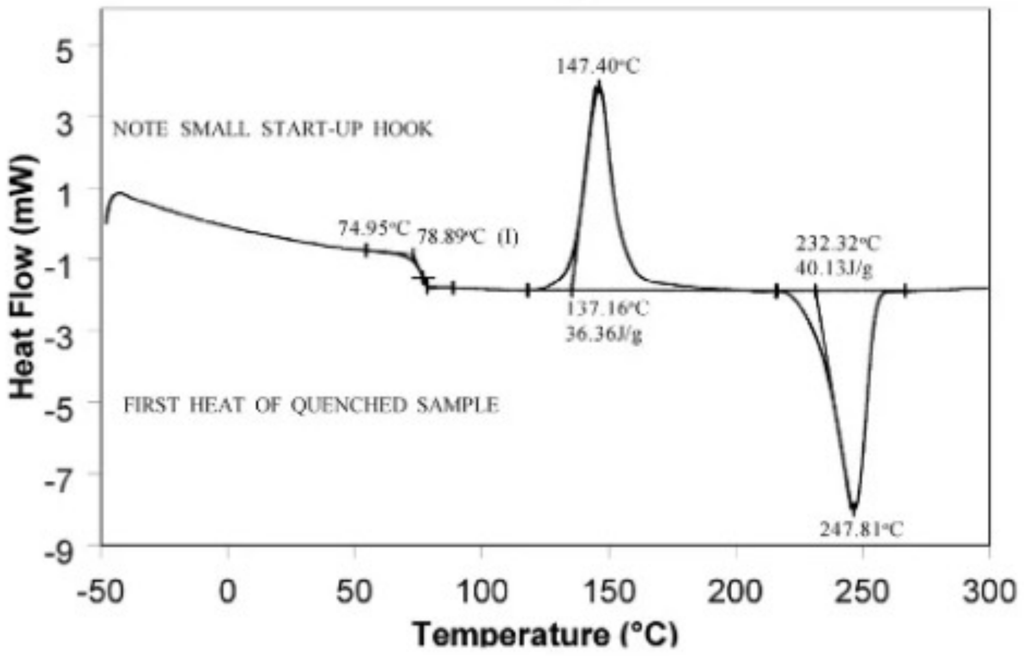
Lecture 6: Processing and Sustainability

Prof. Daryl W. Yee

Email: (daryl.yee@epfl.ch)

EPFL

Exercise 4:



The sample became more crystalline during the scan!

b) If the polymer is 100% crystalline, the heat from melting would be 60 J/g. Using the DSC scan above, calculate the degree of crystallinity of the polymer at the start of the scan.

Hint 1: What is the heat of melting from this polymer? How much of that came from crystallization that happened during the DSC scan itself?

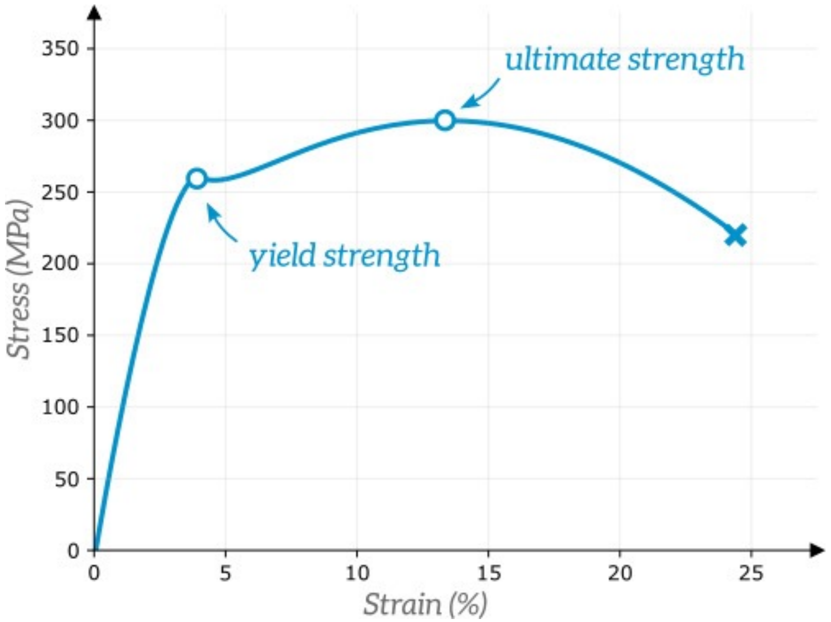
Hint 2: The degree of crystallinity can be approximated by:

$$\frac{H_{melt}^{obs}}{H_{melt}^{100\%}} \times 100\%$$

Where H_{melt}^{obs} is the observed heat of melting, and $H_{melt}^{100\%}$ is the heat of melting of a 100% crystalline polymer.

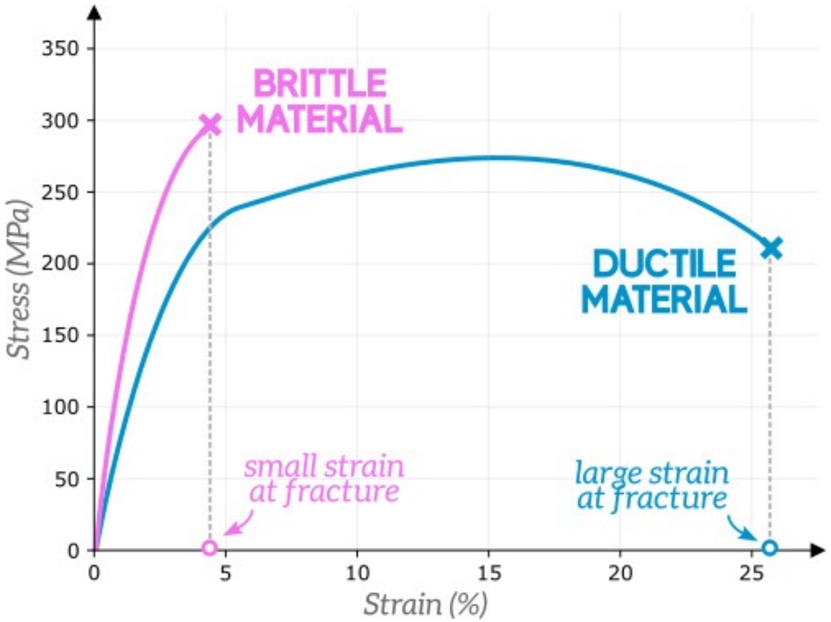
Common question from last week: What is toughness?

Strength



Strength is a measure of the stress that a material can withstand

Ductility



Ductility is a measure of the ability of a material to deform **plasticially** before failing

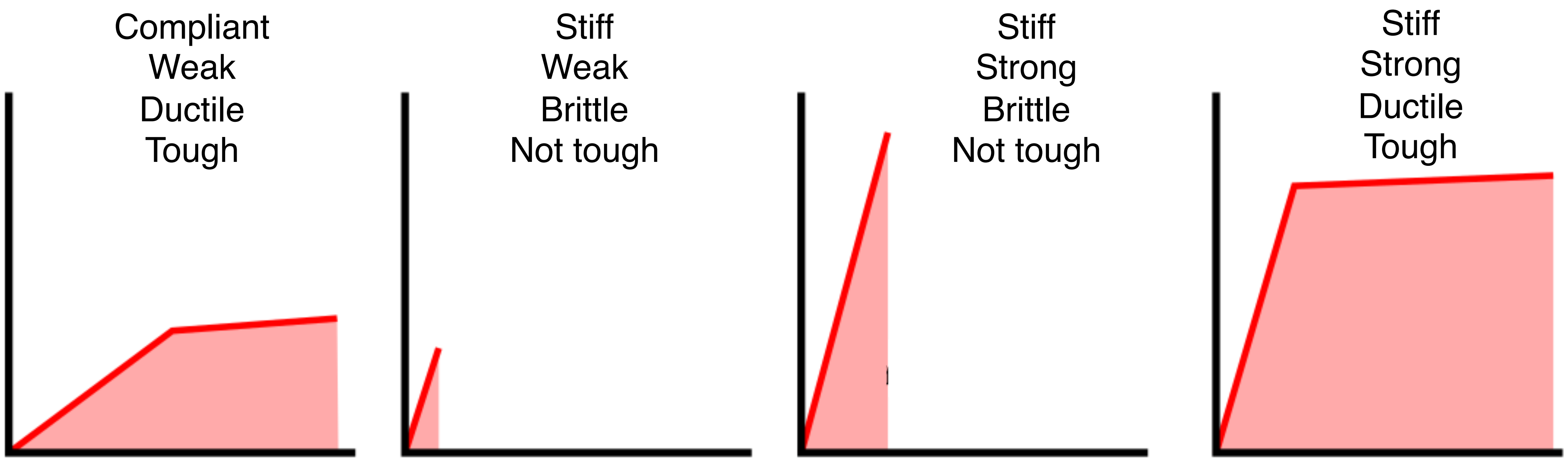
Toughness

Toughness is a measure of the ability of a material to absorb energy up to failure

Stiffness: Measure of the stress needed for elastic deformation

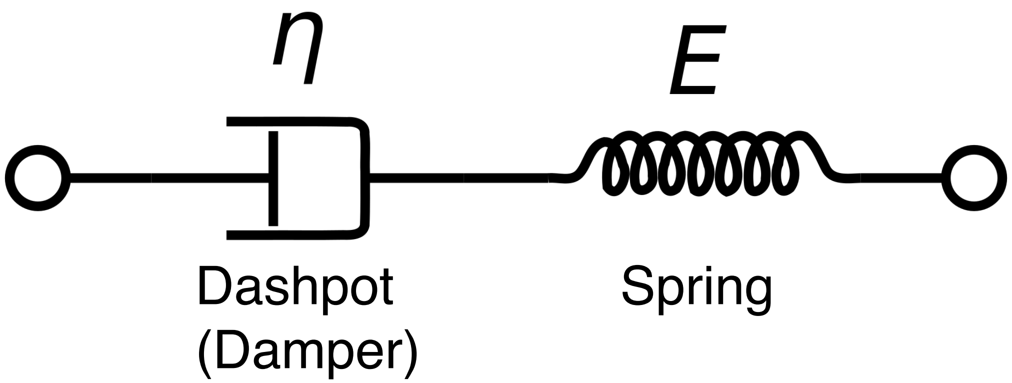
Plastic deformation is needed

Common question from last week: Strong vs Tough



Week 6 Recap: Polymers are viscoelastic

Maxwell model

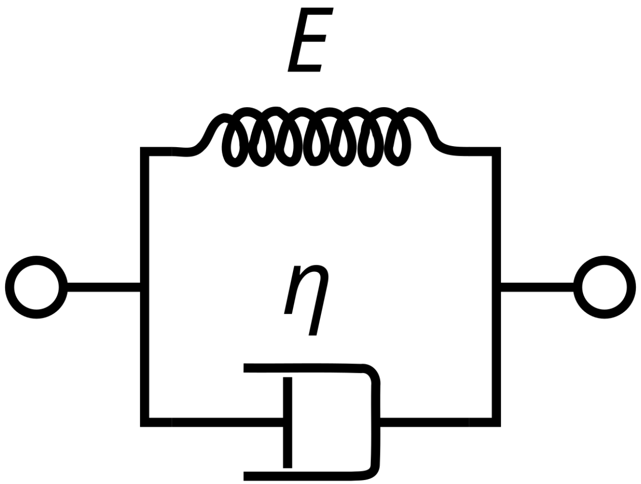


Spring has an elastic constant E

Dashpot has a viscosity η

Connected in series

Kelvin-Voigt model



Spring has an elastic constant E

Dashpot has a viscosity η

Connected in parallel

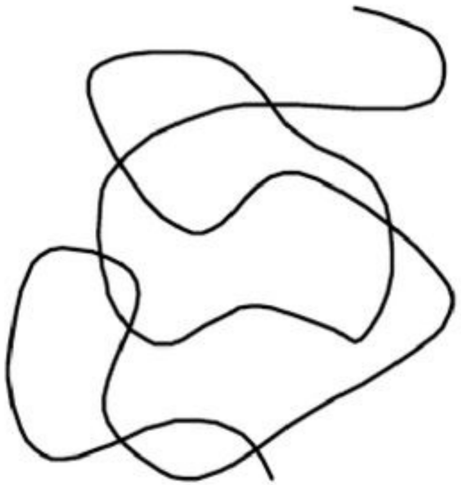
Maxwell model can demonstrate stress relaxation but not creep

Voigt model can demonstrate creep but not stress relaxation

*viscoelasticity can be an entire course in itself!

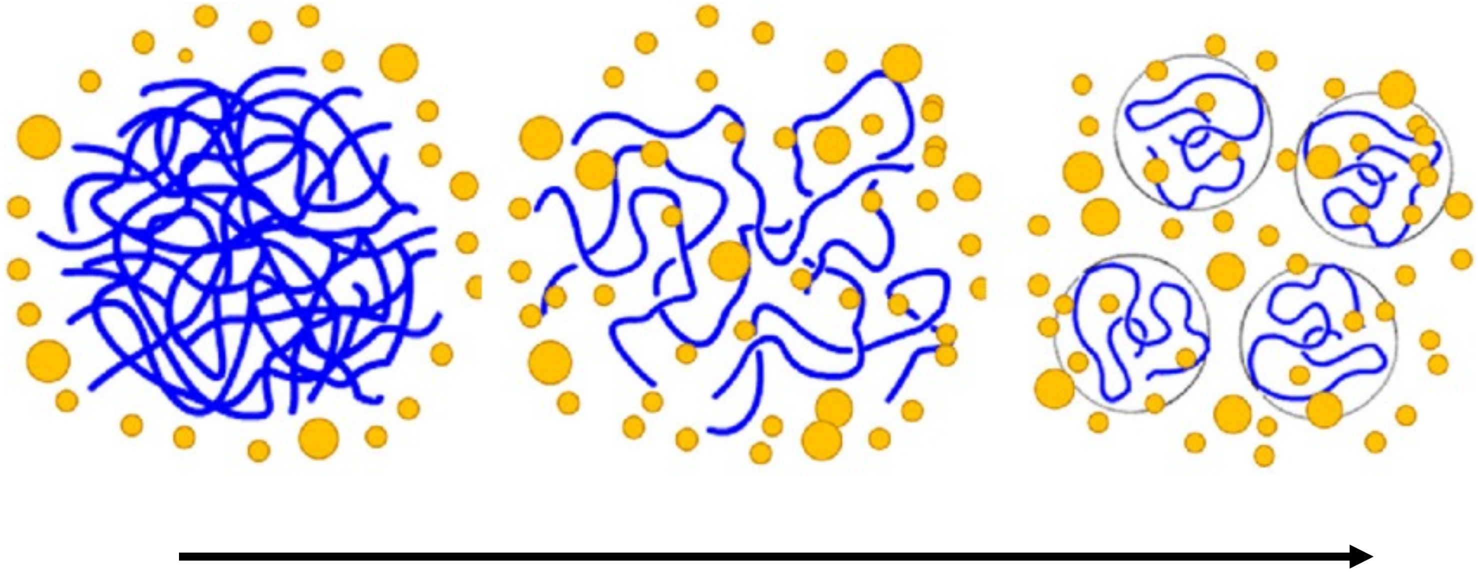
Week 5 Recap: Polymers dissolve in good solvents

<u>Good solvent</u>



Monomer-solvent interactions more favorable than monomer-monomer interactions

Schematic of polymer dissolution

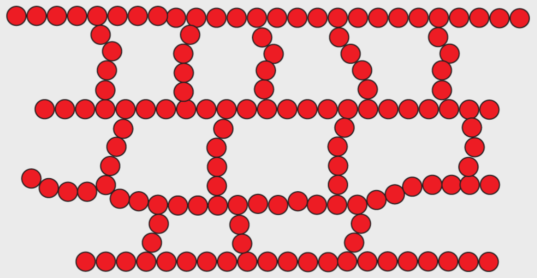


Note 1: Polymer does not degrade, it dissolves. No loss of monomer!

Note 2: Polymer chains remain coiled even when dissolved. Why?

Week 5 Recap: Chemical and physical crosslinks

Chemical crosslinks

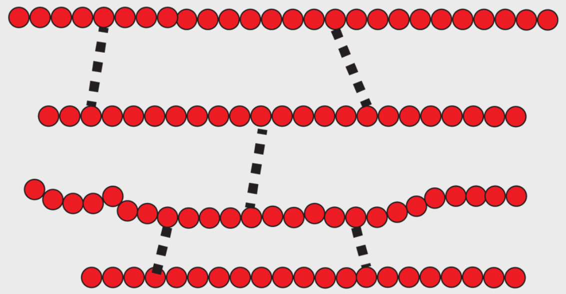


Covalent chemical bonds between polymer chains

Strength of covalent bonds are strong!

Covalent bonds are permanent. Not transient

Physical crosslinks



Non-covalent bonds between polymer chains

Strength of noncovalent bonds are weak!

Noncovalent bonds are transient. Often time-dependent

Chemically crosslinked polymers are often stronger

Common to have both chemical and physical crosslinks!

Physically crosslinked polymers are stimuli-responsive

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Week 5 Recap: General Polymer Properties

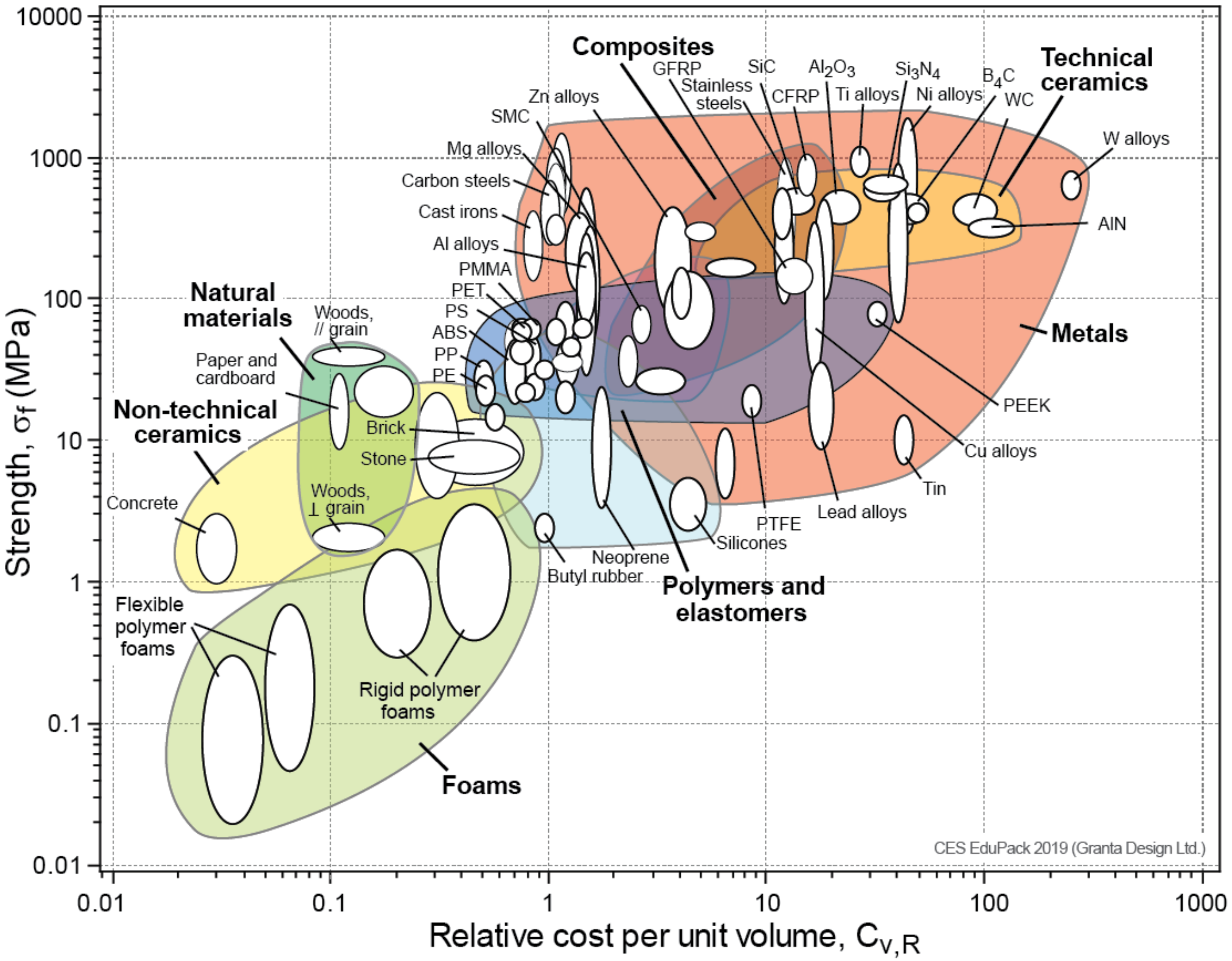
Polymers are very light for their properties

Polymers are flexible and soft compared to ceramics and metals

Polymers have low thermal stabilities compared to ceramics and metals

Polymers are insulators

Polymers are cheap



Week 5 Recap: Classic Polymer Manufacturing Processes

- **Injection molding**
- **Extrustion**
- Thermoforming
- Blow Molding
- Compression Molding
- Transfer Molding
- Vacuum Casting
- Rotational Molding

Typically used for large-volume production

General concept for many of these processes:

1. Heat up polymer feedstock to a liquid state or to a softened state
2. Deform softened polymer or fill mold with liquid polymer
3. Cool polymer down to solidify it.

Week 6 Learning Objectives

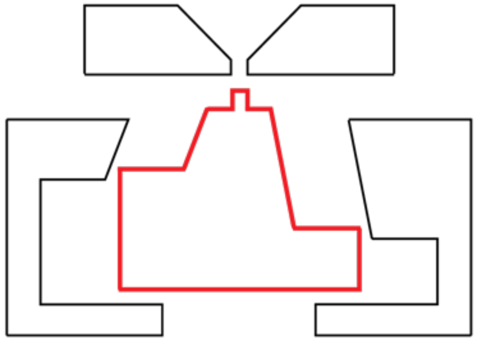
- Understand the basic working principles of material extrusion and vat photopolymerization additive manufacturing
- Understand the basic working principles of photolithography and its applications
- Understand that polymers as we know it today are unsustainable
- Recognize the multiple efforts being undertaken to improve polymer sustainability
- Recognize that sustainability is a complex challenge that involves multiple stakeholders

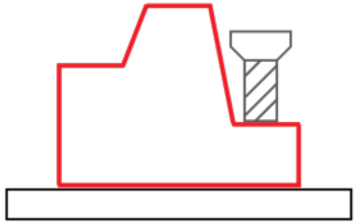
LESS CLASSIC POLYMER MANUFACTURING PROCESSES

Additive Manufacturing (AM)

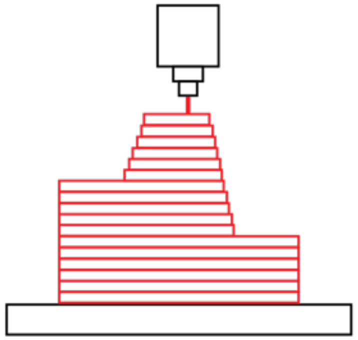
Some challenges with "traditional" polymer manufacturing approaches:

- Limited part complexity
- Difficult to pivot between part designs
- Optimized for scale — start up cost is very high
- Subtractive approaches* can be wasteful





Additive Manufacturing



Part is built in a layer-by-layer^ manner

- "Complexity for free"
- Easy to pivot between multiple designs
- Can be more material efficient
- Small-scale

^This definition is evolving with volumetric methods *we didn't cover this but an example is machining

Additive Manufacturing — Versatile, On-demand manufacturing

Injection Molding

High throughput
Rapid
High startup cost
Not easy to pivot to different part
Not suited for small-medium production volume

Additive Manufacturing

Low throughput
Slow
Low startup cost
Easy to pivot to different parts
Suited for small-medium production volume

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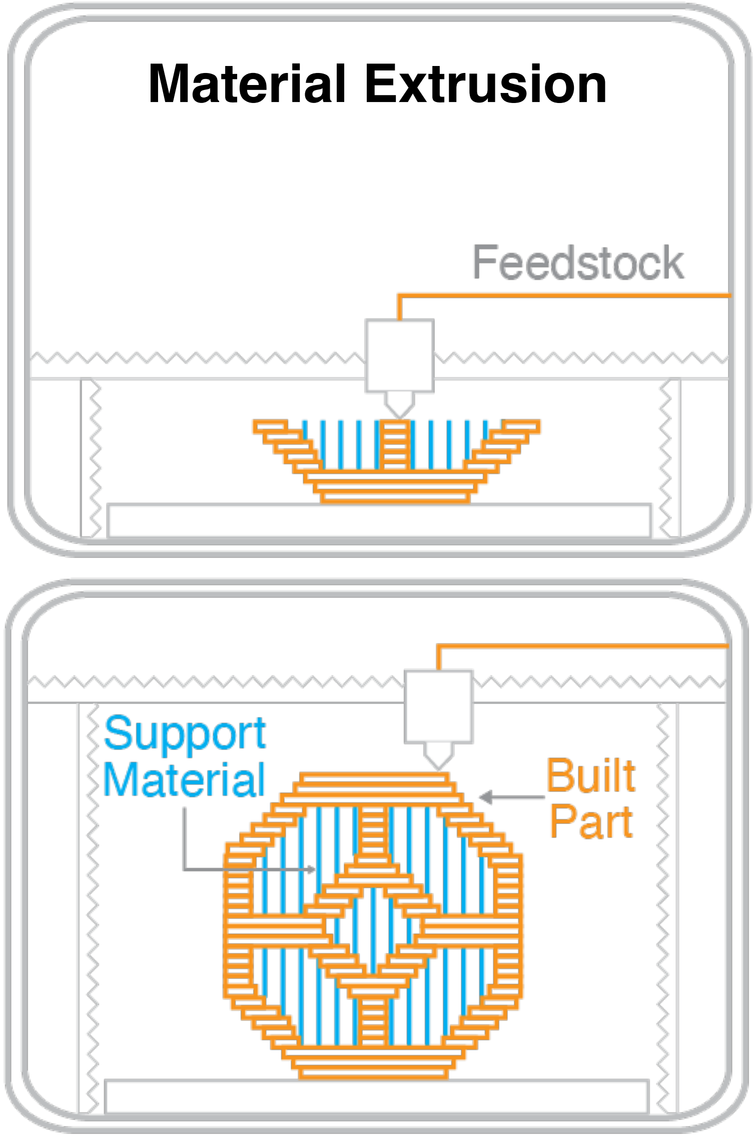
Polymer Additive Manufacturing: Material Extrusion

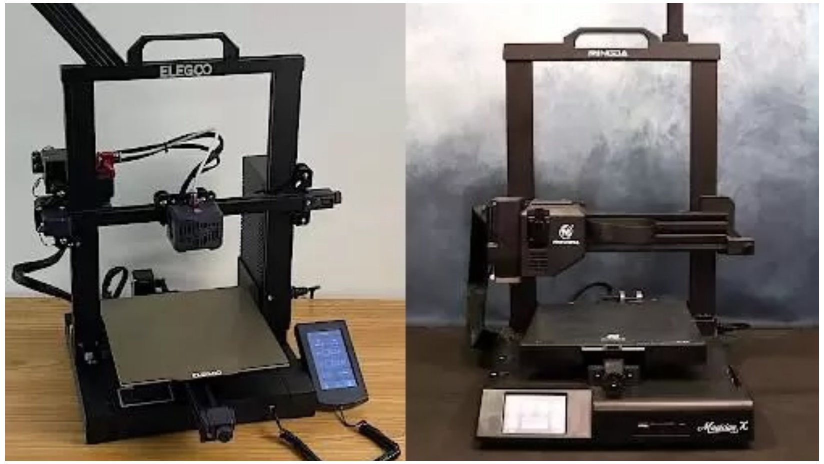


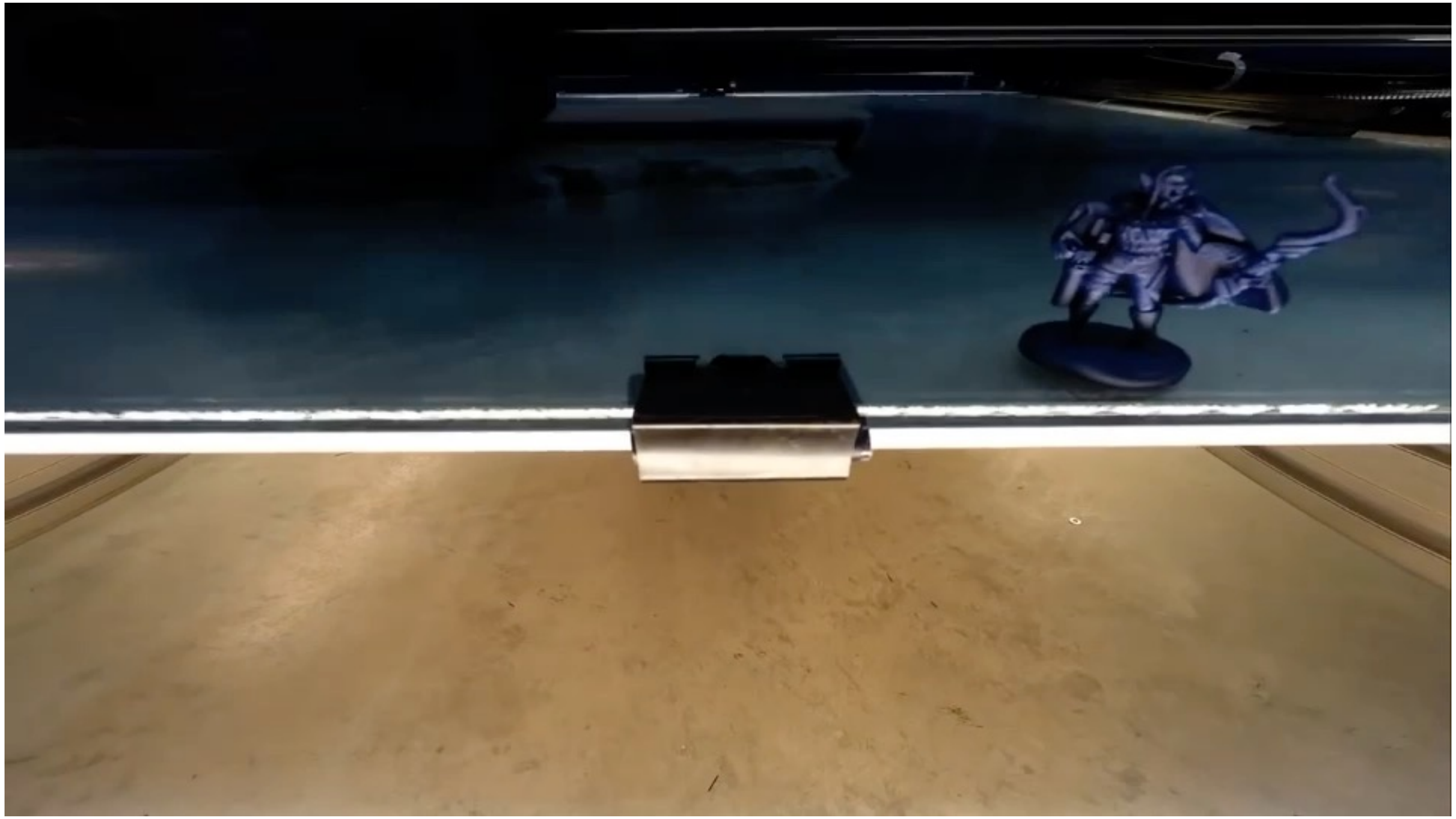
Family of AM techniques where a material is deposited through a nozzle onto a substrate

Often confused with “Fused Deposition Modeling (FDM)” or ”Fused Filament Fabrication (FFF)”.

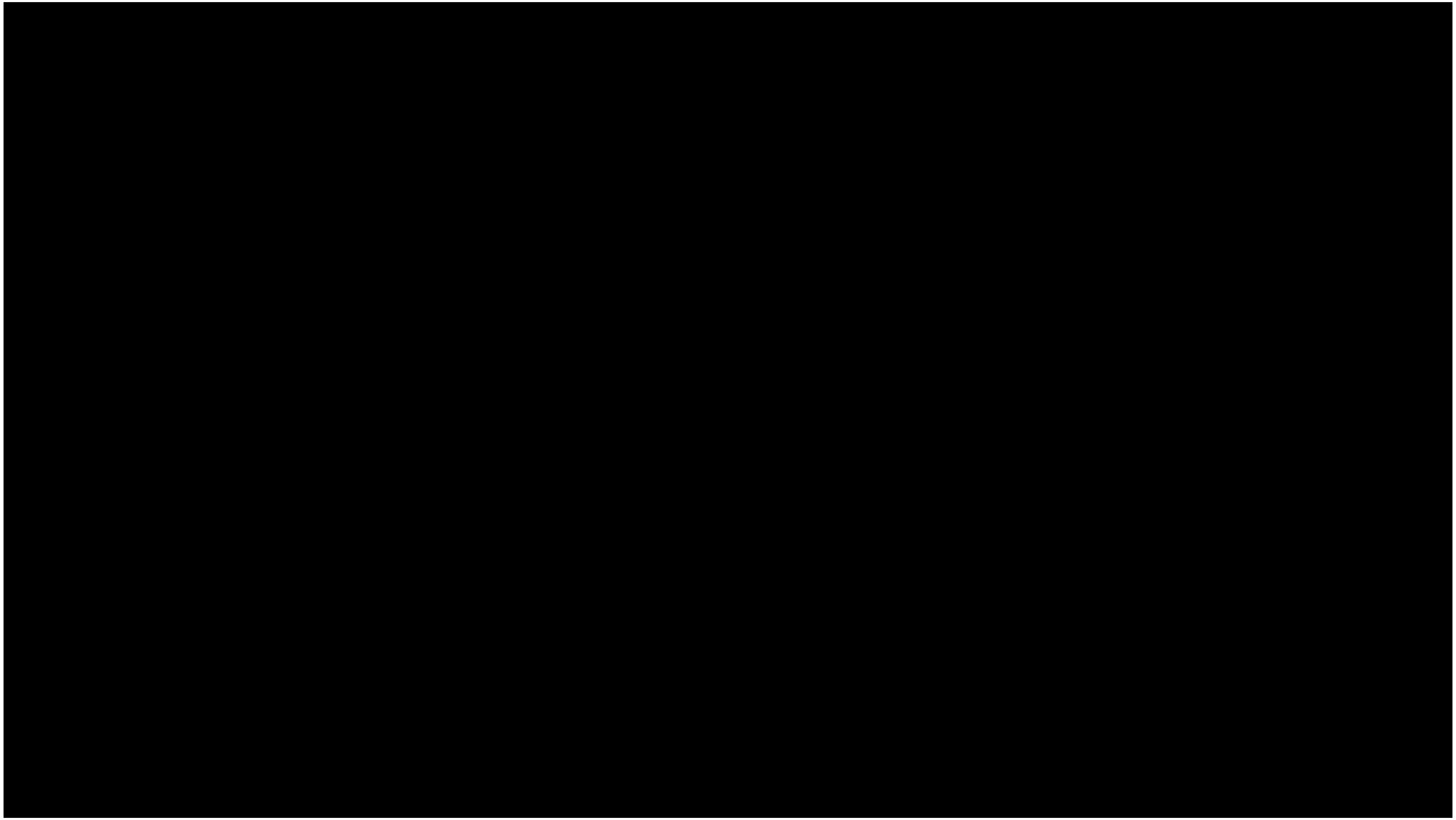
FDM and FFF belong to the family of techiques called Material Extrusion

Polymer Additive Manufacturing: Material Extrusion



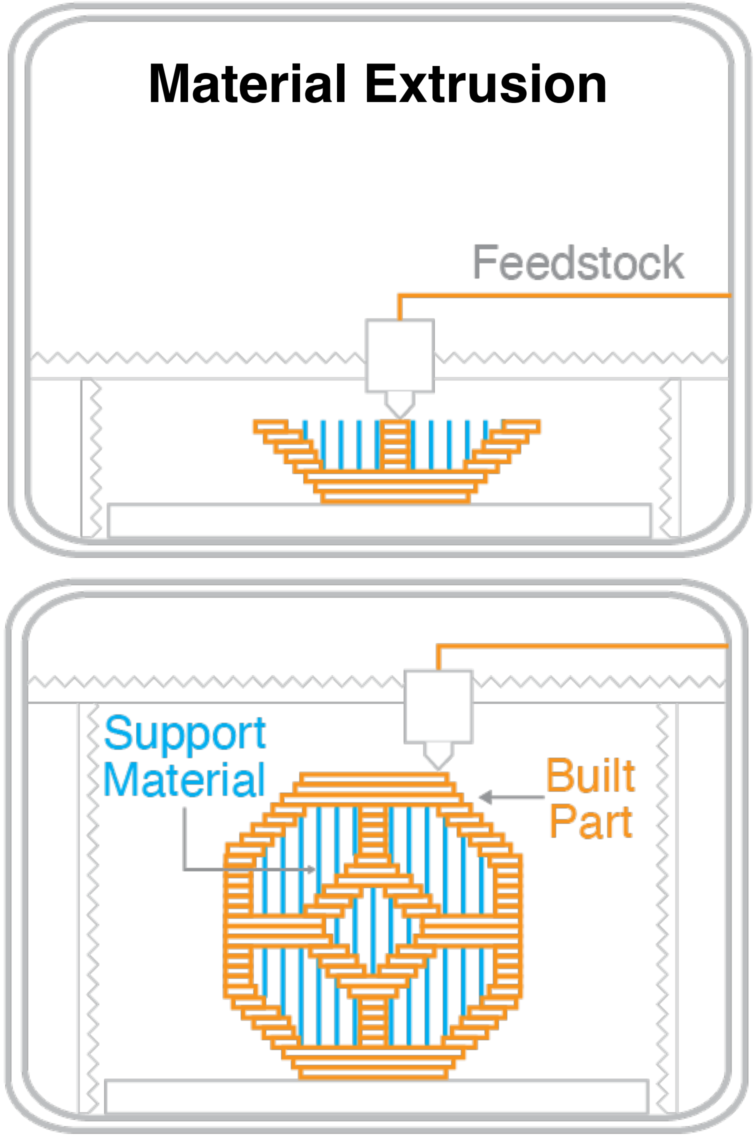


Polymer Additive Manufacturing: Material Extrusion



Jennifer Lewis, Harvard University

Polymer Additive Manufacturing: Material Extrusion



Operating Principle

Feedstock: Polymer, polymer composite, nanoparticle dispersions

Heat and/or pressure is used soften the material and allow it to flow through the nozzle

Material is deposited spatially

Material solidifies after deposition

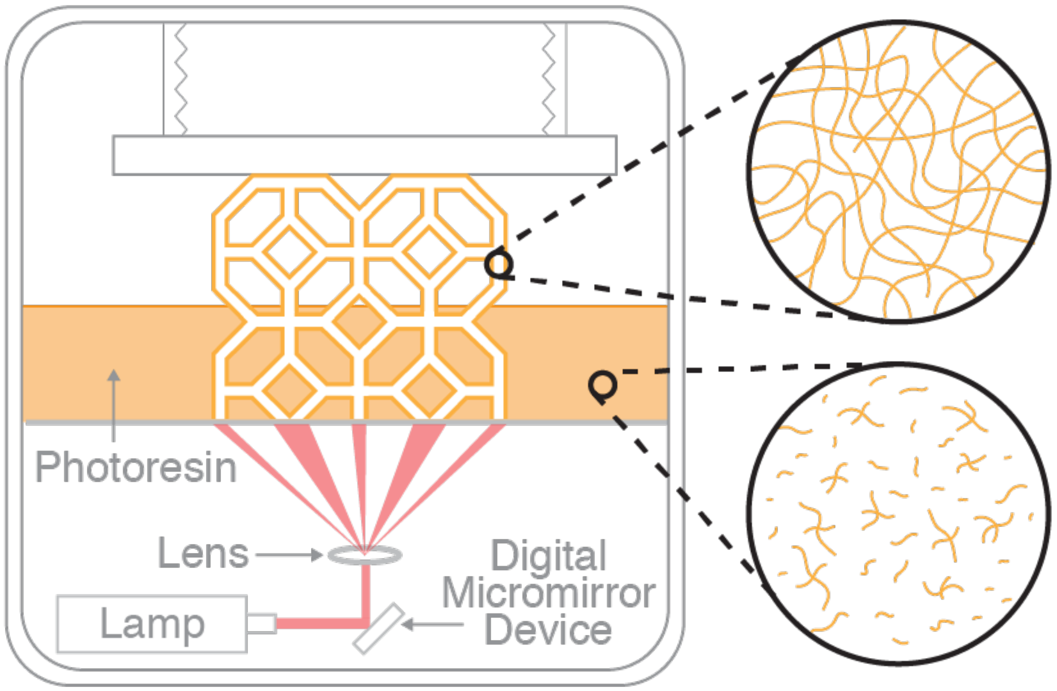
Pros

- Simple and inexpensive
- Low toxicity
- Ease of multimaterial

Cons

- Supports needed for complex geometries
- Warping due to thermal gradients
- Anisotropic properties
- Best used with thermoplastics

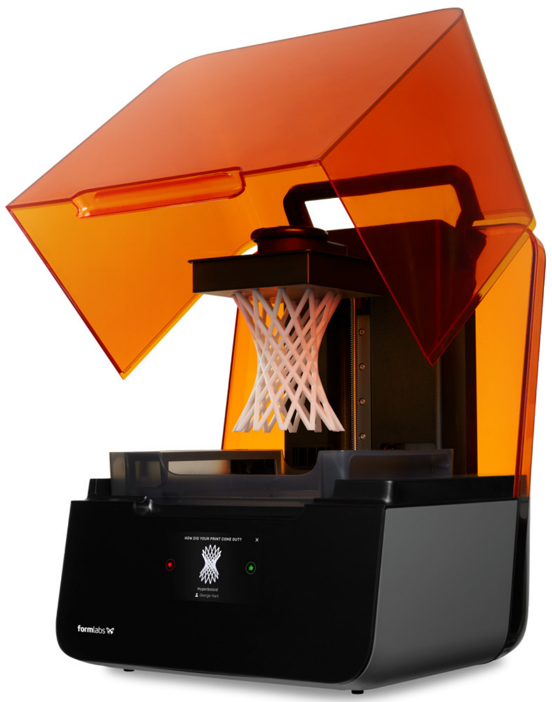
Polymer Additive Manufacturing: Vat Photopolymerization



Often confused with “stereolithography”.
Stereolithography is a subset of vat photopolymerization

Family of AM techniques where a liquid photopolymer in a “vat” is cured via photopolymerization

Often termed as “resin printing”



Form 3

Azul 3D

Polymer Additive Manufacturing: Vat Photopolymerization

Operating Principle

Resin: Monomer, oligomer, photoinitiator, solvent, etc.

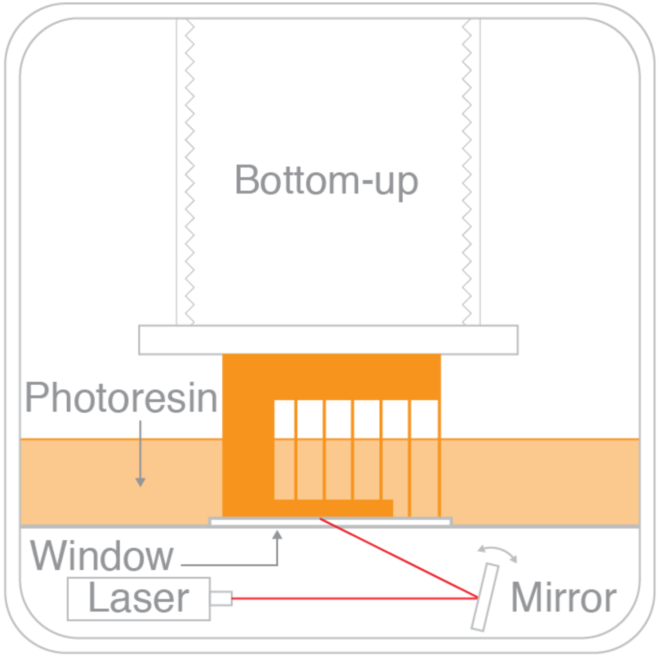
Light is used to spatially photopolymerize the monomer and form the polymer solid

Usually chain-growth polymerization

Different techniques apply light in different ways

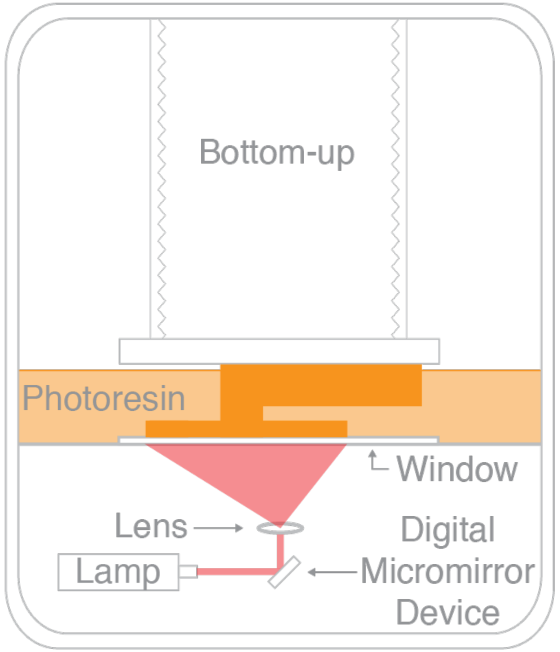
Stereolithography

Laser is rastered on resin



Digital Light Processing Printing

Pattern is projected onto resin



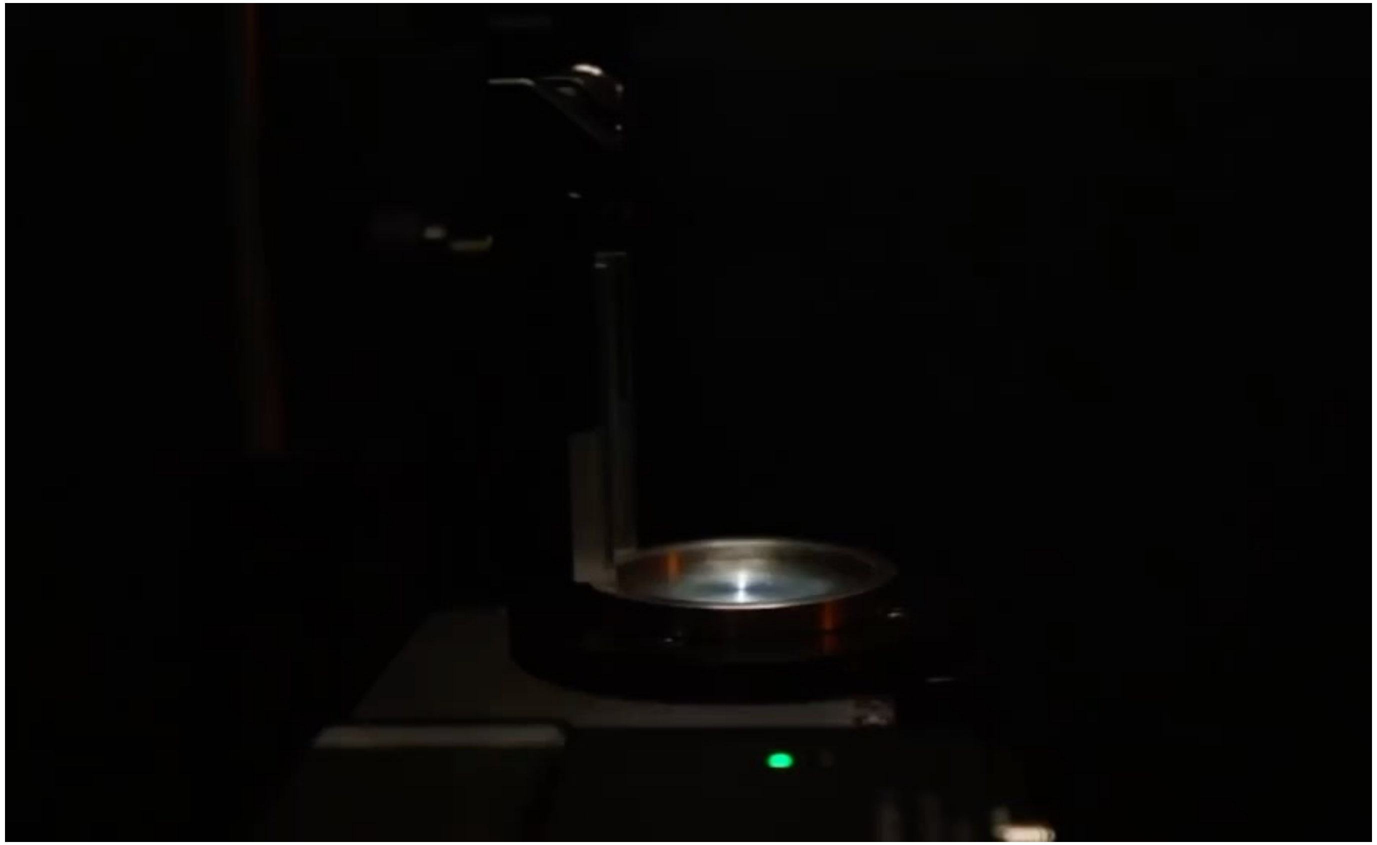
Other techniques in this family: LCD printing, multiphoton lithography, microstereolithography, continuous liquid interface production, volumetric printing, etc.

Polymer Additive Manufacturing: Vat Photopolymerization

Two Photon Lithography

Capable of ~100-150nm resolution

Volumetric Printing



Pioneered by Prof. Christophe Moser at EPFL!

Polymer Additive Manufacturing: Vat Photopolymerization

Pros

- Simple and inexpensive
- High resolutions (as low as 100 nm. Typically ~30 μm)
- Complex geometries easily achievable
- Rapid printing (especially with projection methods)

Cons

- Resin is often toxic. Difficult to handle at home
- Multimaterial is challenging to achieve
- Best used with thermosets
- Anything that scatters light will make the print difficult
- Polymer needs to be compatible with photopolymerization

SOME MICROENGINEERING RELEVANT POLYMER PROCESSING

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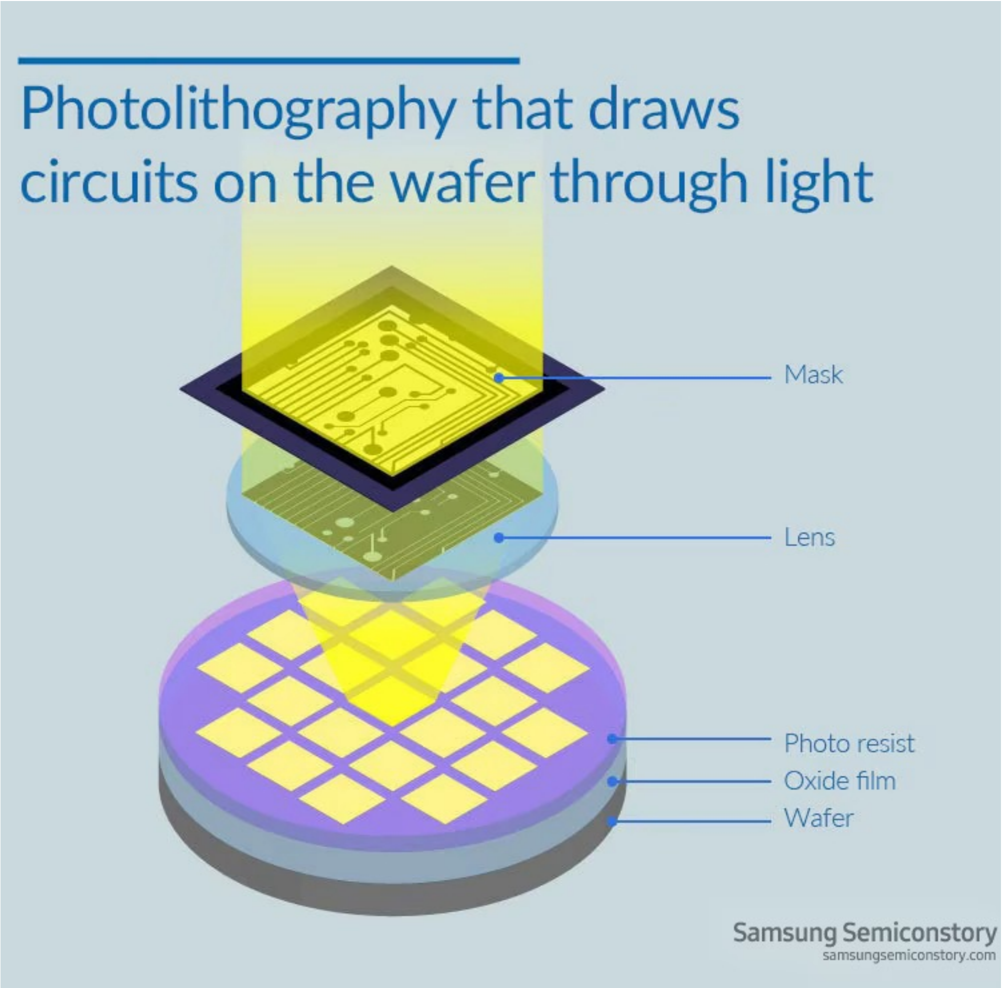
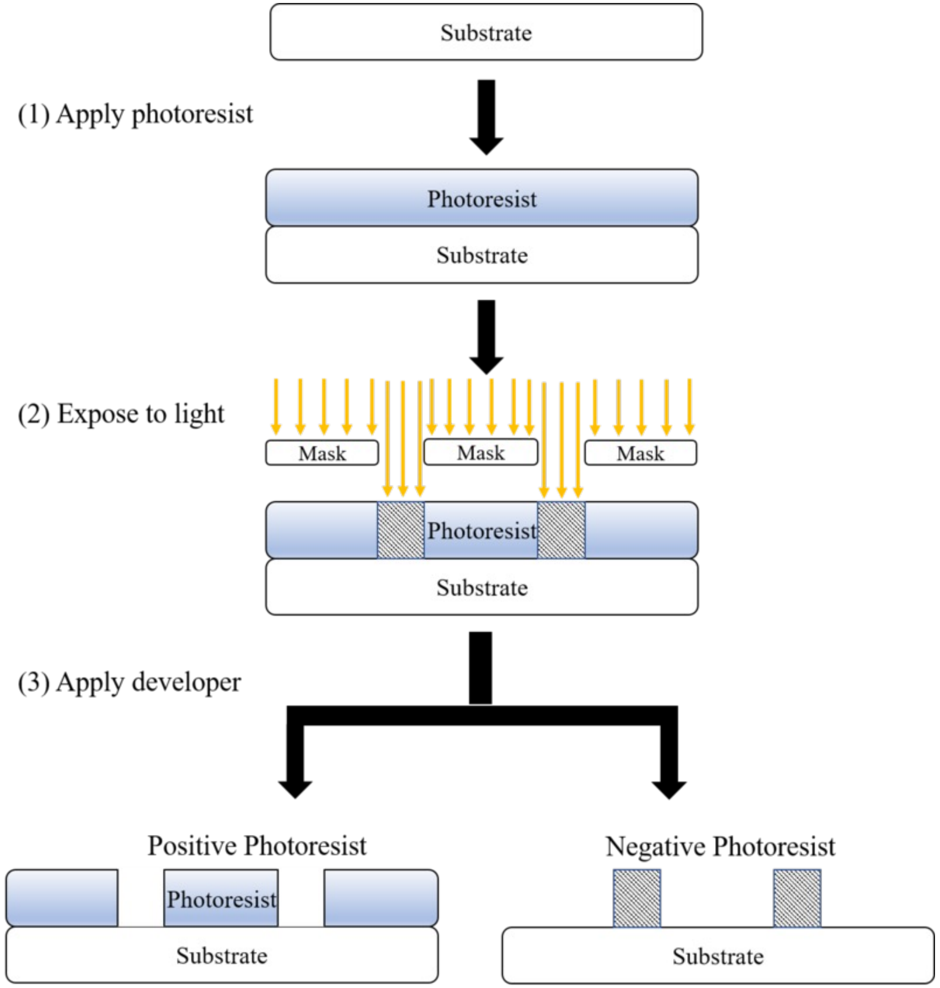
Photolithography





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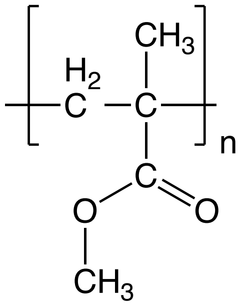
Positive Resist: Exposed = Dissolve

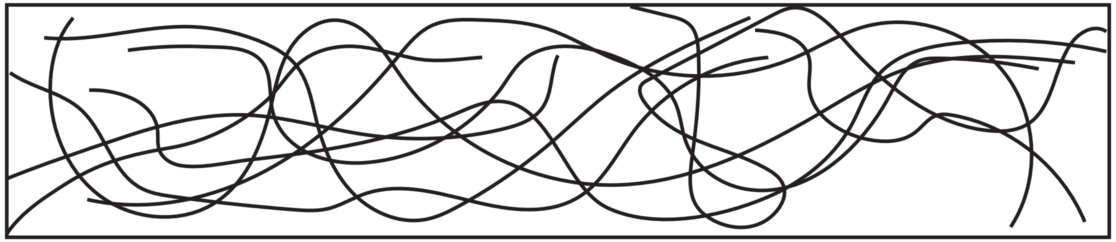
Poly(methyl methacrylate)



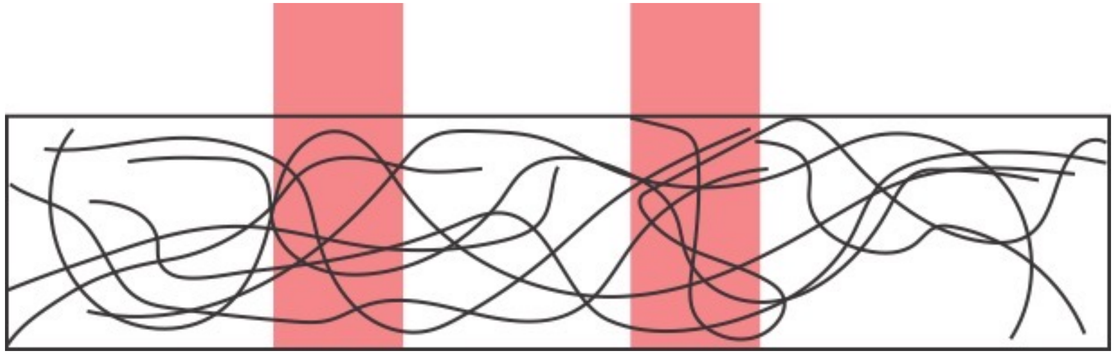
PMMA is commonly used as a high resolution positive resist for electron beam, deep UV, and X-ray lithography

The coating, exposure, and dissolution process parameters are all impacted by the molecular weight!

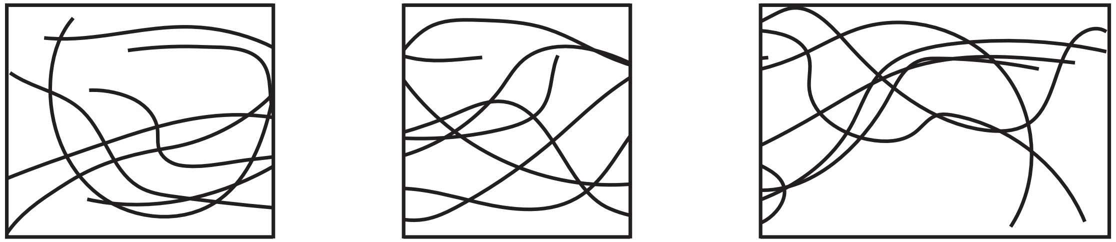
PMMA film coated onto substrate



Exposure causes chain scission, lowering molecular weight

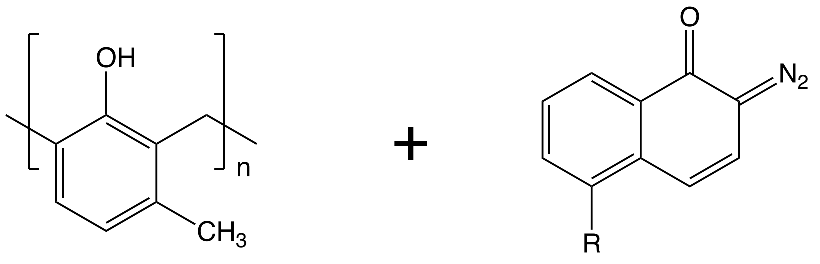


Lower molecular weight regions can be dissolved away



Positive Resist: Exposed = Dissolve

Novolac-DNQ

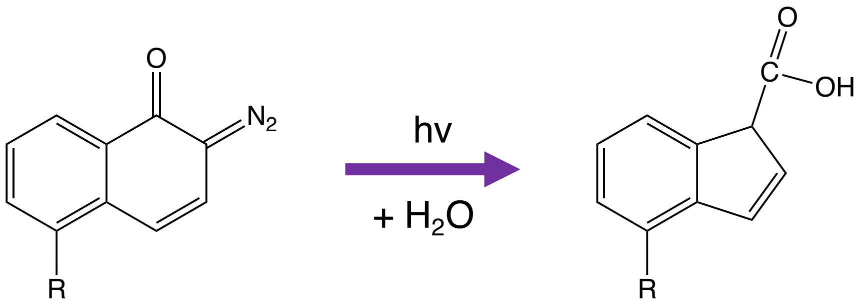


Novolac resin

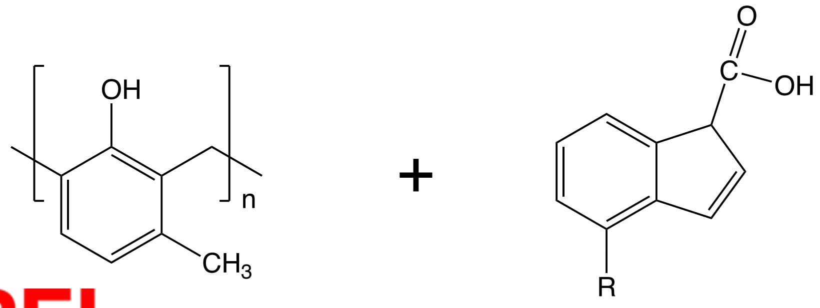
Diazonaphthoquinone (DNQ)

DNQ is a dissolution inhibitor

Slow dissolution

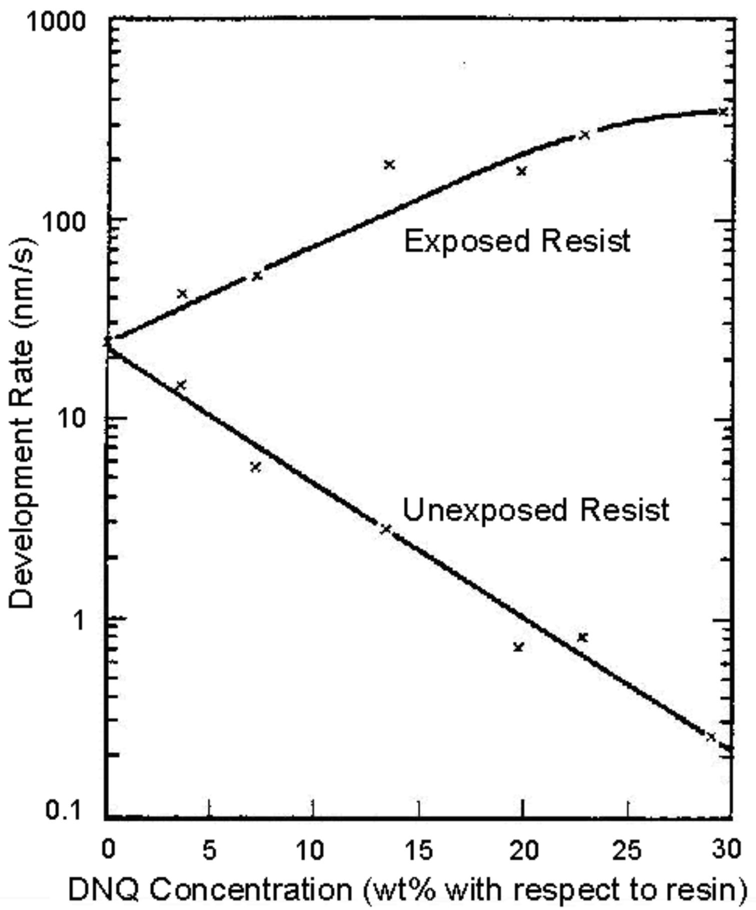


Indene-Carboxylic acid Photoproduct (ICA)



ICA is a dissolution promotor

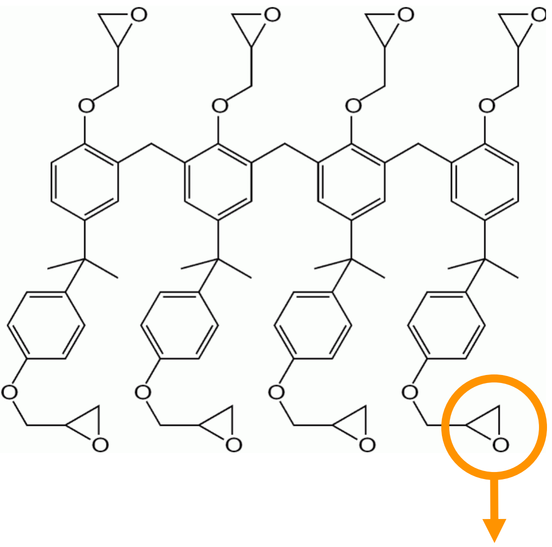
Fast dissolution



Design of polymer impacts the rate of dissolution

Negative Resist: Exposed = Stay

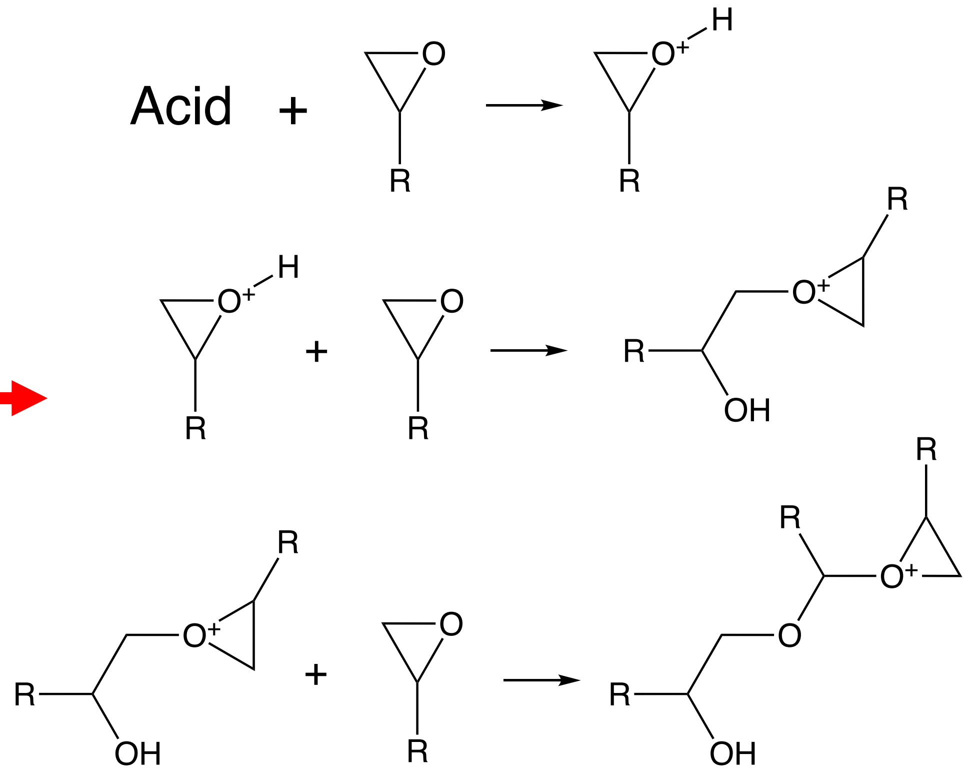
SU-8



\+

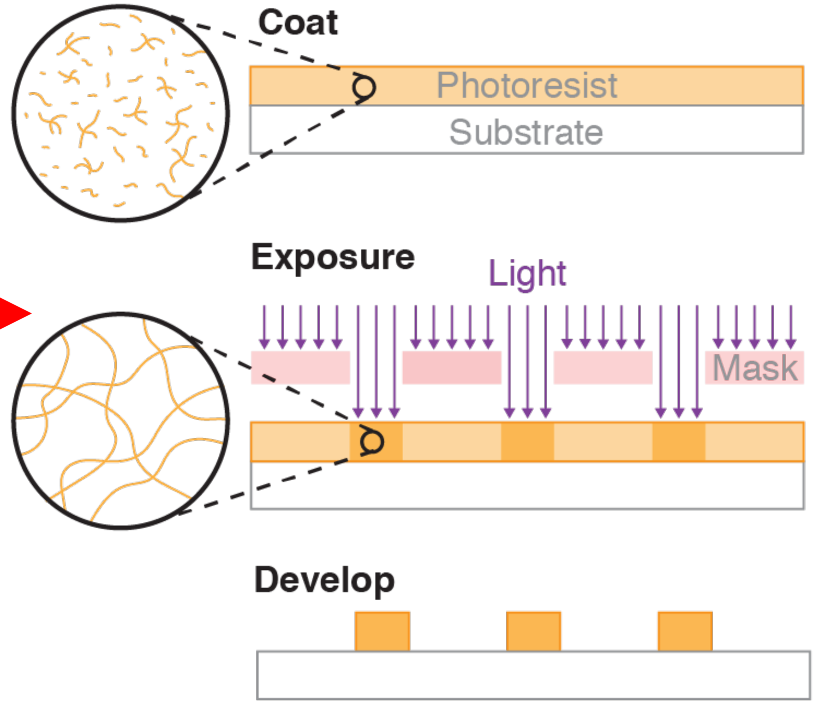
Photoacid Generator* (PAG)

PAGs react with light to generate acids
Epoxides can react with acids!



Chain-growth polymerization!

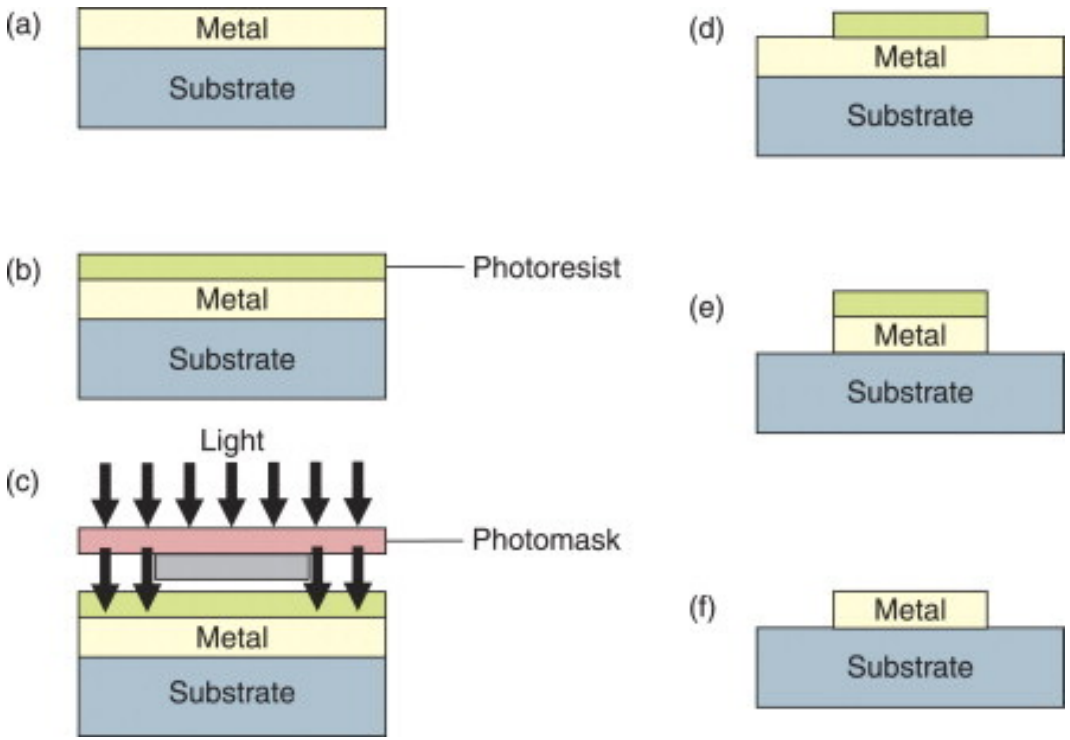
Areas exposed with light crosslink and become insoluble



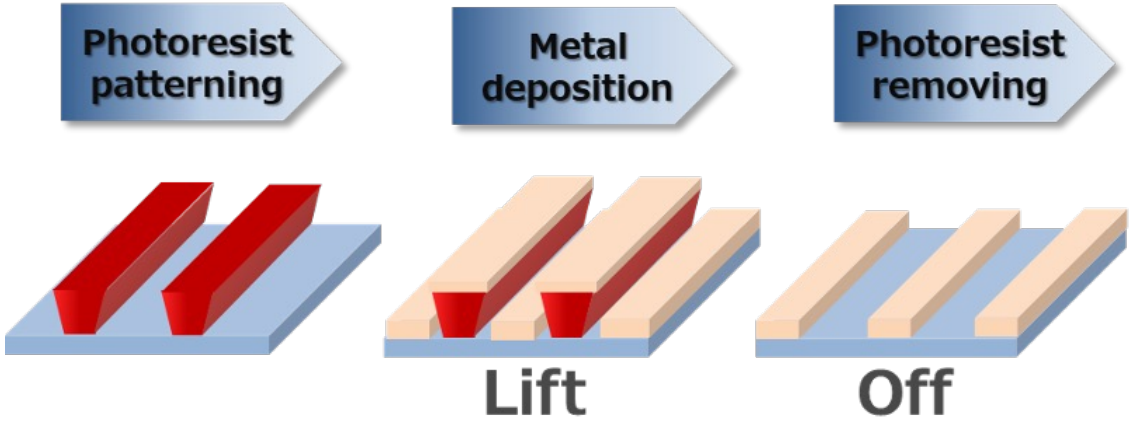
*if you're interested, the PAG for SU-8 is triarylsulfonium/hexafluoroantimonate salt

What is Photolithography used for? – Metal Patterning

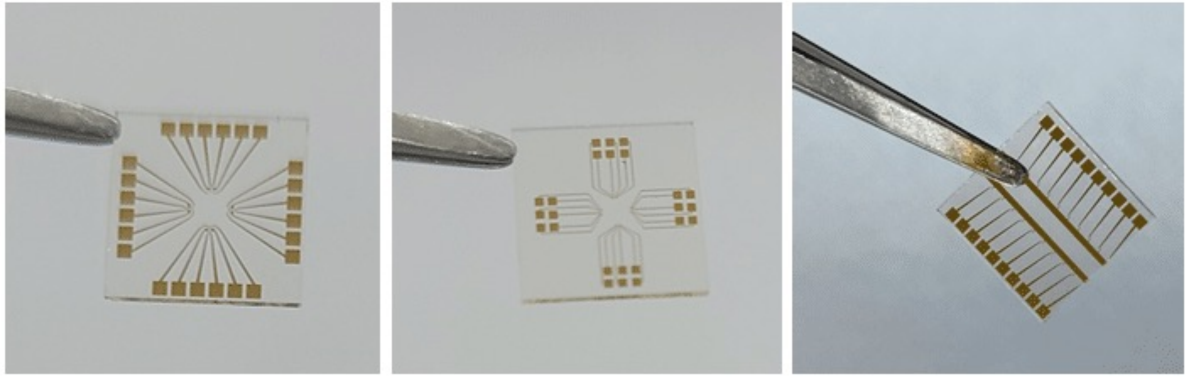
Metal patterning via use of an etch mask (subtractive)



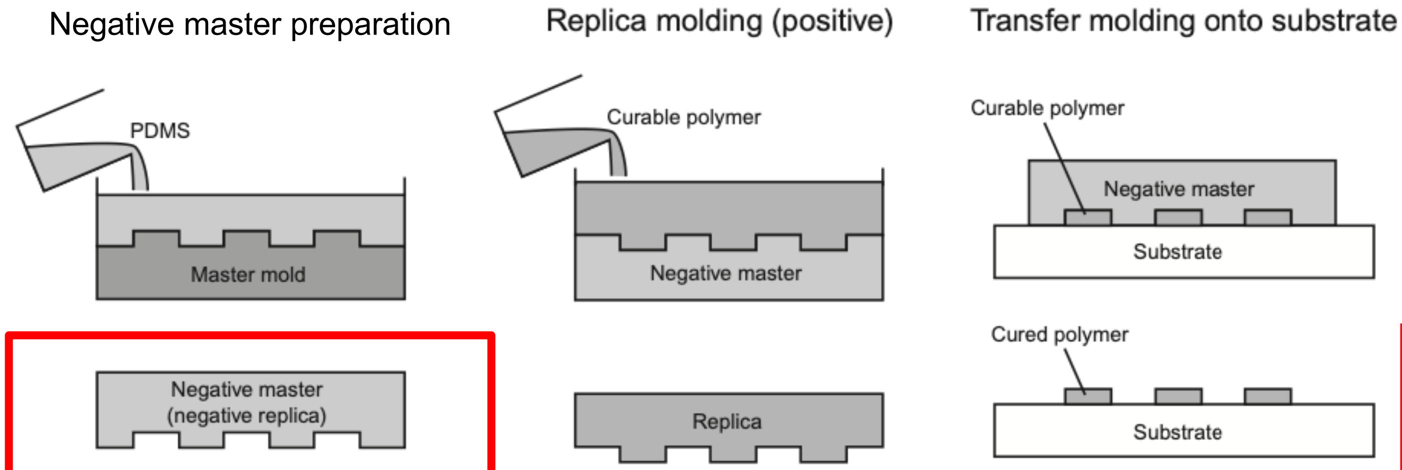
Metal patterning via lift-off (additive)



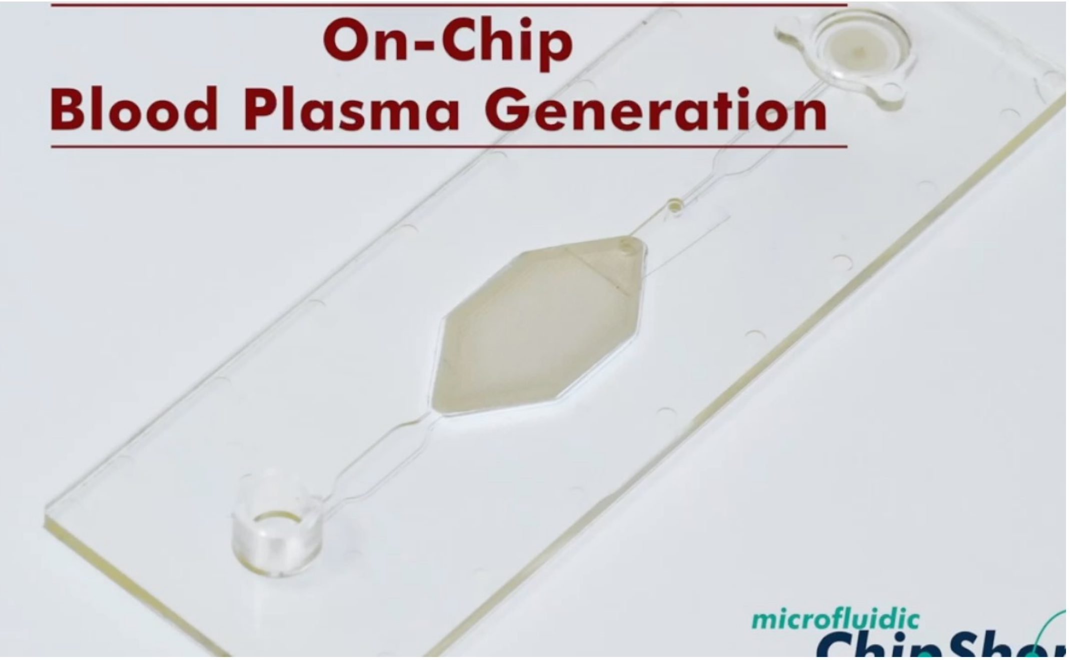
Used to make these microelectrodes

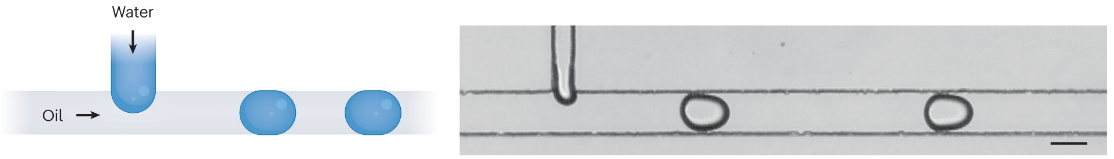


What is Photolithography used for? – Soft Lithography

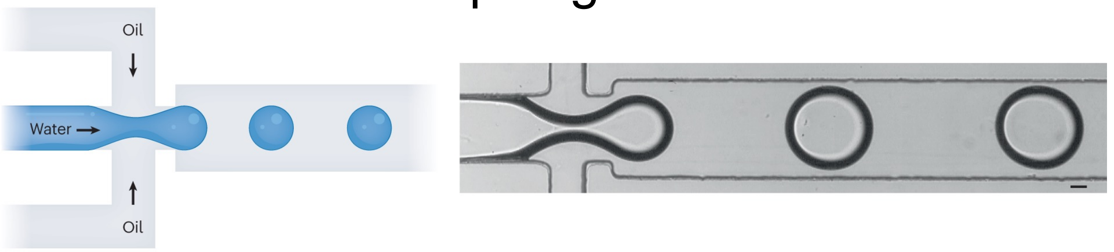


Can be bonded to a substrate to make microfluidic devices!



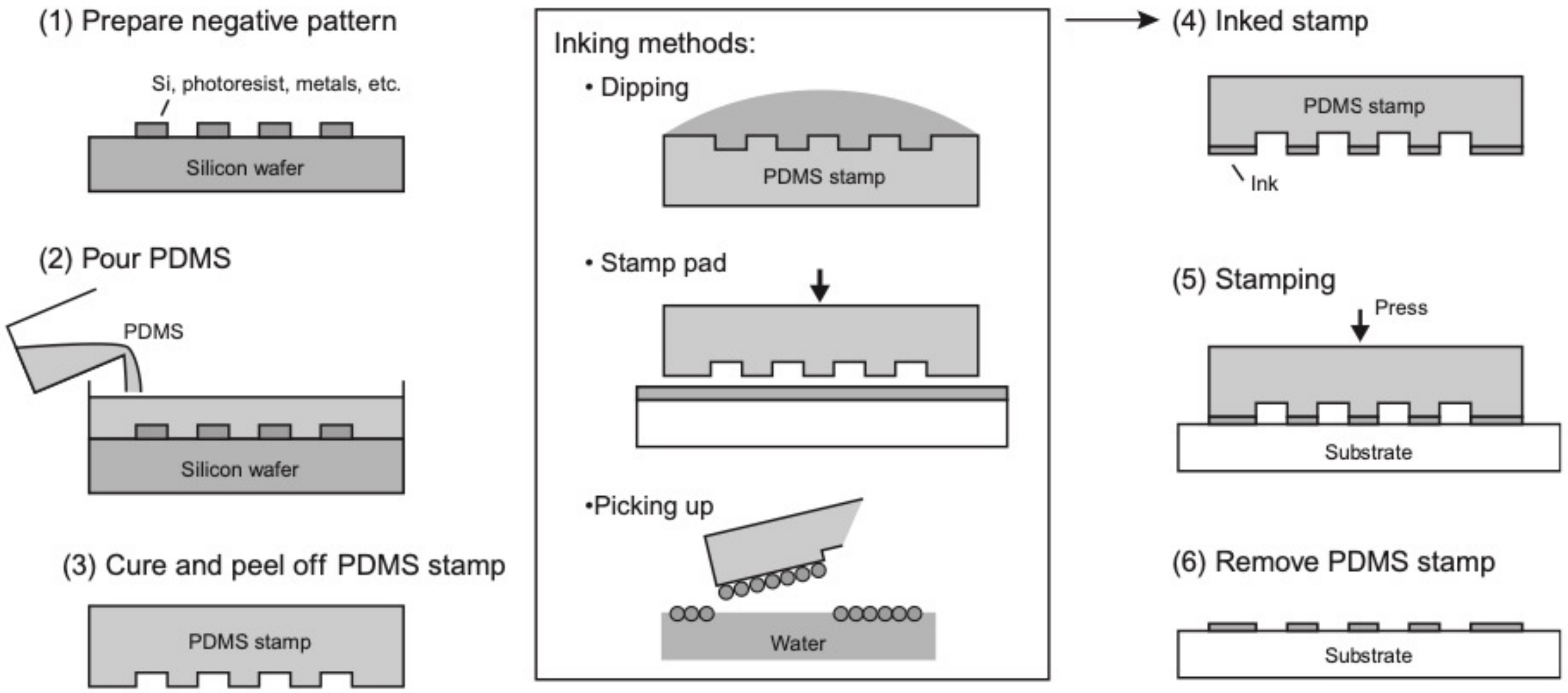


Droplet generation

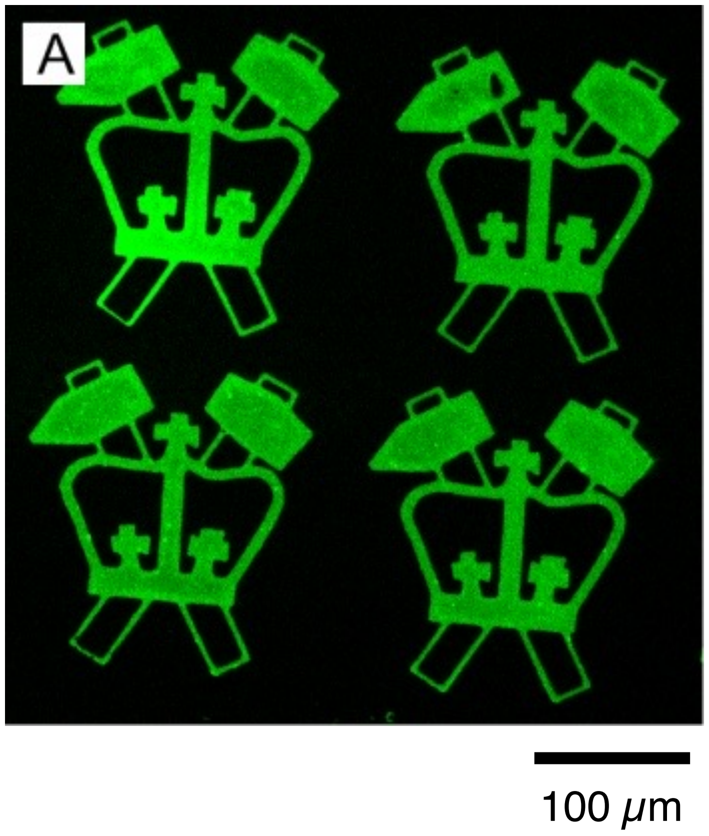


What is Photolithography used for? – Soft Lithography

Microcontact Printing



Fluorescent protein



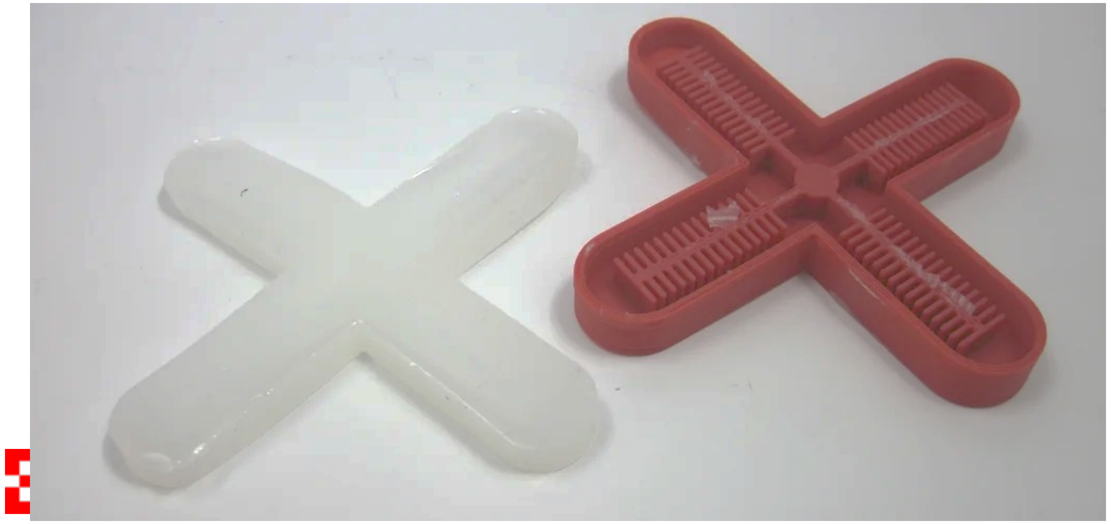
Molding is something you'll probably do a lot of in SMT

1. 3D print mold

2. Pour and cure polymer

3. Remove polymer

4. Profit



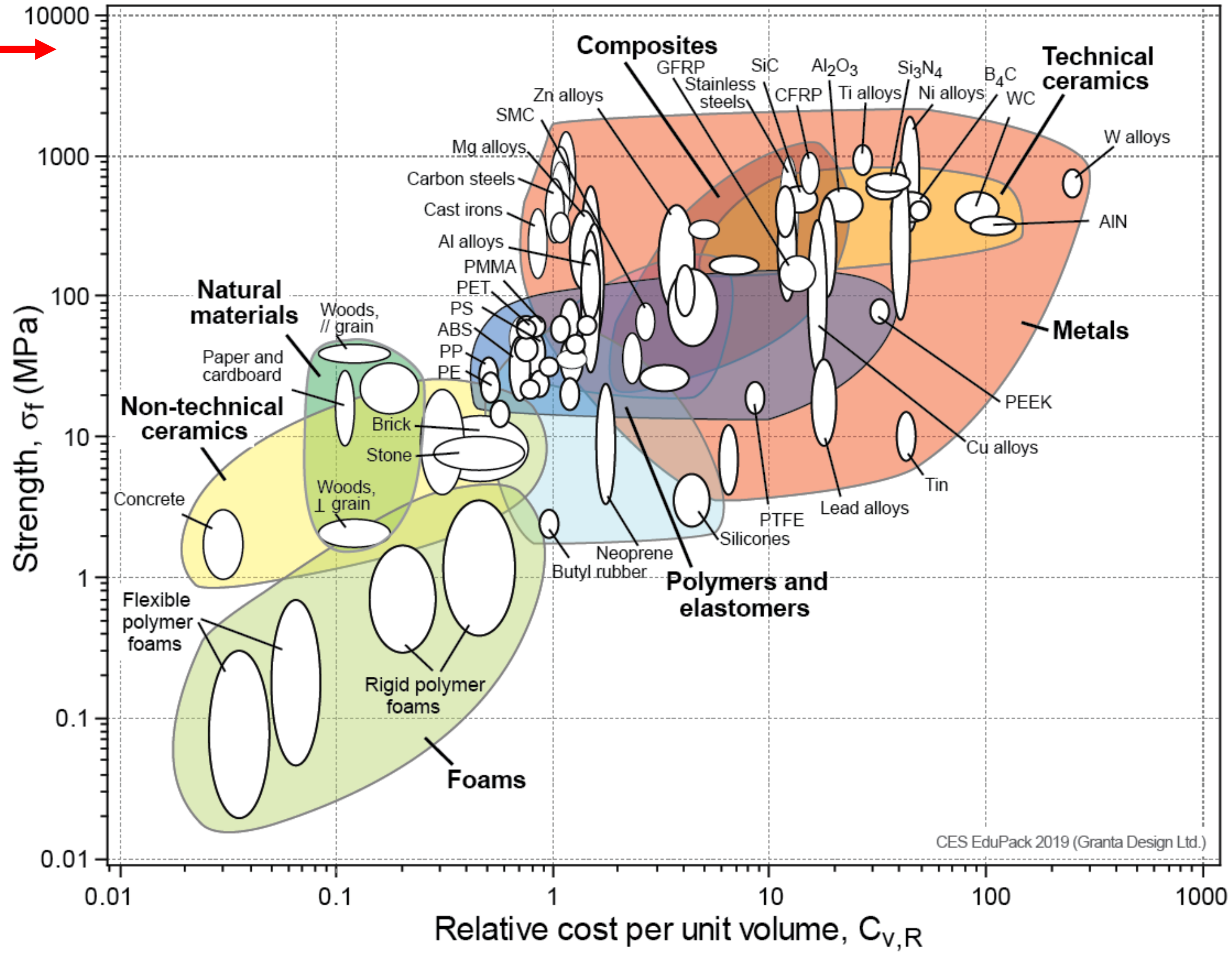
Multiple ways to cure polymer: Heat and light

Tune X_n → Tune properties

3D printing and molding → Simple way to make parts

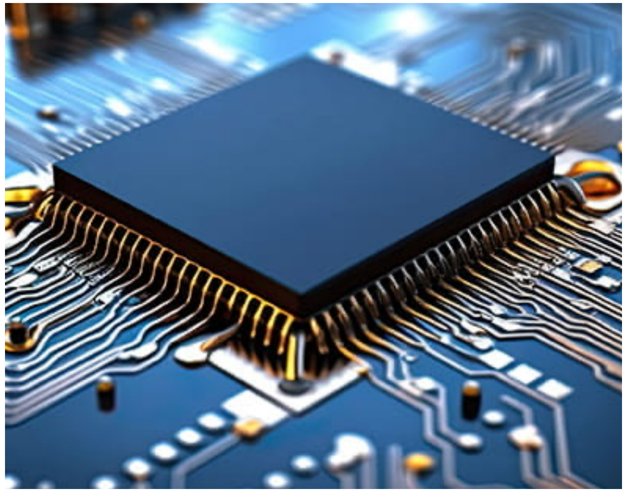
Short Summary about Manufacturing

- Polymers are easy to manufacture! — Relatively low processing temperatures compared to metals and ceramics
- Traditional polymer manufacturing is optimized for high-volume production
- Additive manufacturing an emerging alternative manufacturing method for small/medium volume production
- Polymer processing and manufacturing is relevant to microengineers as well!
- Polymers are cheap!

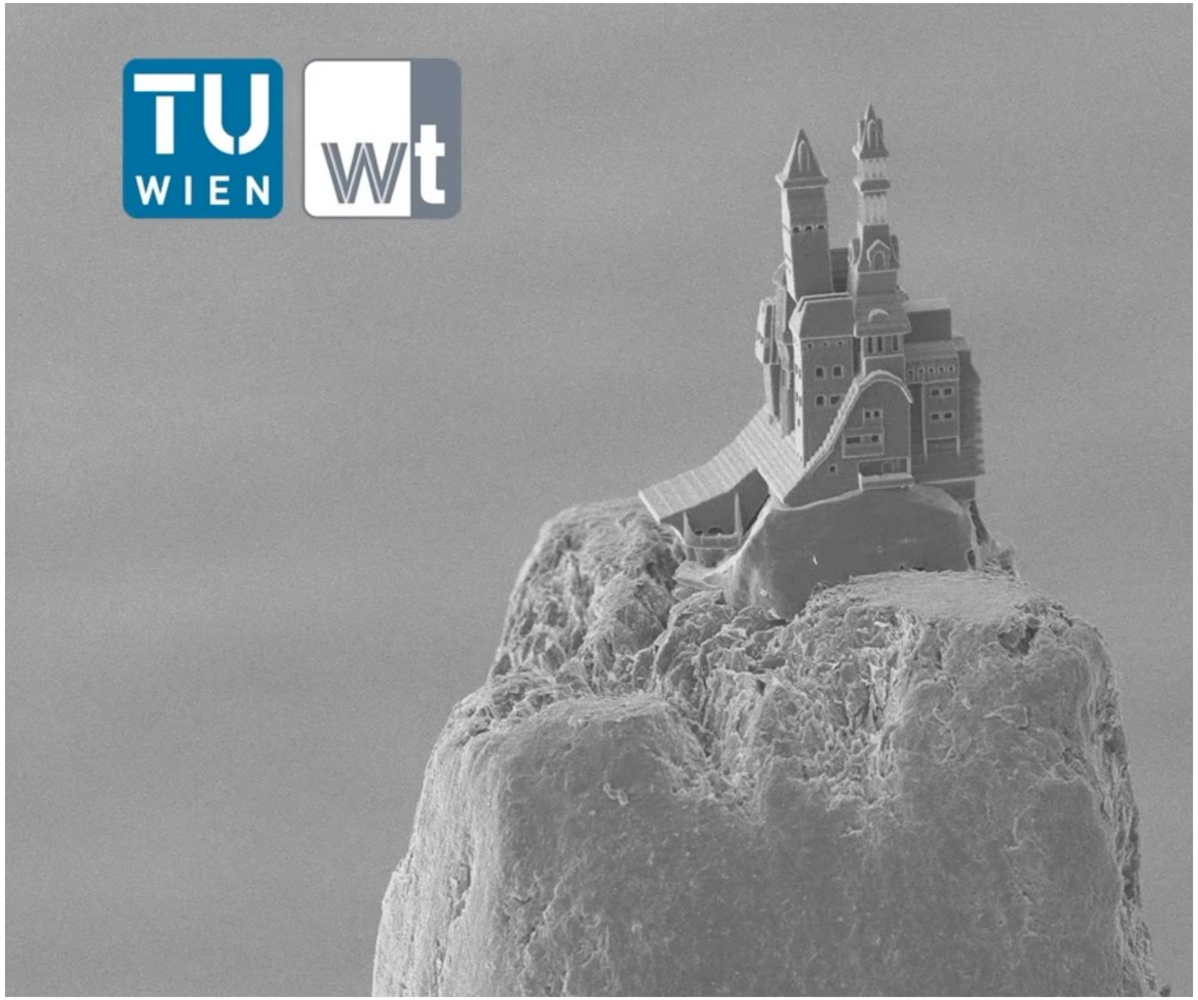


Past 5.5 weeks: Polymers are cool!

All your daily products



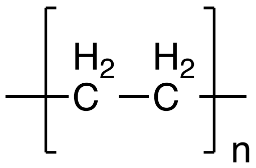
Big or small…



WHAT'S THE CATCH?
POLYMERS AND SUSTAINABILITY*

*A brief introduction to a very complex topic

Polymers are stable, too stable…



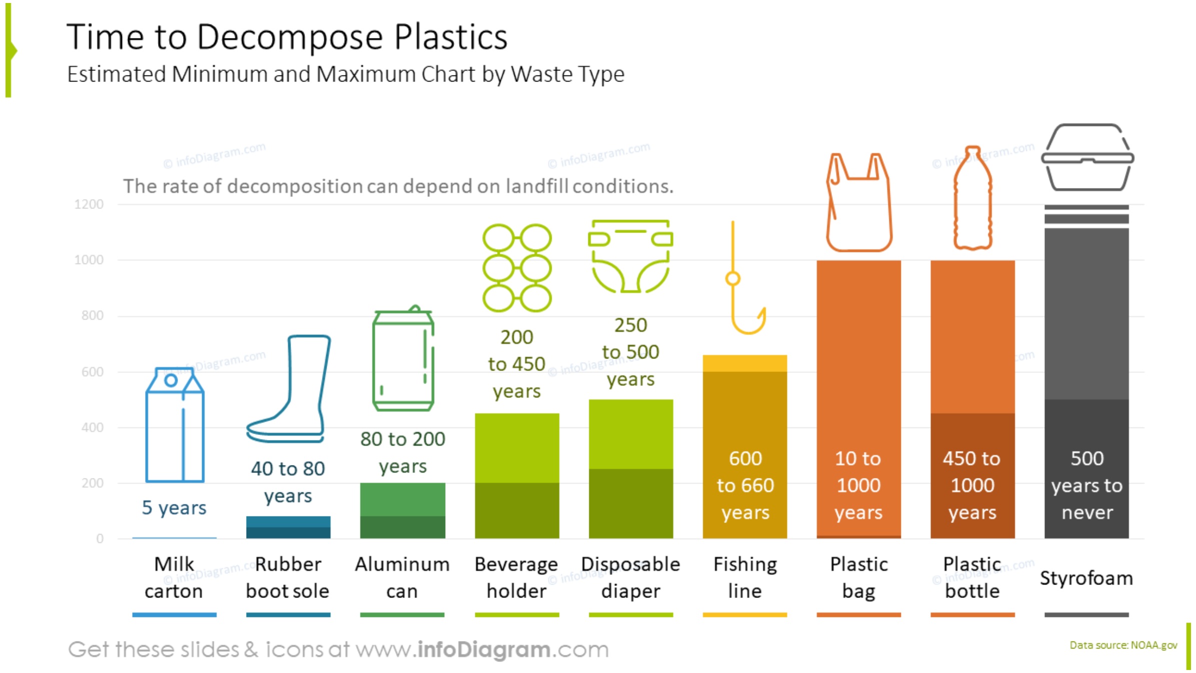
C-C bonds are strong/stable

Polymers are designed to last a long time
→ Great product!

Breakdown of polymers are hard

- Microorganisms do not recognize polymers so they cannot break it down easily
- Breaking down polymers result in the release of toxic small-molecules and microplastics

Flipside → We can't get rid of it!



Why do we keep using polymers then?

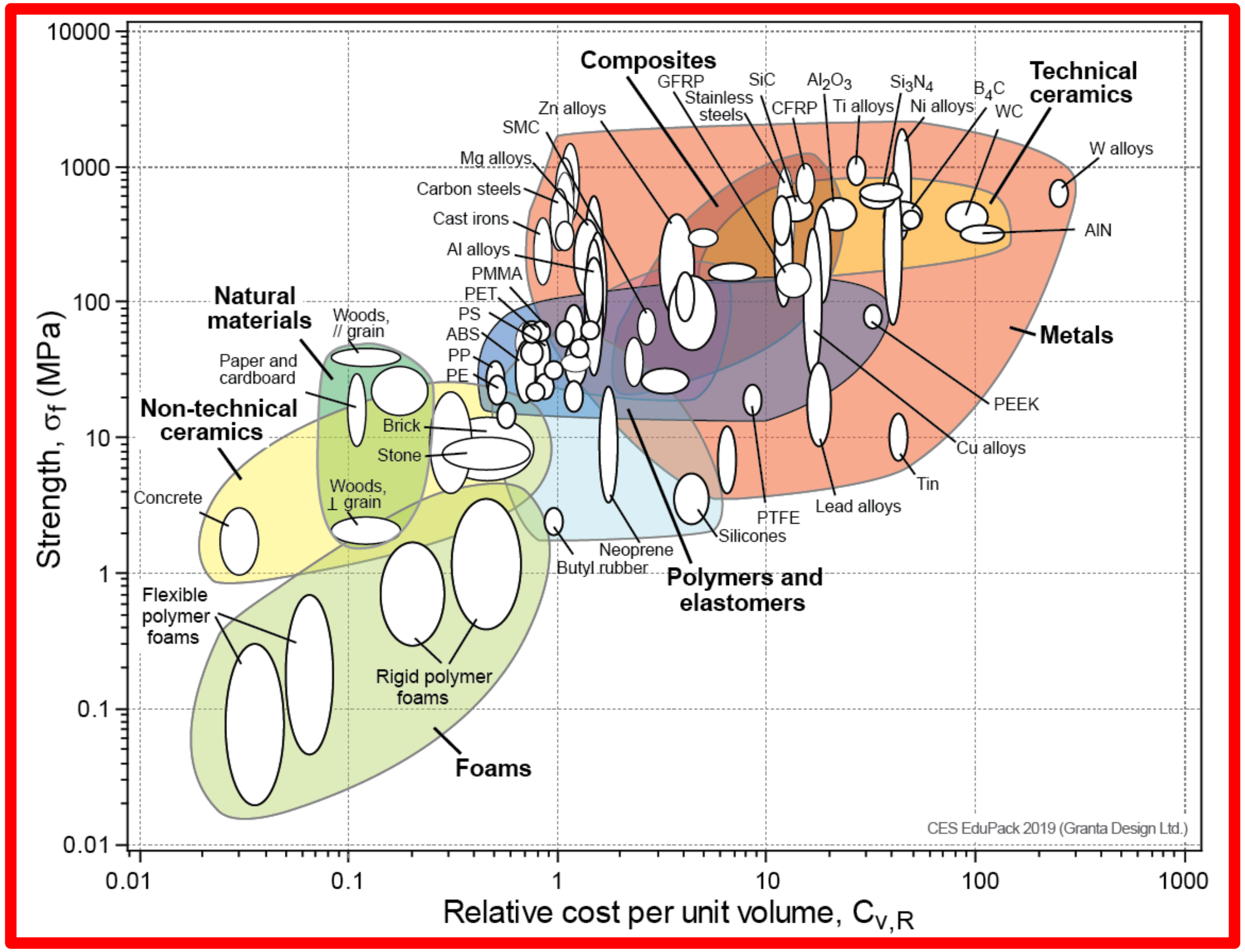
We are used to it making life more convenient

Largely driven by how cheap and useful polymers are!

Why do we keep using polymers then?

Low Cost

(A water bottle can cost ~1 cent to make!)



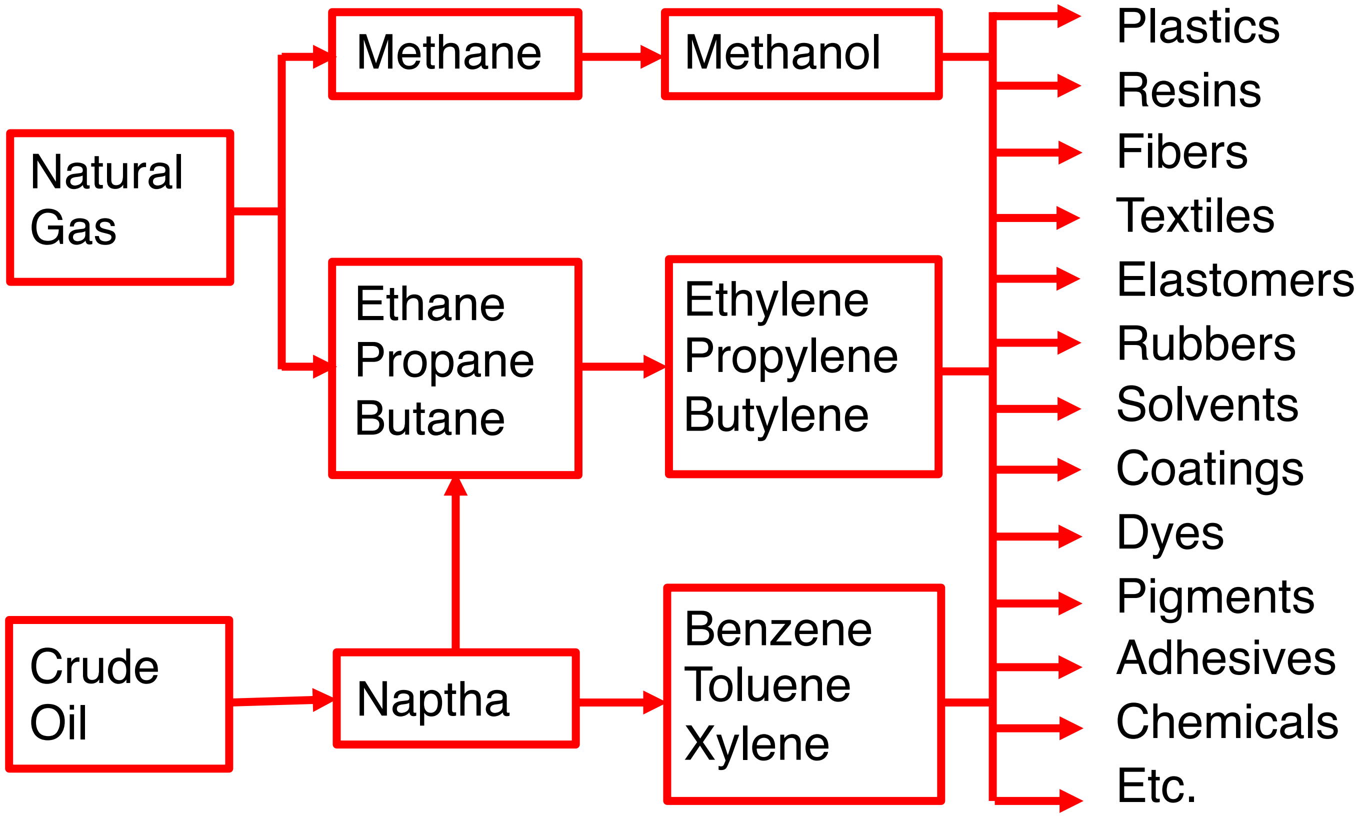
Versatile properties!

- Optical (Transparent → Opaque)
- Thermal (Low → High thermal stability)
- Mechanical (Weak → Strong; Brittle → Ductile)
- Electrical (Insulating → Conductive)
- Chemical (Inert → Reactive)
- Piezoelectric
- Magnetic (very weak, but still magnetic!)
- Stimuli-responsive (pH, heat, light, reagent)
- Lightweight
- Luminescent

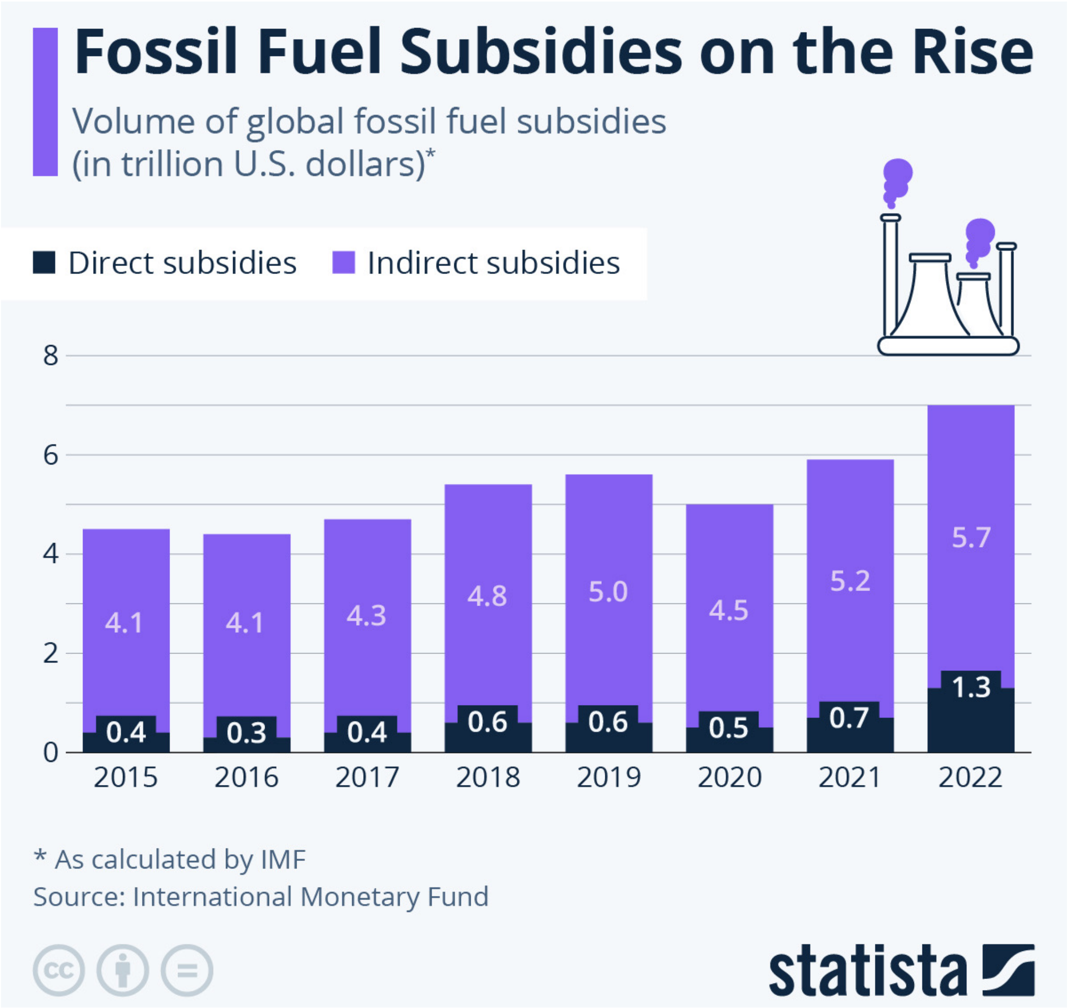
EPFL

Why are polymers so cheap?

Much of the chemicals / monomers used for polymer production comes from oil and gas



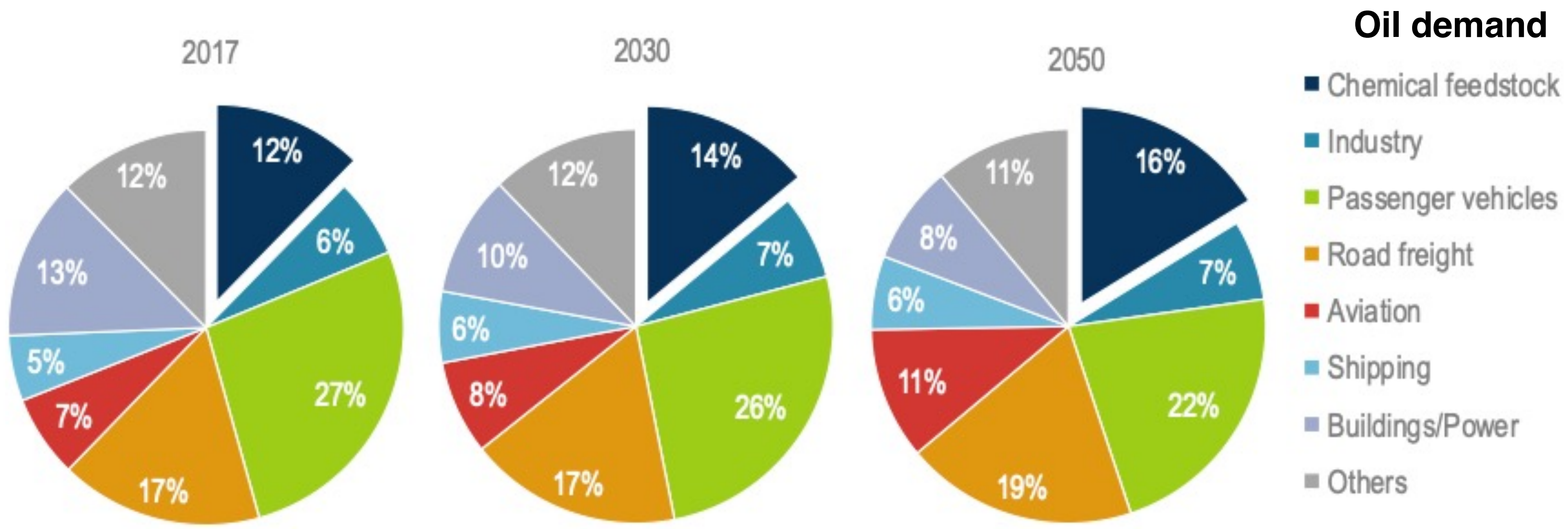
Feedstock is cheap!



Complex relationship between fossil fuel and plastics industries

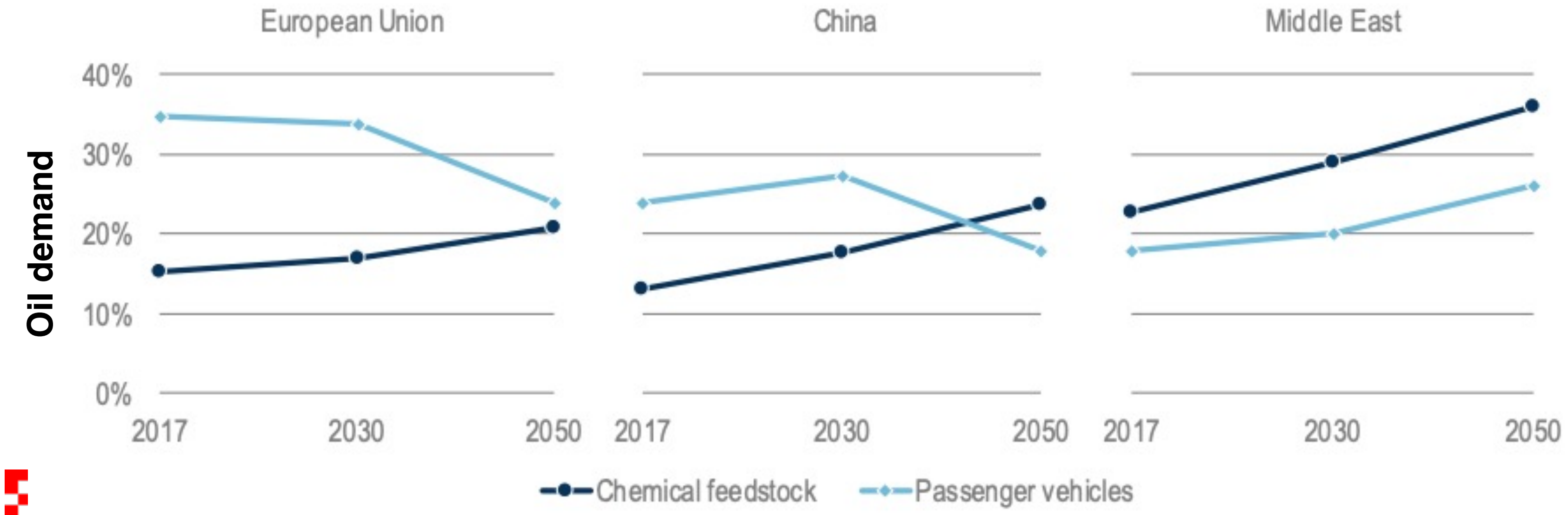
EPFL

Cutting down on fossil fuels also means cutting down on polymers



Vehicle share decrease offset by feedstock increase

Worth noting that this is despite car fleets doubling!

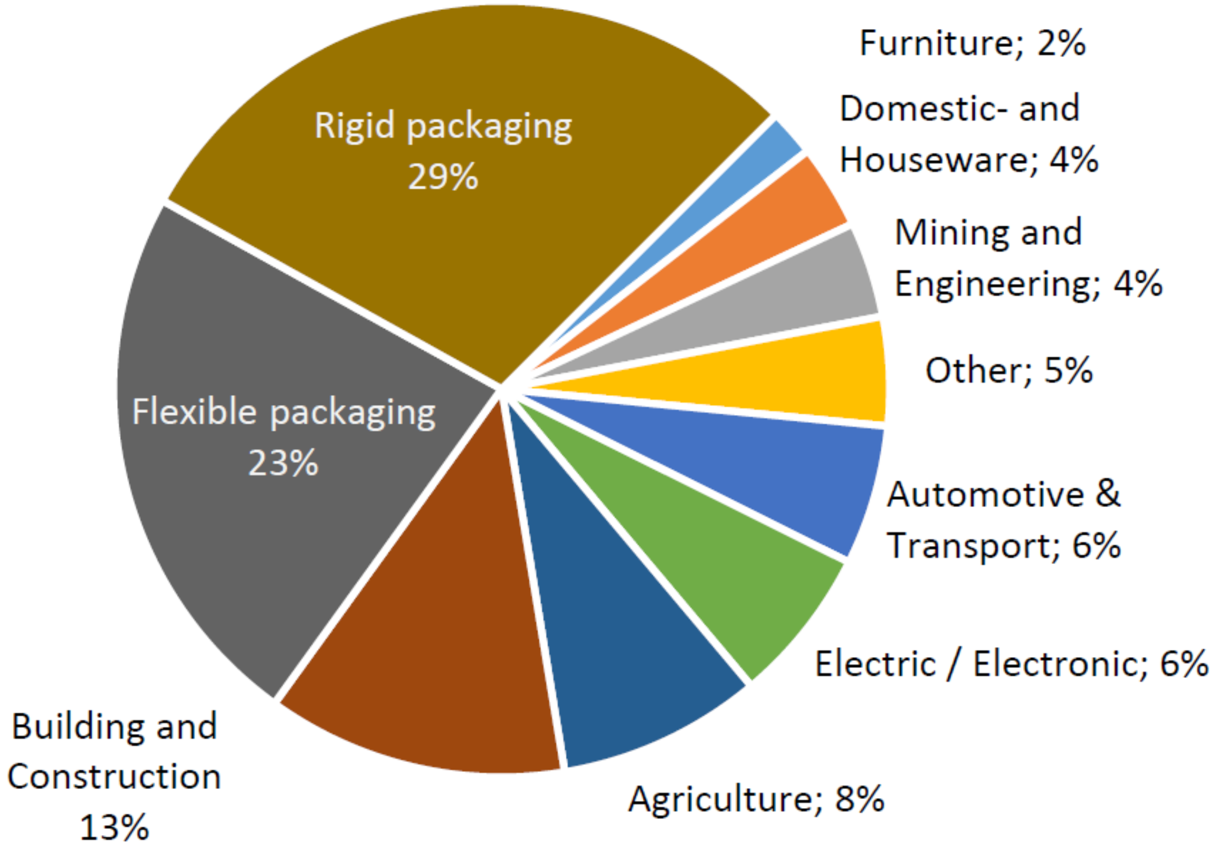


Polymers play a large and growing role in oil and gas demand!

OECD/IEA 2018: The Future of Petrochemicals

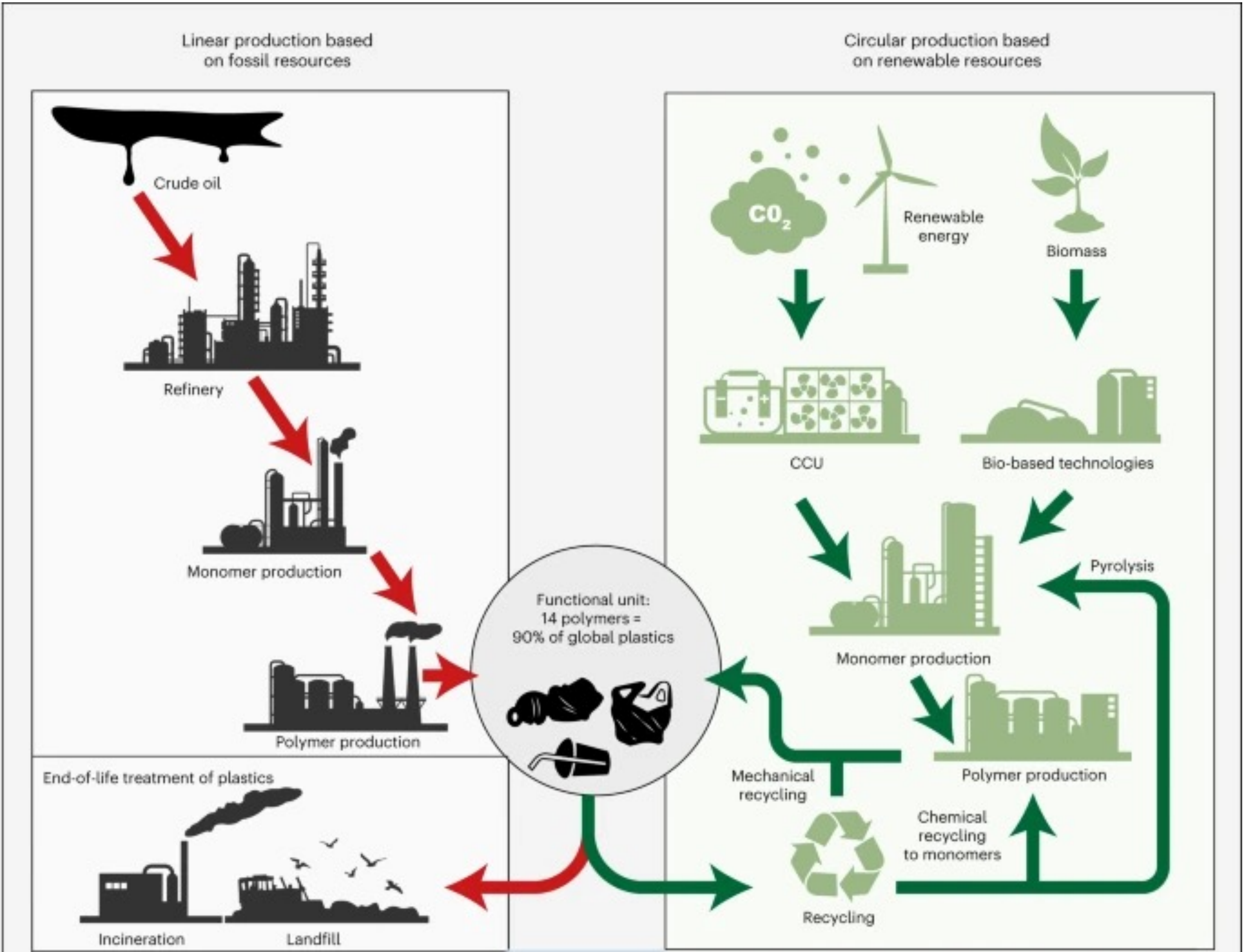
Are polymers inherently bad then?

Polymers are needed for modernization and for economic growth. Important for developing nations!



But at the same time…

From Linear to Circular

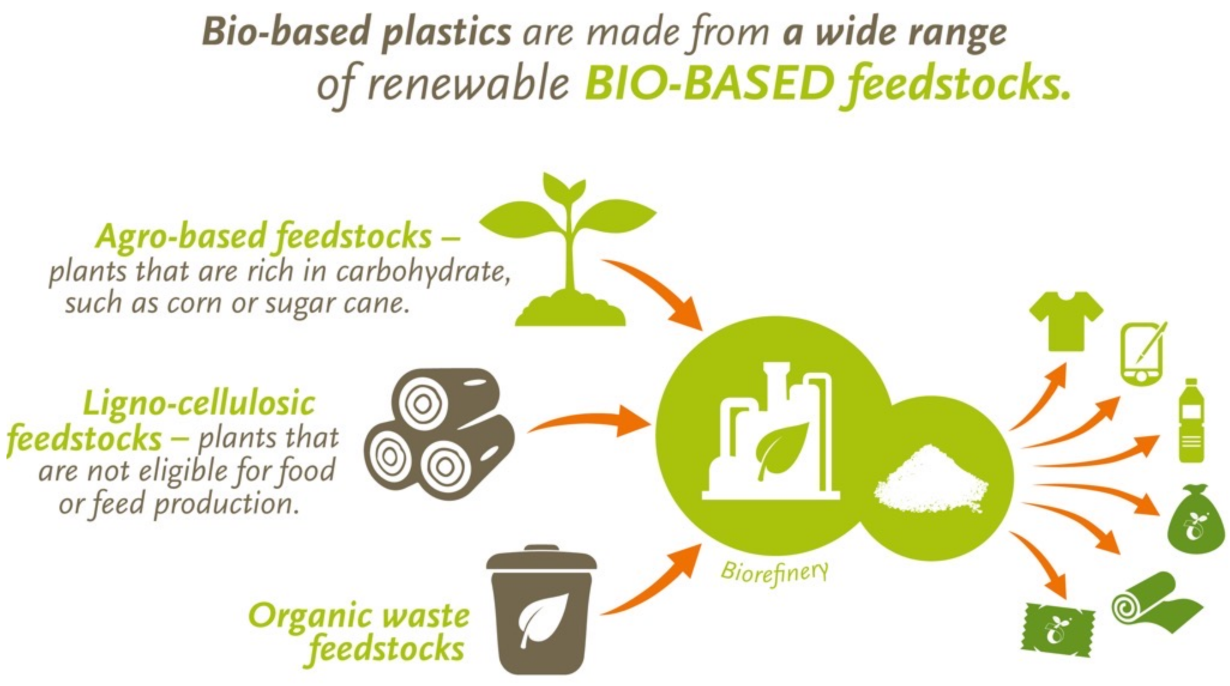


Polymers are not inherently bad, but the way we produce and use them are not sustainable!

Complex challenge that encompasses science, manufacturing, policy, and politics

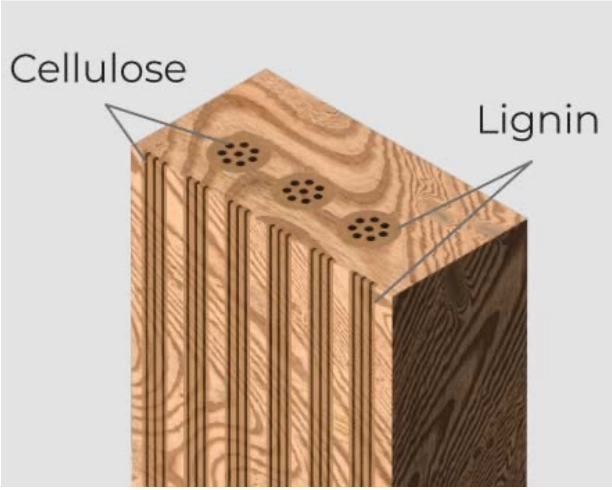
Materials: Bio-based Polymers

<u>Bio-based Feedstock</u>

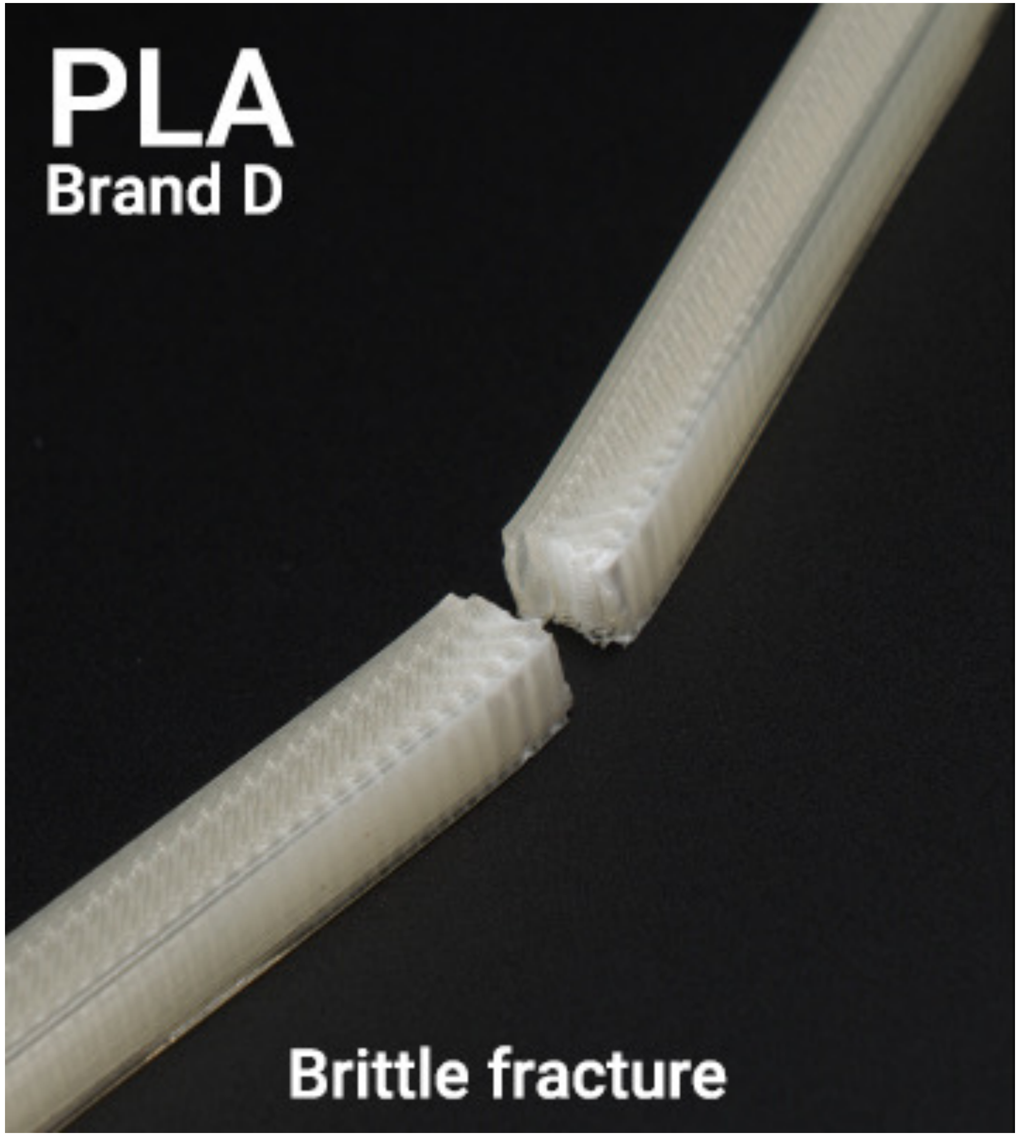


Polylactic acid

Cellulose



Materials: Bio-based Polymers have limited properties



T_g ~ 70˚C

Can’t store hot drinks

Brittle at room temperature

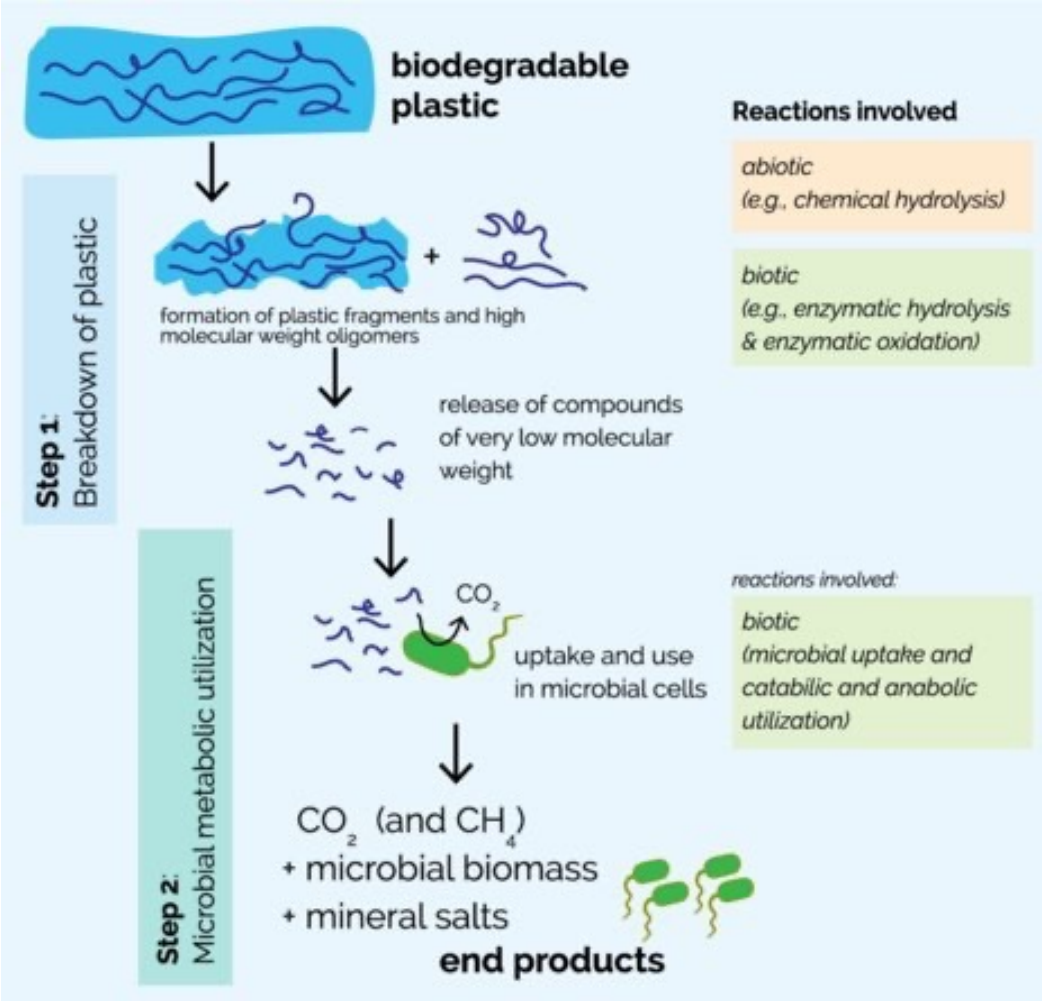
Poor barrier properties

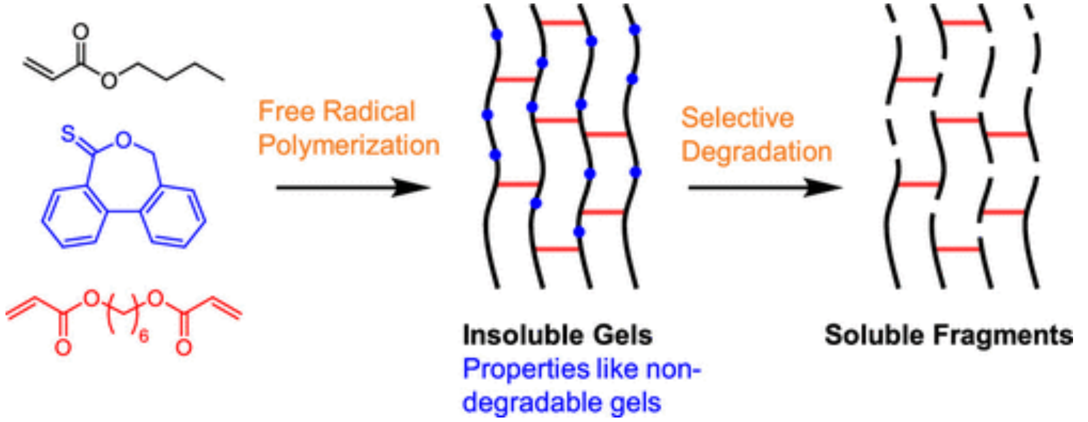
Significant efforts on improving the properties of bio-based polymers

See: ***J. Mater. Chem. A***, 2018,**6**, 9298-9331

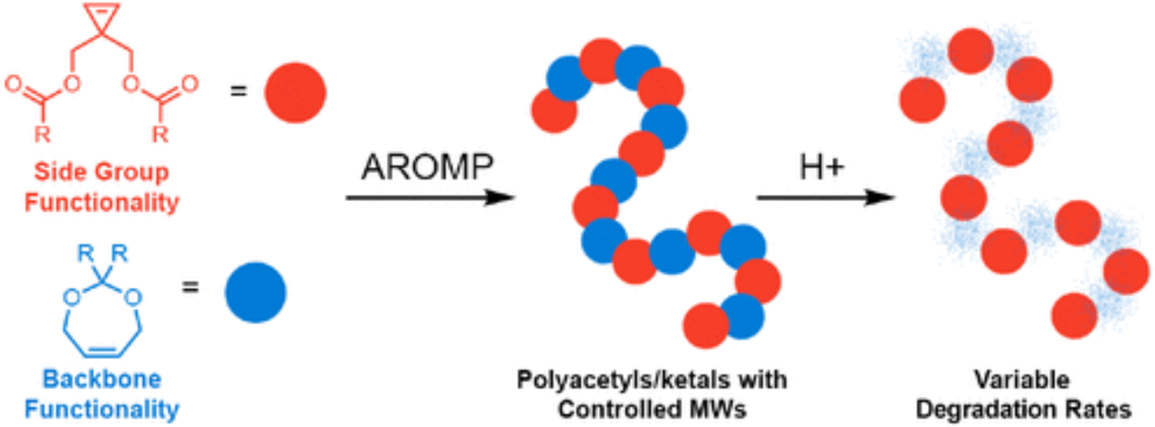
Materials: Biodegradable Polymers

Biodegradable Polymers



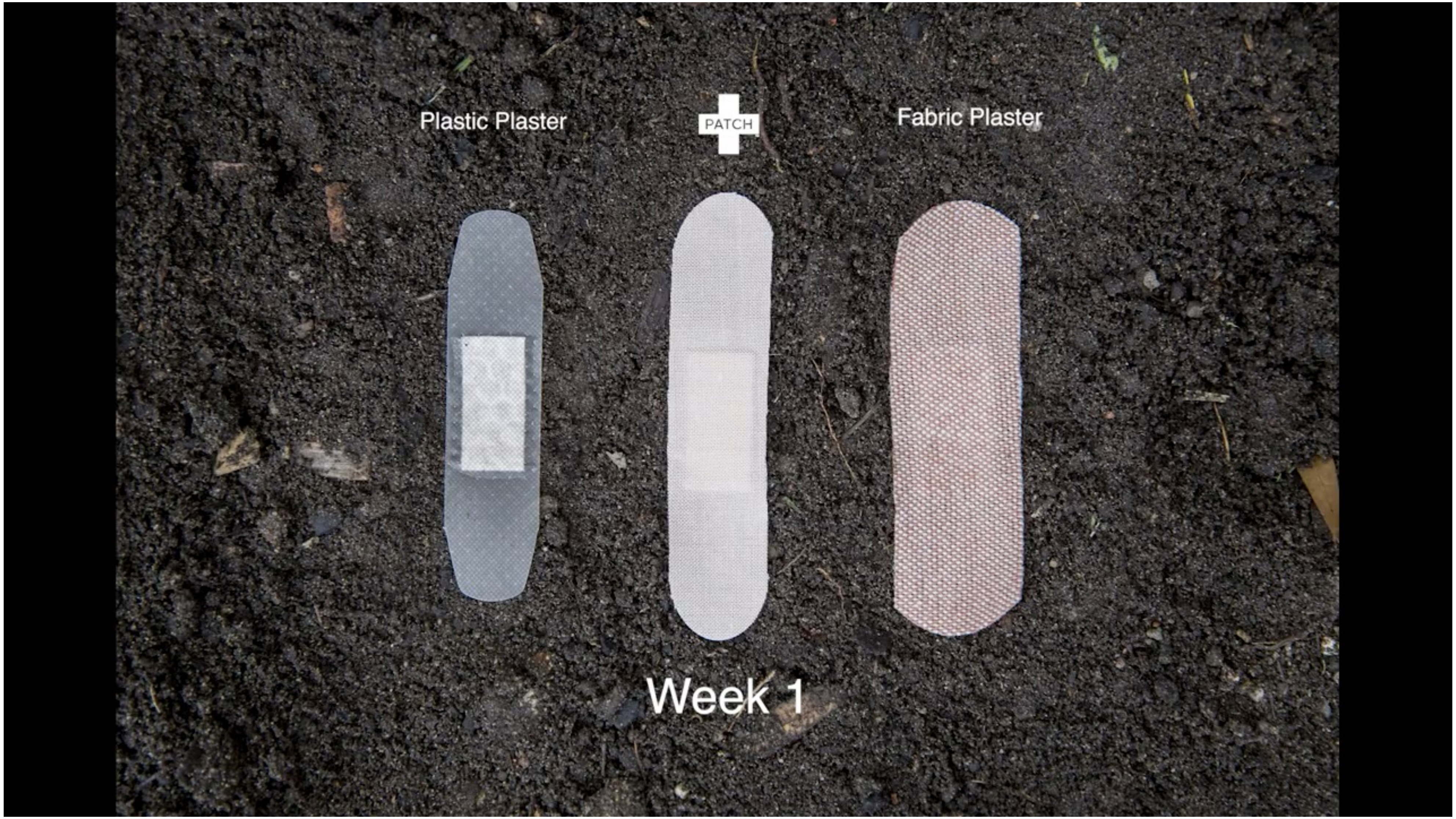


Macromolecules 2022, 55, 15, 6695–6702



ACS Macro Lett. 2020, 9, 2, 180–184

Materials: Biodegradable Polymers

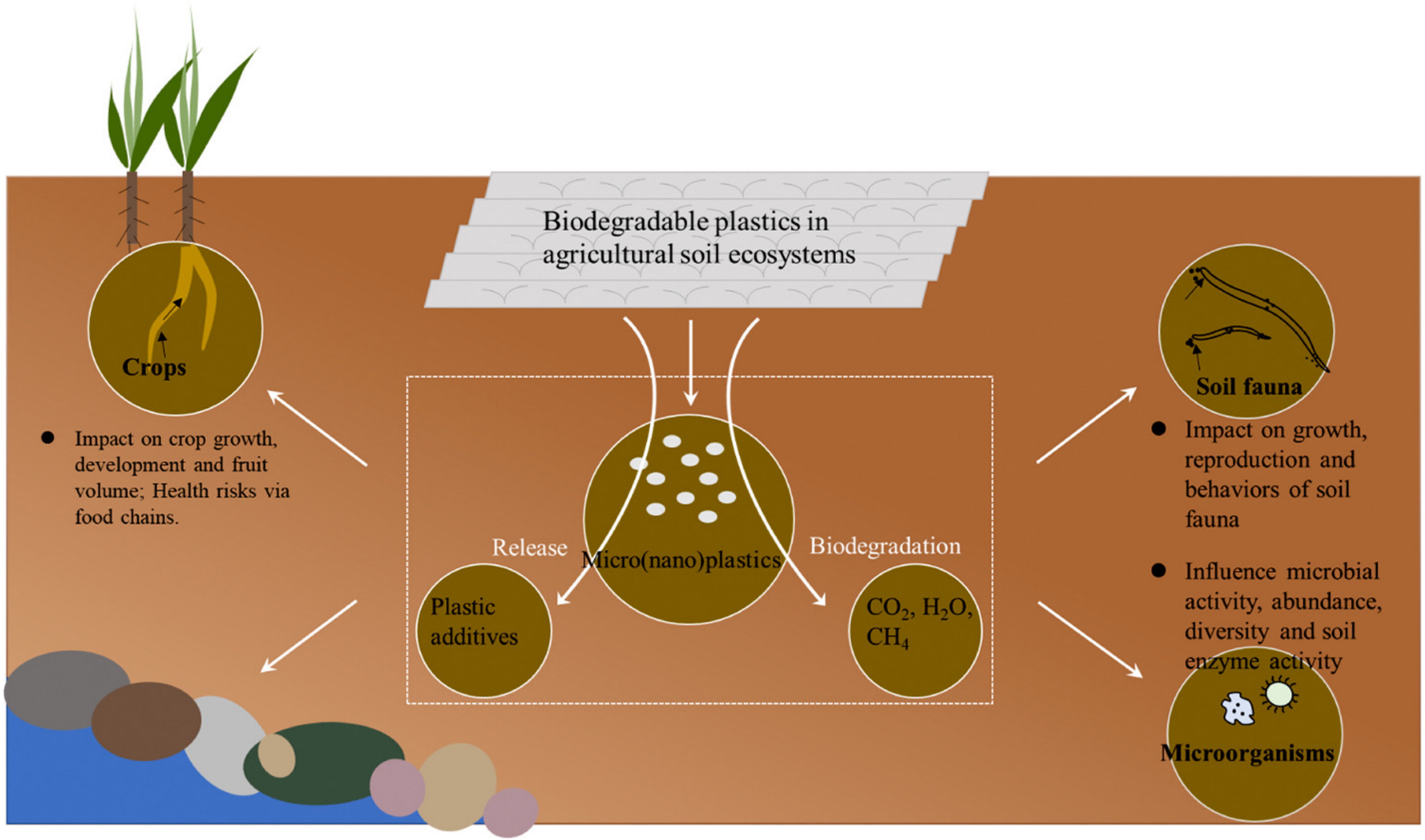


PATCH is made with <u>bamboo fibre</u>

↓

Biodegradable

Materials: Biodegradable Polymers pollute in their own ways



Mo, Aoyun, et al. *Applied Soil Ecology* 181 (2023): 104667.

Materials: Depolymerization

Recap: **Exercise 2, Question 6**

Many of the step reactions covered in the lecture are actually equilibrium reactions, i.e., it is more accurate to depict them as such:

$$\sim\!\sim COOH \;+\; \sim\!\sim OH \;\underset{}{\overset{K}{\rightleftharpoons}}\; \sim\!\sim CO-O\sim\!\sim \;+\; H_2O$$

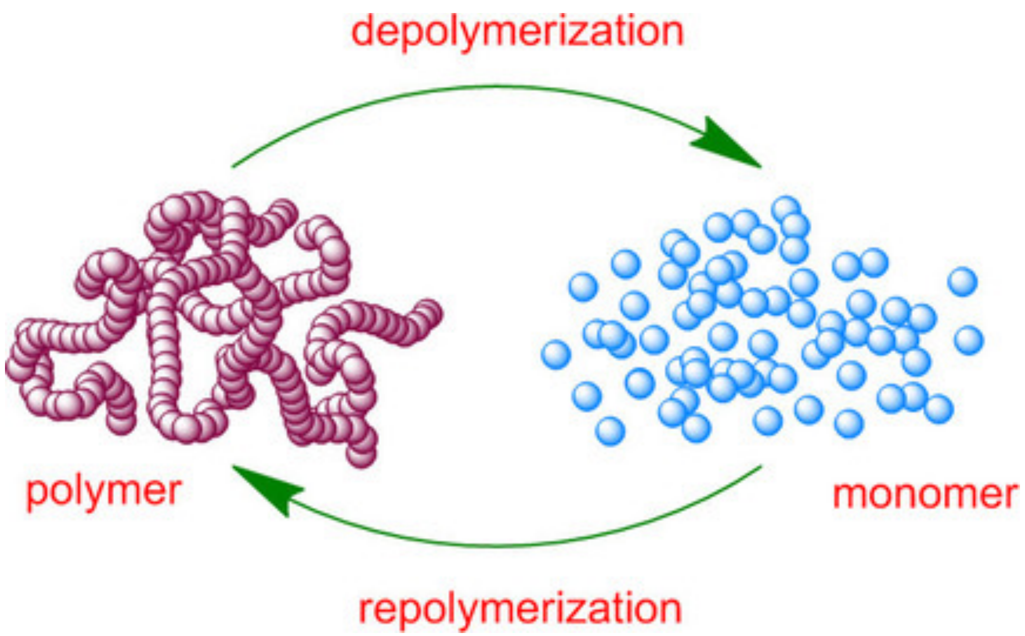
(Carboxylic acid) (Hydroxyl group) (Ester)

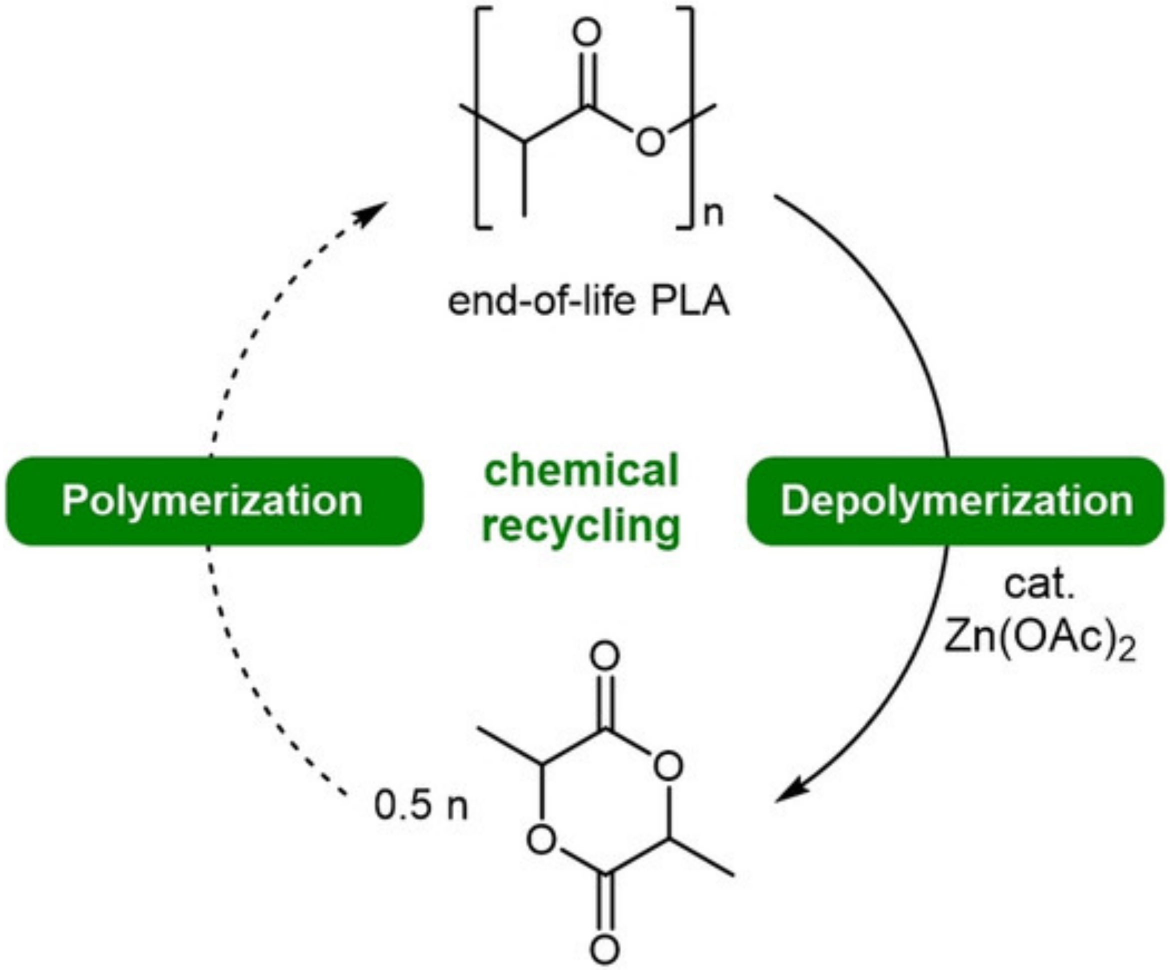
c) What is one important sustainability implication of the fact that these reactions are in an equilibrium?

Ans: The fact that these reactions can be reversed implies that these polymers can be depolymerized. (Polymer can break down to its constituent monomers)

EPFL

Materials: Depolymerization





Slightly distinct from biodegradation

Biodegradation → Degrade in environment

Depolymerization → Recover monomer for reuse

Alberti, Christoph, and Stephan Enthaler. *ChemistrySelect* 5.46 (2020): 14759-14763.

Production: Life Cycle Assessment

Understanding and reducing the environmental footprint of a product

Quantitative and holistic way of measuring the impact of a product across its entire lifecycle

<u>Example: Electric Vehicles</u>

- Lower greenhouse gas emissions during use phase
- Higher resource consumption for battery production
- Hazardous disposal of batteries

LCA lets us identify "hot-spots" where we can take action to reduce the environmental impact

When possible, do an LCA when you pick materials for your devices

Production: Life Cycle Assessment

LCA is useful but can be misleading if not all variables are taken into account

Study by University of Pittsburgh in
Environ. Sci. Technol. 2010, 44, 21, 8264–8269

Table 1. Metrics for Green Design Principles

metric
atom economy
density
TRACI health and ecotoxicity impacts
Total Energy Demand
percent from renewable sources
feedstock distance
percent recycled
biodegradability
price

Table 3. Rankings for Each of the Polymers Based the Normalized Green Design Assessment Results and the Normalized Life Cycle Assessment Results

Material	Green Design Rank	LCA Rank
PLA (NatureWorks)	1	6
PHA (Utilizing Stover)	2	4
PHA (General)	2	8
PLA (General)	4	9
High Density Polyethylene	5	2
Polyethylene Terephthalate	6	10
Low Density Polyethylene	7	3
Bio-polyethylene Terephthalate	8	12
Polypropylene	9	1
General Purpose Polystyrene	10	5
Polyvinyl chloride	11	7
Polycarbonate	12	11

Did not consider:

Impact of recycled polymer on the reduction of new polymer production

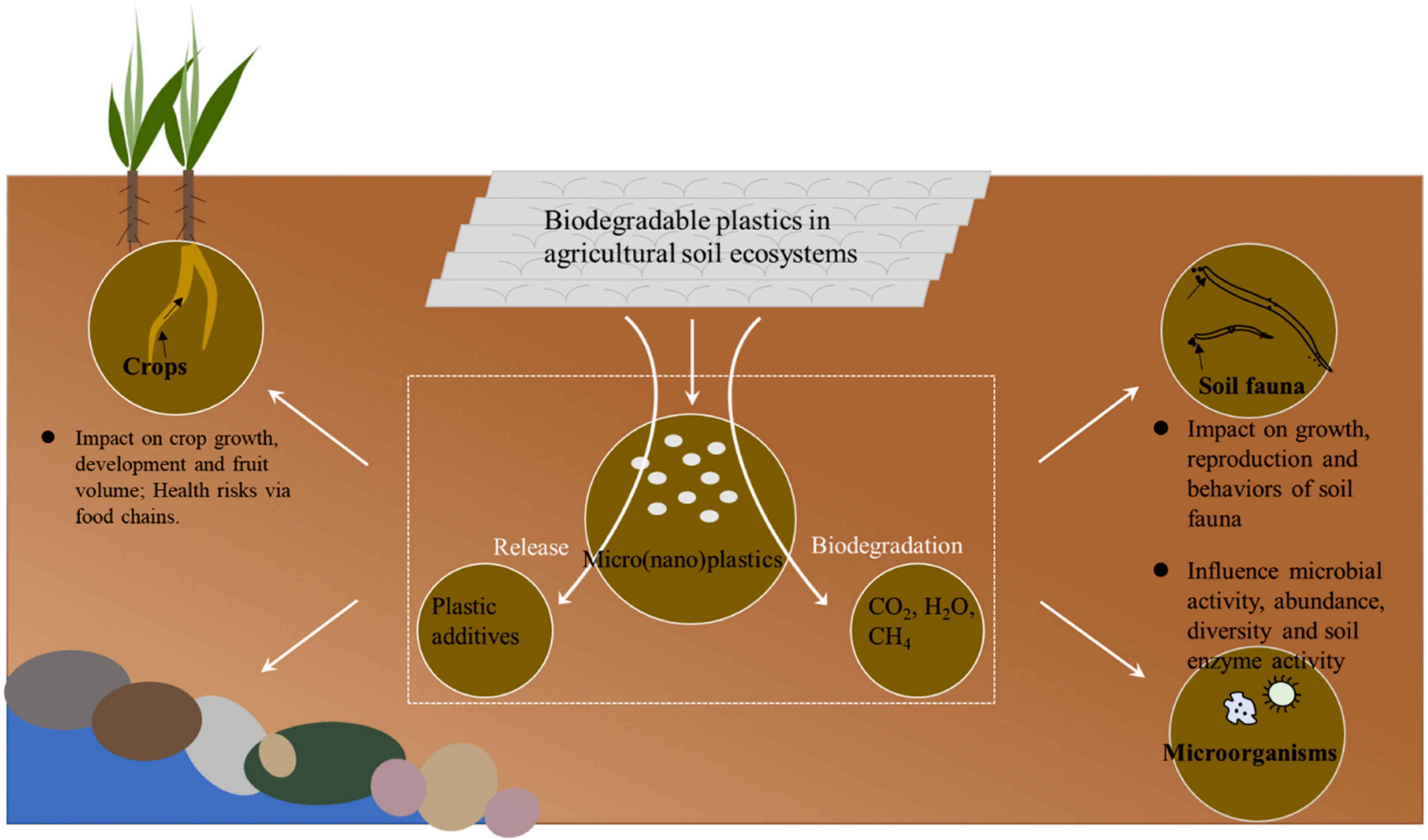
Environmental impact of incineration and land filling

Health impact of byproducts from biodegradation of polymers

LCA is important but diffficult!

Production: Life Cycle Assessment

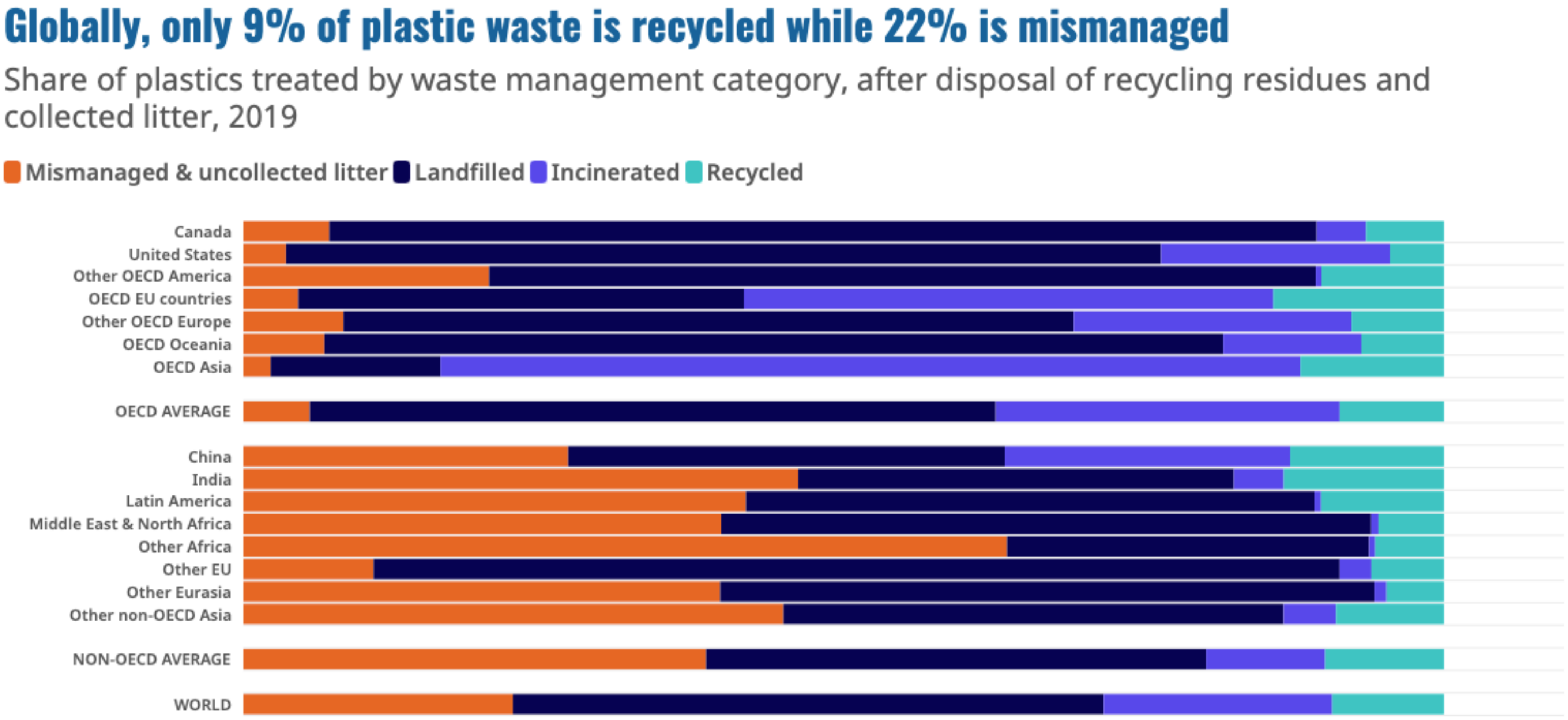
Unintended consequences!



But we recycle our polymers!

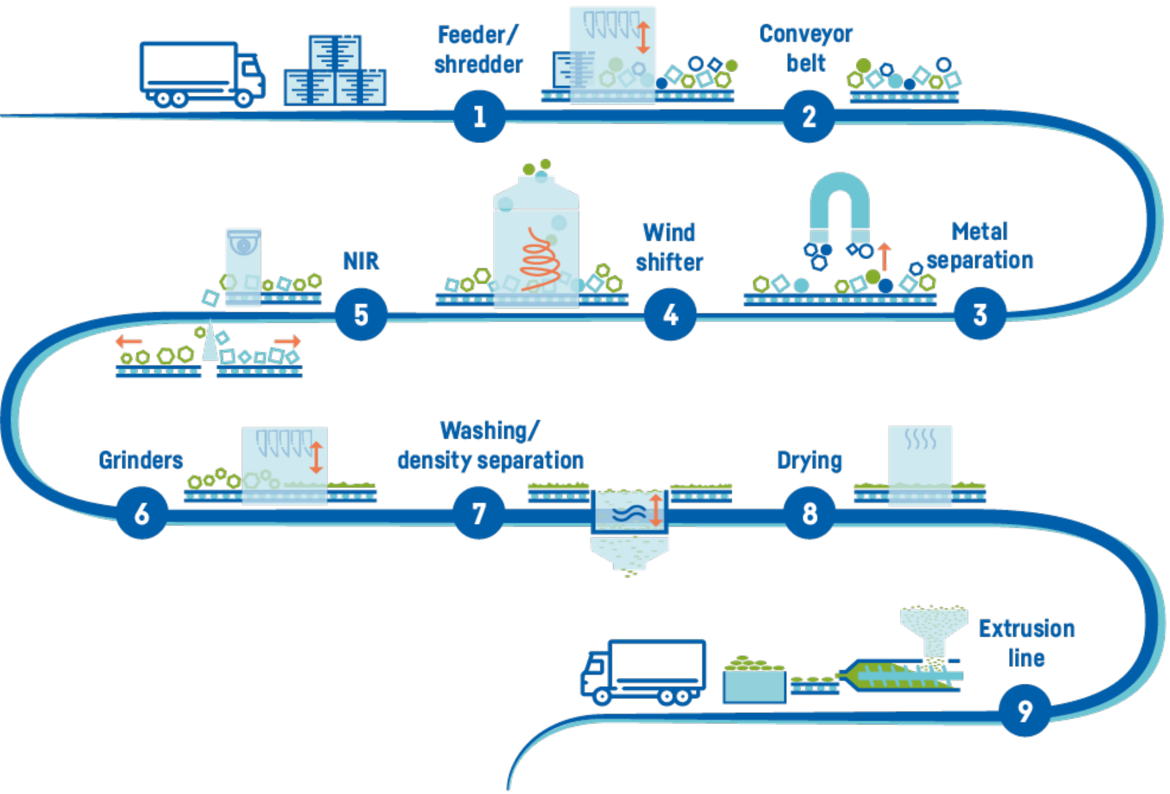
Recycle: When you can’t Reduce or Reuse

Recycling reduces the impact associated with the production of new/virgin polymers

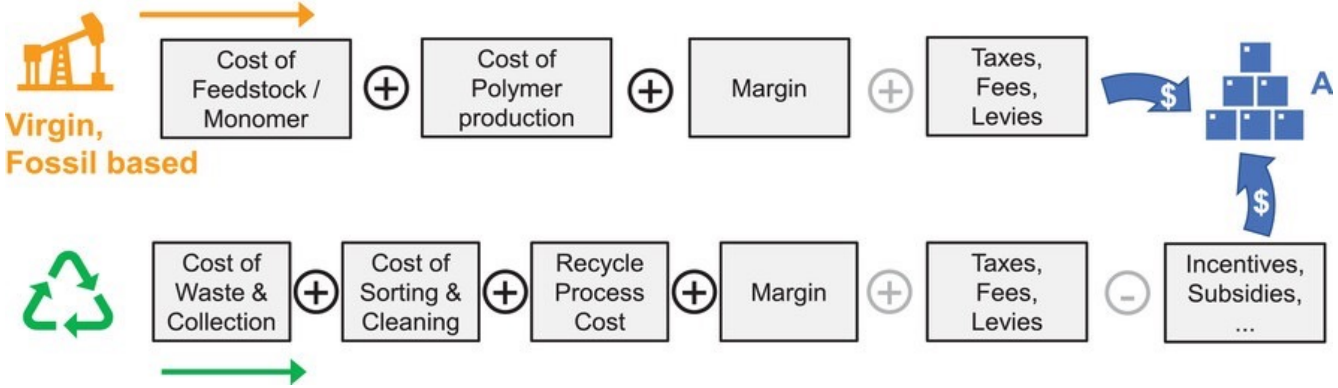


Recycle: Not an Easy Task

Recycling is not easy or cheap to do.



Sorting and repurifying of materials can be expensive and very time consuming

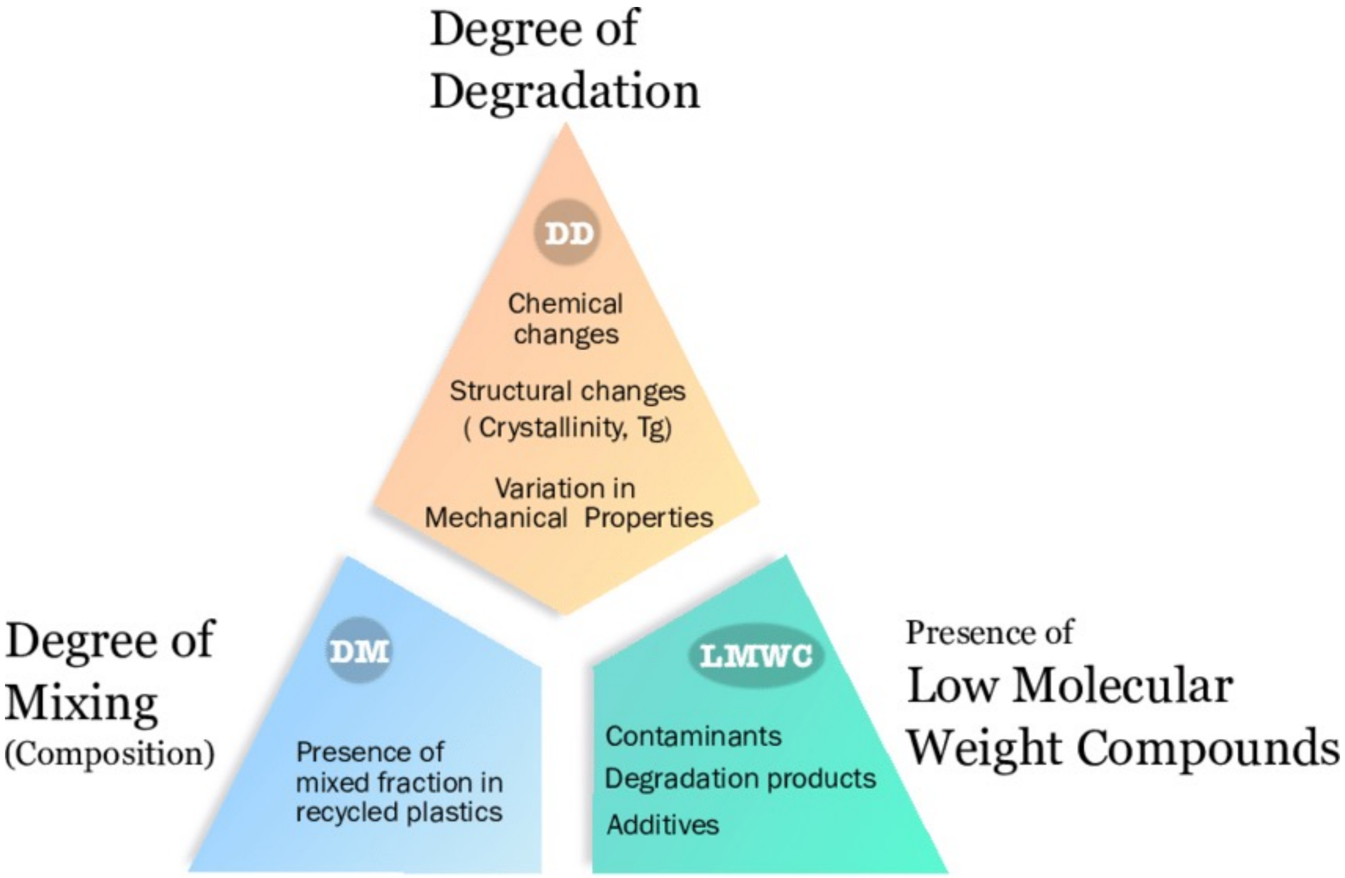


It is still much cheaper to make polymers from new feedstock than from recycled ones

In part because feedstock from oil and gas are subsidized!

A lot of ongoing research on how to simplify polymer recycling

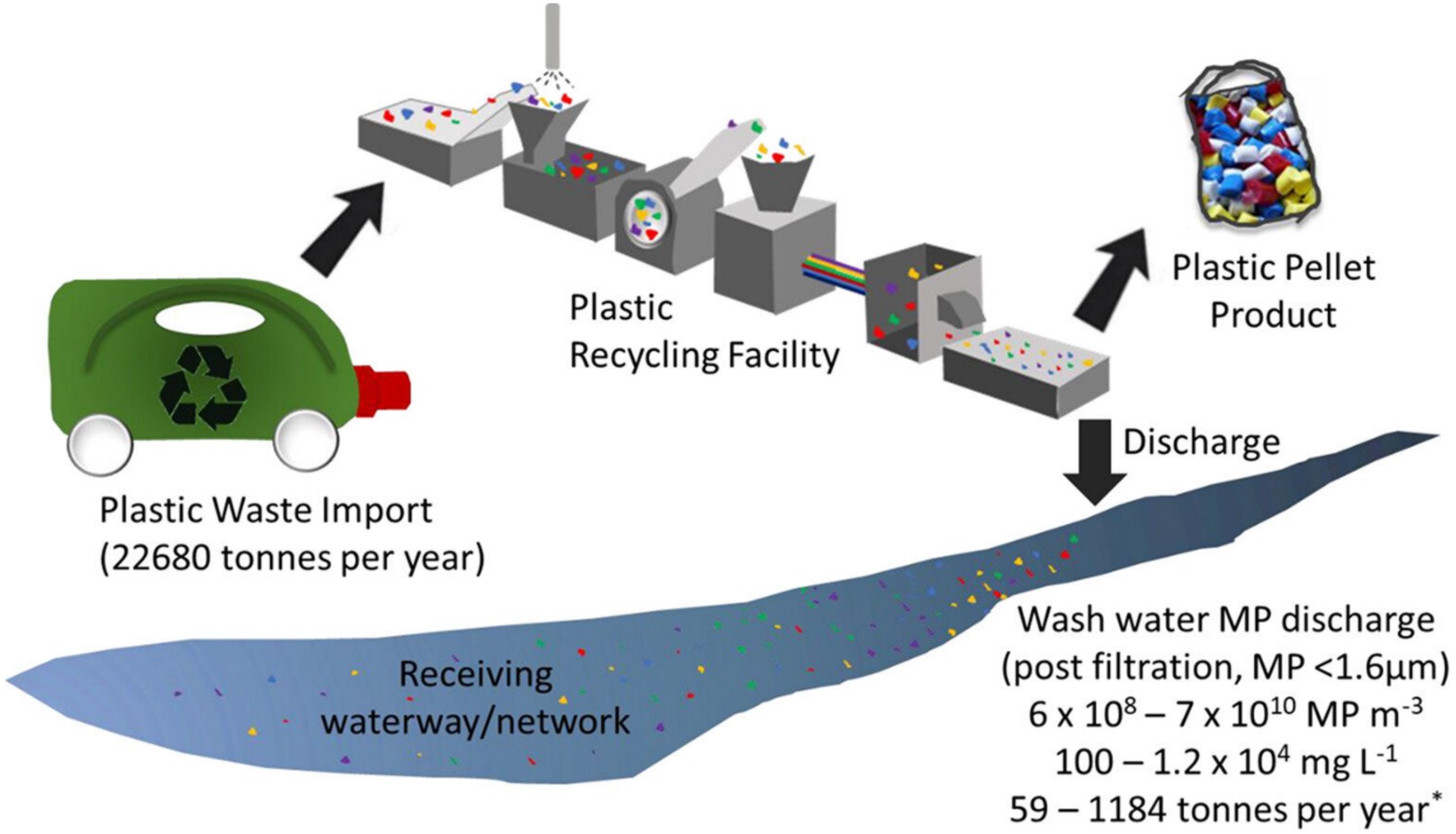
Recycle: Changes in Properties / Unintended Consequences



Miscible or immiscible blends can form → Not always a positive thing

Recycle: Changes in Properties / Unintended Consequences

Microplastics

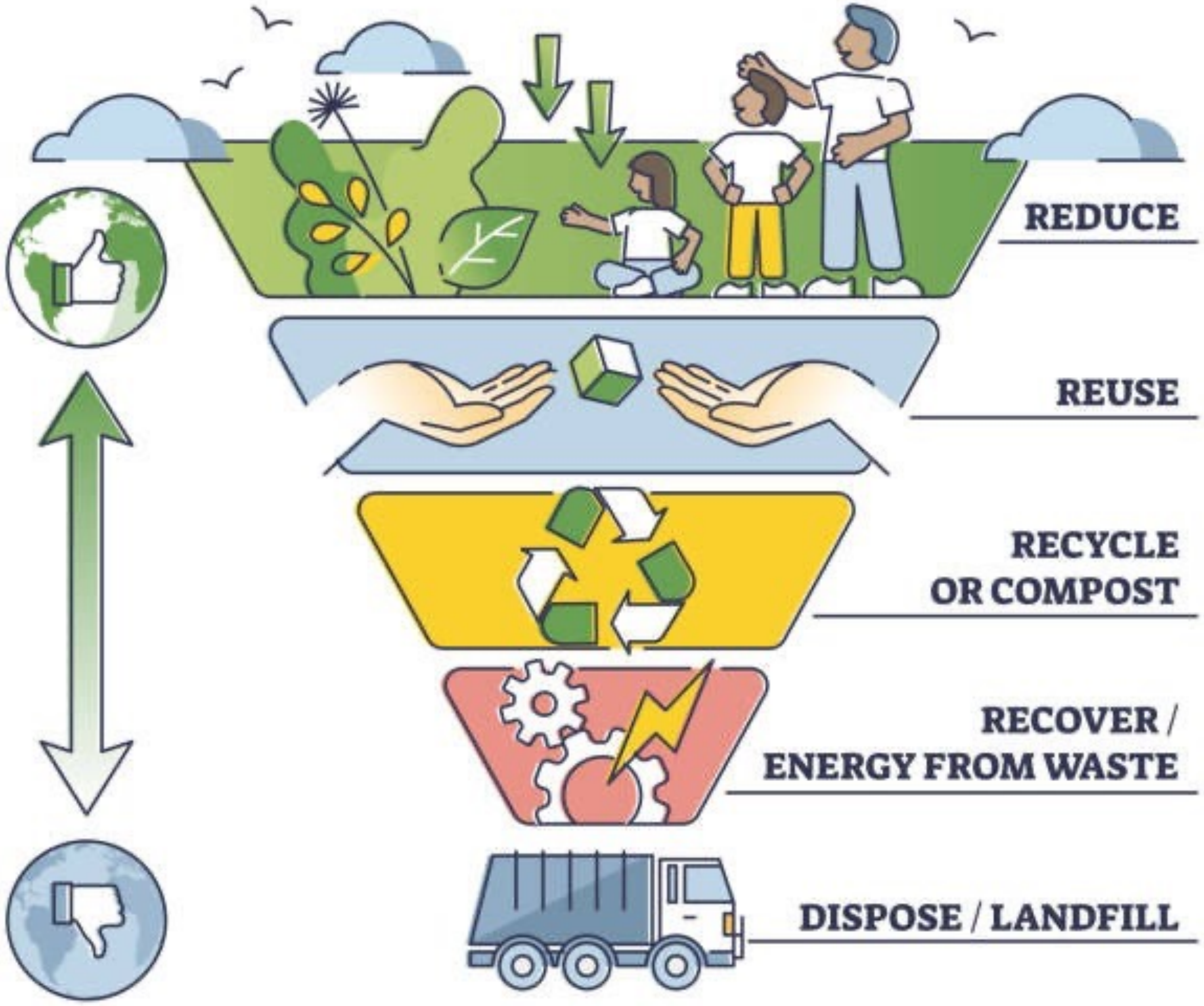


Lots of active research on improving recycling

Recycling is important but challenging and we have a way to go

We should aim to reduce and reuse more!

Reduce > Reuse > Recycle



Policy: The Most Effective Way Forward?

Public awareness of climate change and sustainability has driven a lot of new legislation targeted at polymers

Some recent legislation

Ban on single-use plastics →

Mandated use of recycled polymers in new products

Tax on non-recycled polymer waste

Tax on production of new polymers

Timeline

Key dates related to the Directive on single-use plastics

4 February 2022 — **Commission adopts Implementing Decision 2022/162**

Implementing Decision 2022/162 lays down rules for the calculation, verification and reporting on the reduction in the consumption of single-use plastic food containers and beverage cups

1 October 2021 — **Commission adopts Implementing Decision 2021/1752**

Implementing Decision 2021/1752 lays down rules for the calculation, verification and reporting of data on the separate collection of waste single-use plastic beverage bottles

3 July 2021 — **The EU no longer allows certain single-use plastic items to be placed on the Member States market; and marking requirements enter into force**

Find out more about the marking specifications and download the pictograms

31 May 2021 — **Commission adopts guidelines on single-use plastics products, and implementing decision on reporting on fishing gear**

View the guidelines in all EU languages

View the implementing decision on reporting on fishing gear

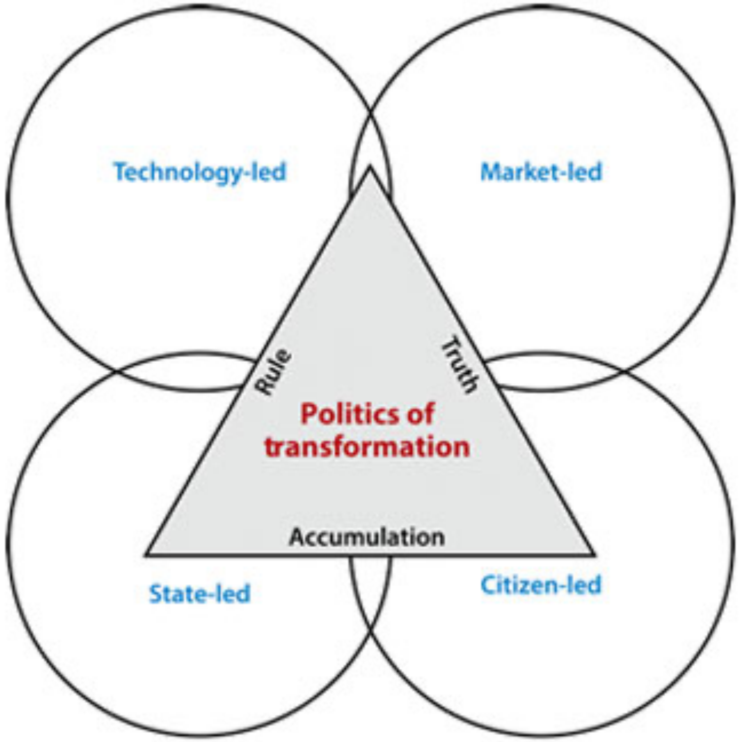
2 July 2019 — **Directive on single-use plastics enters into force**

Hide 2 items

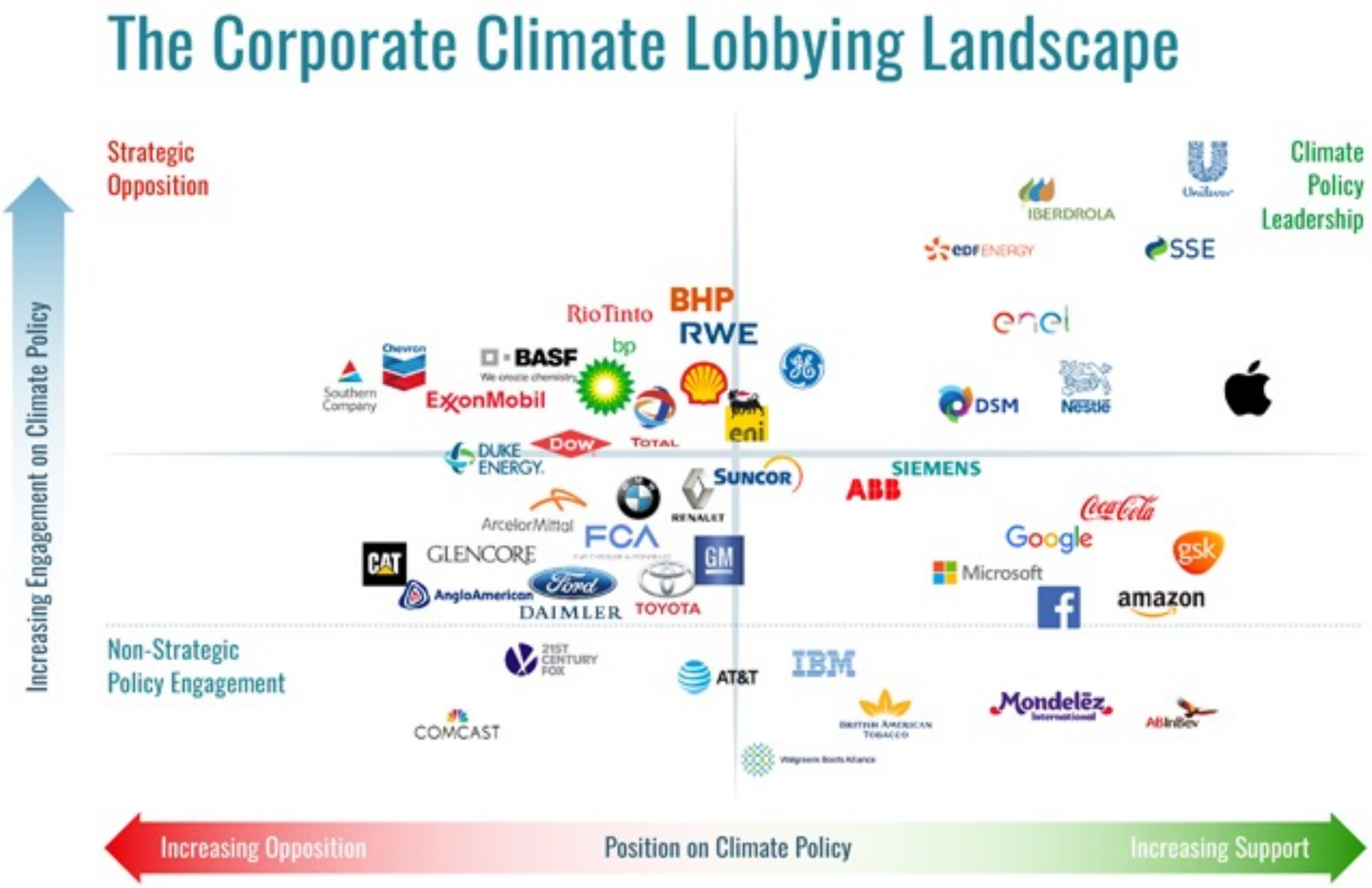
16 January 2018 — **Publication of the EU plastics strategy - outlining the need for a legislative proposal on single-use plastics**

EPFL

Policy is a battle between various stakeholders

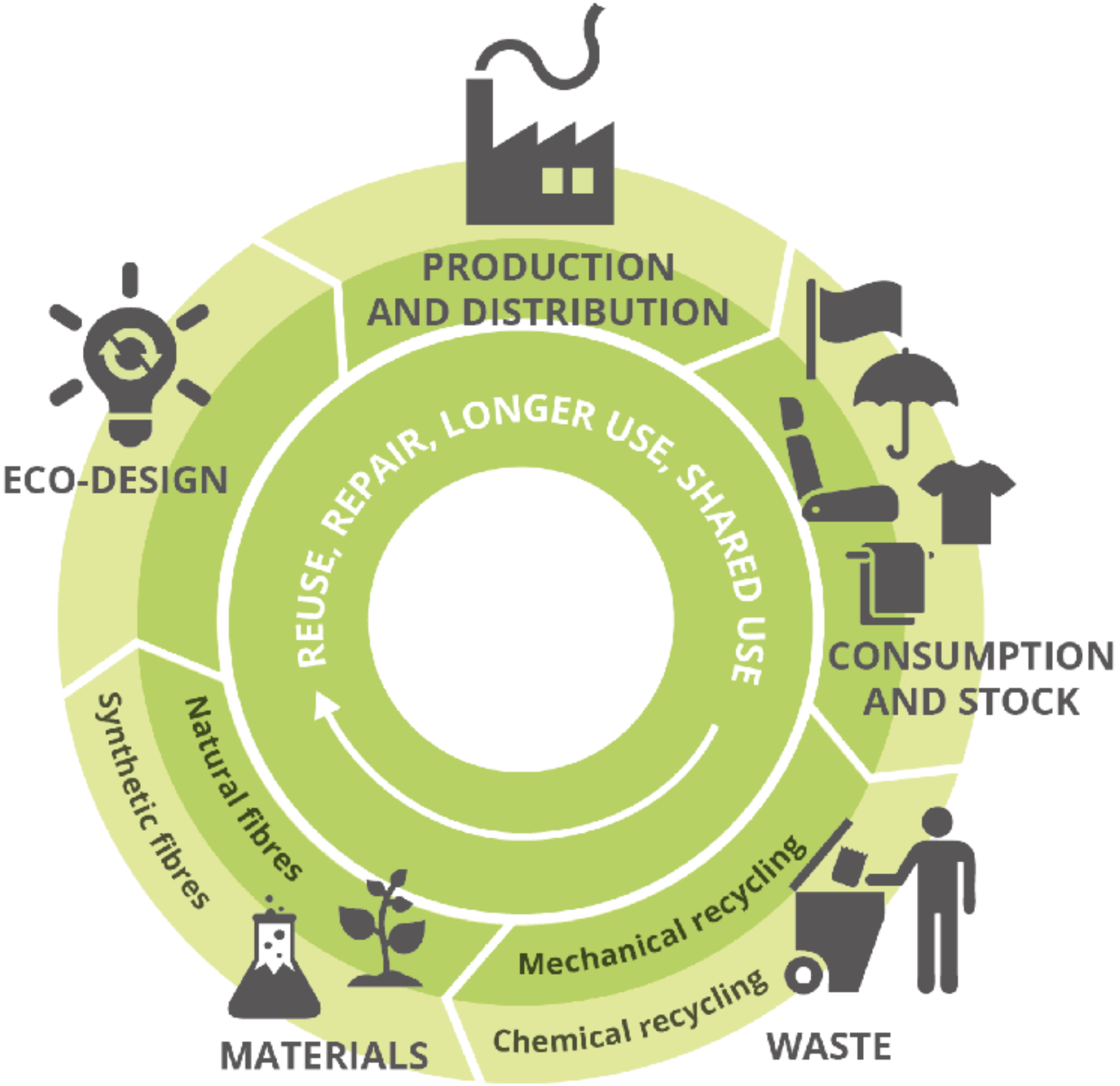


Annual Review of Environment and Resources 41 (2016): 293-319.



InfluenceMap 2018

Where we want to be



Sustainability (of polymers) is a complex problem!

Science is just one part of the solution; production, logistics, education, policy, etc. all play a role in tackling this!

Many roles that you as future scientists, engineerings, educators, politicians, etc. can play to help tackle this crisis

MSE 214 Polymers Summary

- Polymers are made from monomers and that there are many different types of polymers (copolymer, branched, graft, crosslinked, etc.)
- Polymers are characterized by their average molecular weight and dispersity
- Polymers can be made via chain-growth or step-growth polymerization. How are they different? What are their pros and cons?
- The method and conditions of each polymerization impacts the structure and properties of the polymers
- Polymers can be amorphous and semi-crystalline depending on the structure and chemistry of the polymer. Crystallinity plays a key role in dictating polymer properties
- The glass transition (T_g) and melting (T_m) temperatures are important in deciding the application of polymers

MSE 214 Polymers Summary

- The mechanical properties of polymers are dependent on the temperature and the polymer chemistry
- Polymers are viscoelastic and have mechanical properties that are time-dependent.
- Polymers have great strength-to-weight ratios (light and strong!)
- Polymers are a huge contributor to climate change and pollution
- Making polymers sustainable is a complicated challenge that involves multiple partners working together to address

Polymers are complex and messy materials!

But I hope this class helped you understand them better and gave you a better appreciation for the wonders of chemistry!