Plastics & Bioplastics MSE 493

Prof. Tiffany Abitbol

2024

“Better Living Through Chemistry” - 1935

- Neoprene
- Nylon
- Teflon
- Lycra
- Kevlar

"Throaway living" - 1955

FEEDING BOWL for pets comes with a wrought-iron stand and disposable, waterproof bowls to eliminate washing-up chore. Stand and six dishes cost $1.

DISPOSA-PAN eliminates scouring of pots after cooking. It consists of steel frame and heavy foil pans to throw out. Frame with eight pans is $2.98.

BARBECUE GRILL is meal cooker with stand, asbestos shell and wire grill, charcoal to last one hour and excelsior topping for a quick light. It costs 79¢.

Throwaway Living

DISPOSABLE ITEMS CUT DOWN HOUSEHOLD CHORES

The objects flying through the air in this picture would take 40 hours to clean—except that no housewife need bother. They are all meant to be thrown away after use. Many are new; others, such as paper plates and towels, have been around a long time but are now being made more attractive.

At the bottom of the picture, to the left of a New York City Department of Sanitation trash can, are some throwaway vases and flowers, popcorn that pops in its own pan. Moving clockwise around the photograph come assorted frozen food containers, a checkered paper napkin, a disposable diaper (seriously suggested as one reason for a rise in the U.S. birth rate) and, behind it, a baby's bib. At top are throwaway water wings, foil pans, paper tablecloth, guest towels and a sectional plate. At right is an all-purpose bucket and, scattered throughout the picture, paper cups for beer and highballs. In the basket are throwaway draperies, ash trays, garbage bags, hot pads, mats and a feeding dish for dogs. At the base of the basket are two items for hunters to throw away: disposable goose and duck decoys.

CONTINUED

"The objects flying through the air in this picture would take 40 hours to clean – except that no housewife need bother. They are all meant to be thrown away after use."

[Life Magazine, 1955]

Plasticene - now

A NEW GEOLOGICAL AGE…(last 60-70 years!)

n. & adj. (2011) an era in Earth's history, within the Anthropocene, commencing in the 1950s, marked stratigraphically in the depositional record by a new and increasing layer of plastic (Stager, 2011, attributed to Matt Dowling). The history and etymology of plasticene in this sense is not related to the word *plasticene*, a common early spelling (for example, Cooper, 1901) of the popular molding clay, plasticine.

A Plasticene Lexicon, Marine Pollution Bulletin,Volume 150, 2020, 110714, ISSN 0025-326X, https://doi.org/10.1016/j.marpolbul.2019.110714.

Commodity plastics

- Approx. 70% of global production is types 1-6

- Biggest single application is packaging = 146 million tonnes (2015), approx. 36% of global production

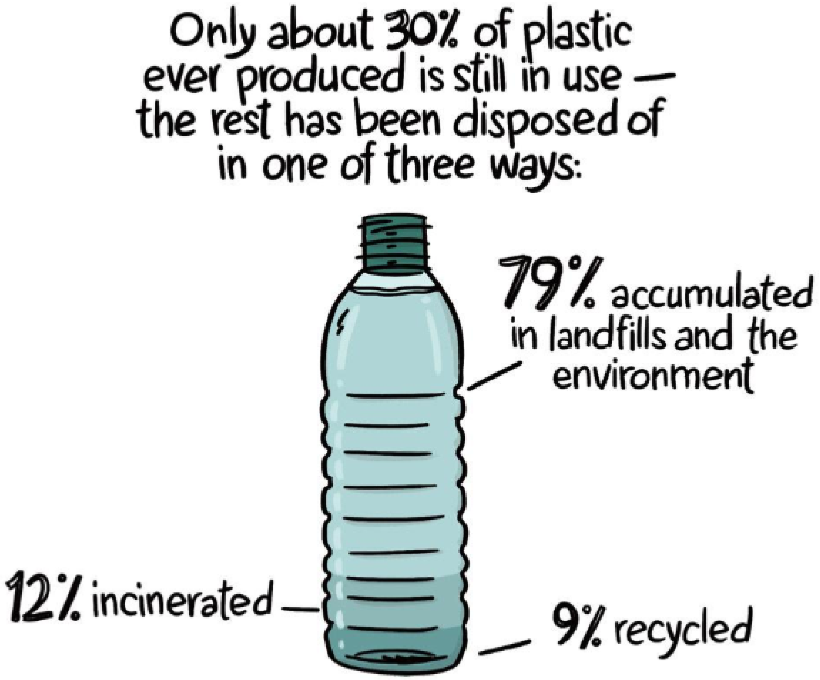
Types of plastics	Symbol	Applications
Polyethylene terephthalate (PET)	1 PET	Beverage bottles, medicine jars, rope, clothing and carpet fibre
High-density polyethylene (HDPE)	2 HDPE	Containers for milk, motor oil, shampoos and conditioners, soap bottles, detergents and bleaches
Polyvinyl chloride (PVC)	3 V	All kinds of pipes and tiles
Low-density polyethylene (LDPE)	4 LDPE	Cling-film, sandwich bags, squeezable bottles and plastic grocery bags
Polypropylene (PP)	5 PP	Lunch boxes, margarine containers, yogurt pots, syrup bottles, prescription bottles, plastic bottle caps and plastic cups
Polystyrene (PS)	6 PS	Disposable coffee cups, plastic food boxes, plastic cutlery and packing foam
Polyethylene (PE) Acrylonitrile butadiene styrene (ABS) Polyamide (PA) or nylons Polybutylene terephthalate (PBT)	7 OTHER	Baby bottles, compact discs and medical storage containers

Common types of plastics

Plastic promises: How'd we do?

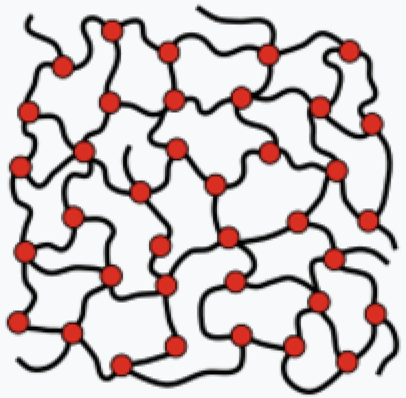
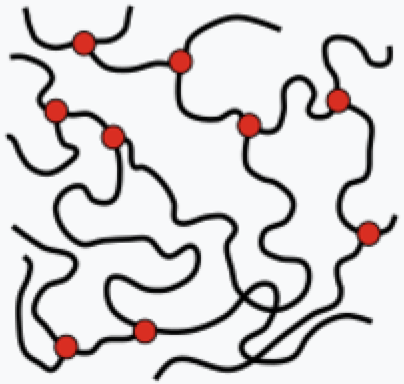
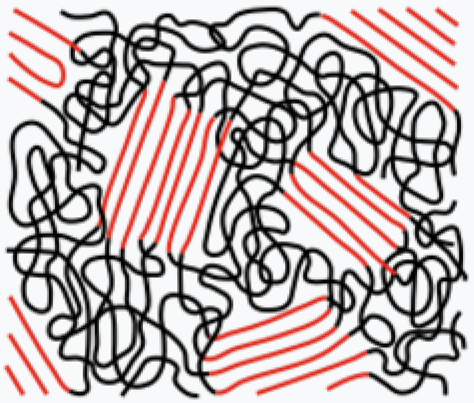
Data from 1950-2015:

- 8300 Mt of plastics
- 6300 Mt of plastic waste
- 12000 Mt in landfill/nature projected by 2050
- Conventional plastics do not biodegrade
- Increased demand for plastics
- Permanent elimination only by incineration



Geyer R. et al., Science Advances 2017, 3(7), 1-5.

Plastics – recyclable or not?

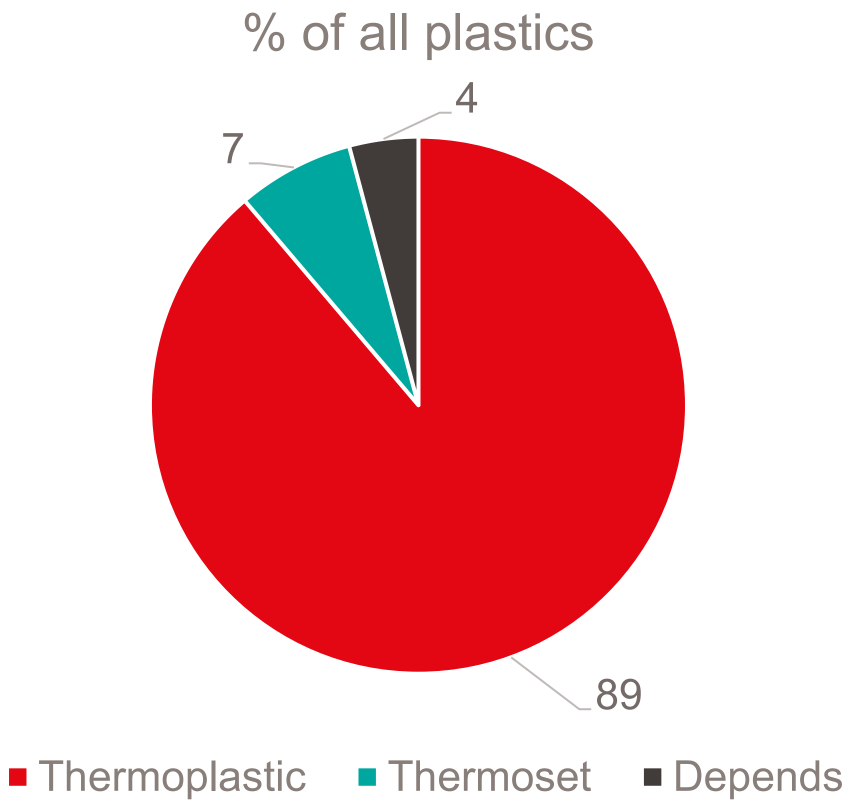
 *Thermosets* consist of closely cross-linked polymers. Cross-links are shown as red dots in the figure.	 *Elastomers* consist of wide-meshed cross-linked polymers. The wide mesh allows the material to stretch under tensile load.	 *Thermoplastics* consist of non-crosslinked polymers, often with a semi-crystalline structure (shown in red). They have a glass transition temperature and are fusible.

Can’t be recycled mechanically

Usually recycled mechanically

Plastic

Thermoplastic or thermoset?



- Rough calculation
- About 75% or more of all commodity plastics are thermoplastics
- So what is the problem? Why are only 9% of all plastics recycled?

Plastic

Recyclable vs. Recycled

- What’s the difference?

Recyclable vs. Recycled

Recyclable		**Recycled**
Can be collected and remanufactured into new products	Vs.	*Has* been collected and remanufactured into new products
up to 75% of commodity plastics are recyclable		<10% of these recyclable plastics have actually been recycled

Plastics Recycling

Recyclable vs. Recycled

Clearly, just because plastics can be recycled doesn't mean they are actually recycled…

- ***Can you think of why?***

[Plastics Recycling]

Why are we so bad at recycling?

- Cost – virgin plastic is cheaper than recycling
- Quality – loss of quality and contamination
- Few established recycling streams (PET and HDPE; types 1 and 2)
- Bans on import of plastic waste (China banned import of low quality plastic waste in 2017 – previously importing majority of waste from North America Europe)
- Mixed plastics
- Insufficient collection and sorting infrastructure

[Why aren't we recycling more plastic?]

[Operation National Sword]

Plastics everywhere - now

- *Microplastics*

- Particles < 5mm in diameter
- Primary or secondary
- Main source is secondary from SUPs

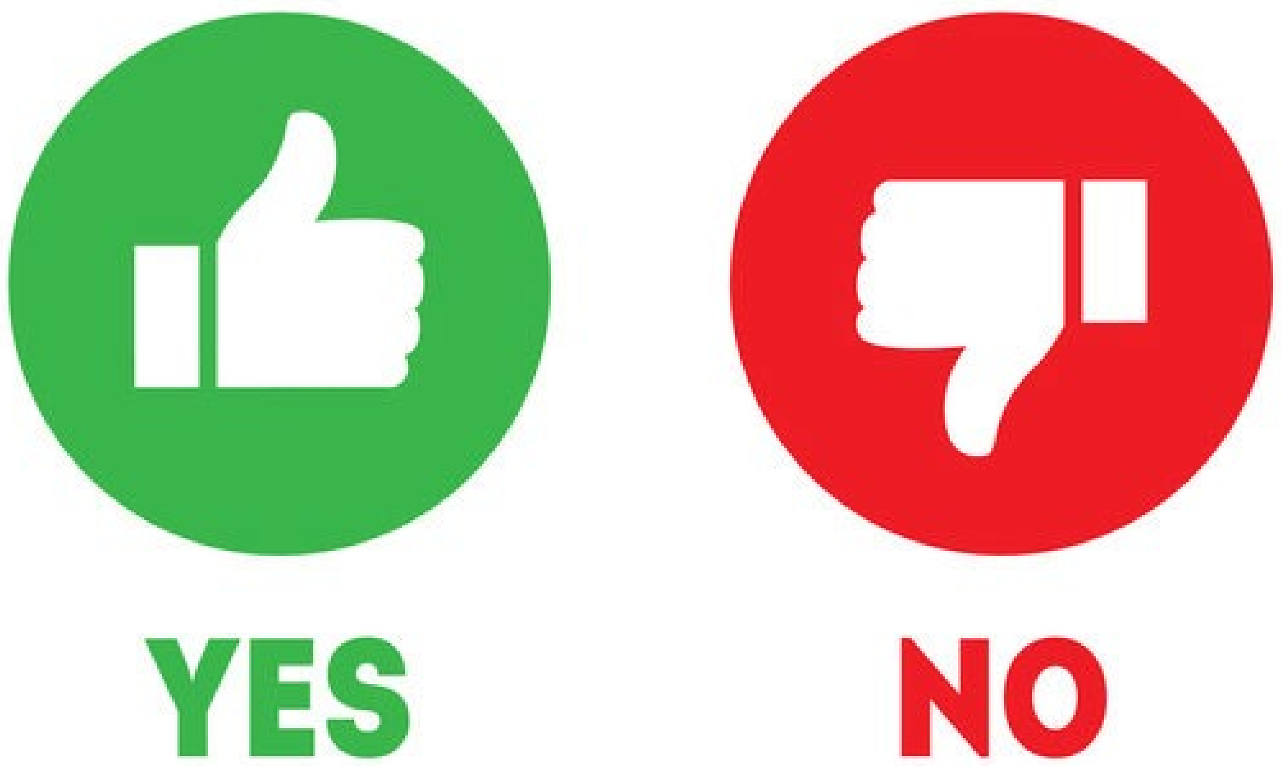
Throwaway living no more

- No widespread ban in Switzerland
  - Geneva banned SUPs in 2020
  - Charge for single use bag
  - Oxo-degradable plastics banned
  - Good waste management infrastructure

[EU SUP ban]

[Swiss plastic policies]

Side note: Can you recycle a thermoset?

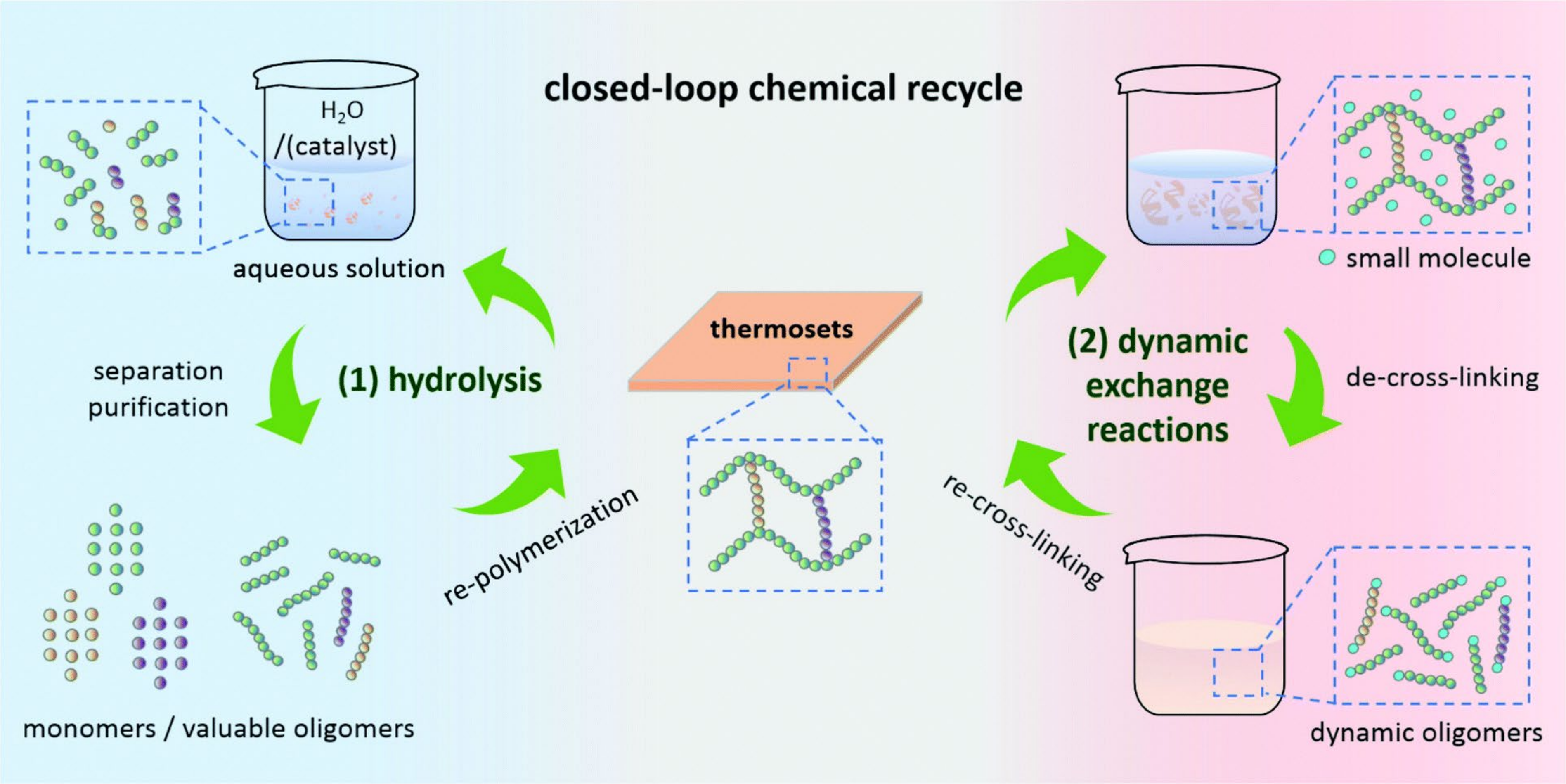


Confusingly, the answer is yes

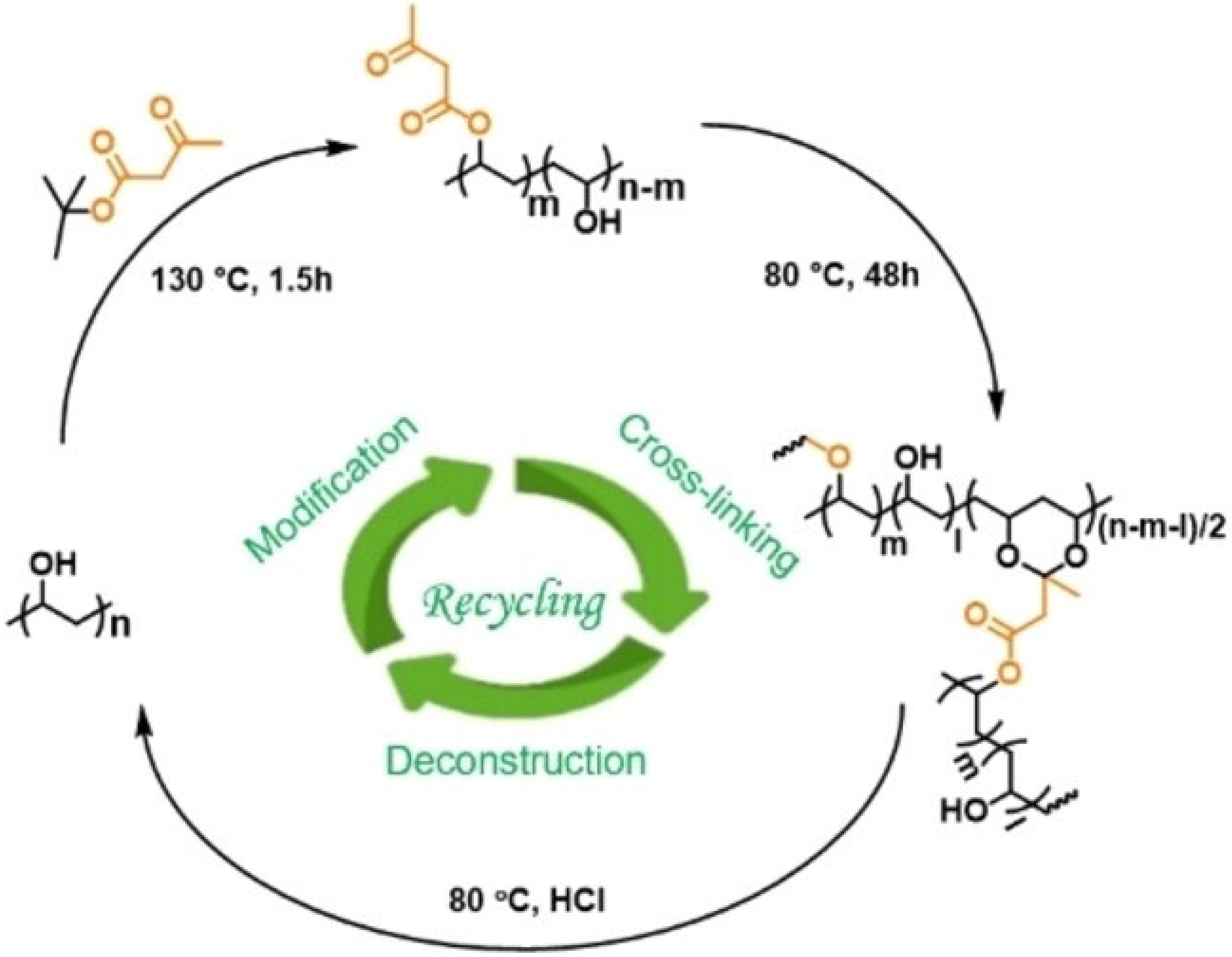
Two different approaches can be used:

https://pubs.rsc.org/en/content/articlehtml/2022/gc/d2gc00368f

1. Cleavable crosslinks (dynamic covalent polymer networtks – DCPN)
2. Chemical recycling to monomer (CRM)



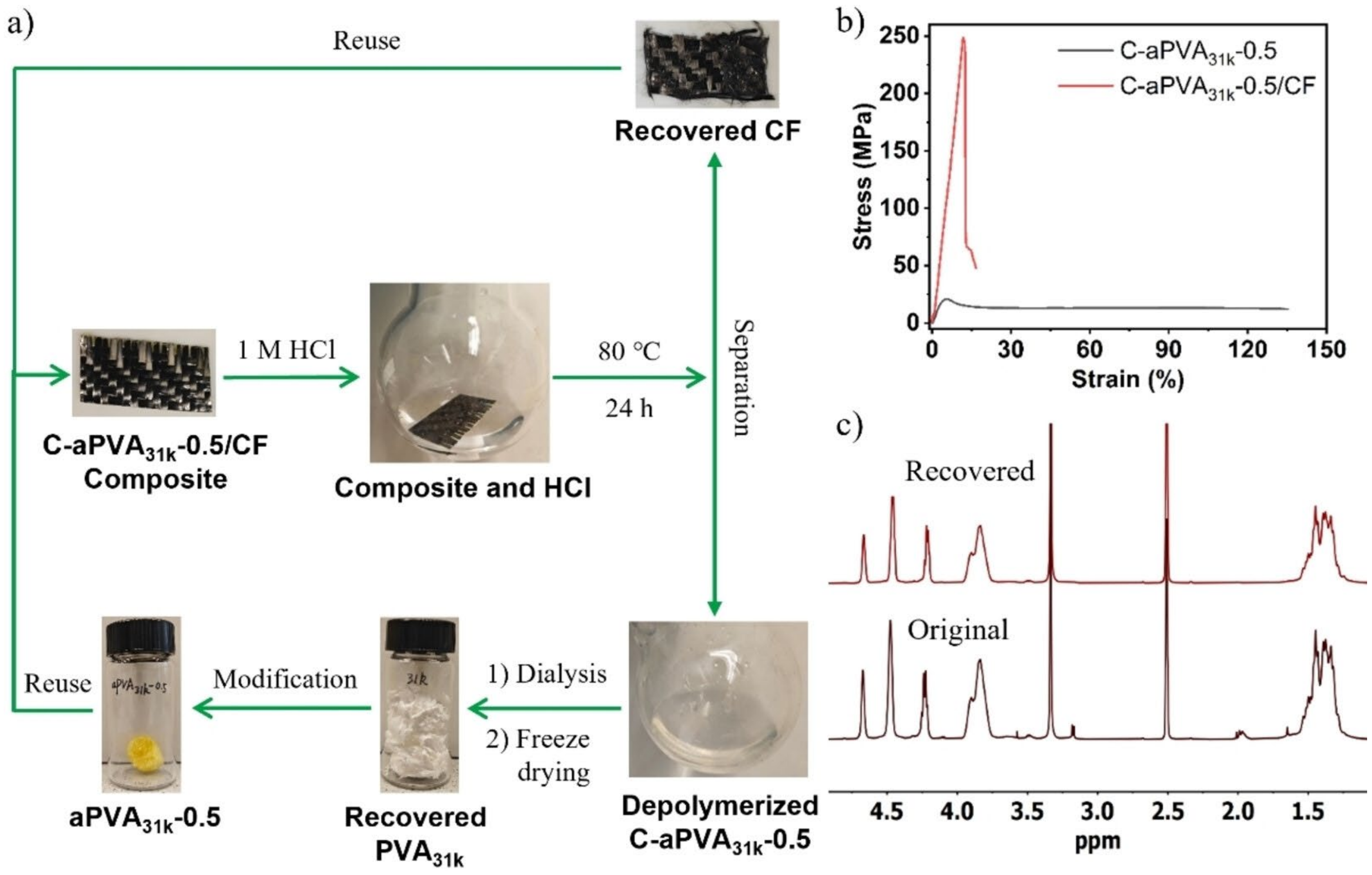
An EPFL example – Stellacci group



https://doi.org/10.1002/anie.202410624

- PVA is a commercial polymer (1,3- diol)
- PVA modified with beta-ketoester crosslinks to give a PVA thermoset
- This thermoset is stable and insoluble under many conditions, but heat and acid can de-crosslink and give back the soluble PVA

Carbon fibre polymer-reinforced composites



https://doi.org/10.1002/anie.202410624

Angewandte Chemie International Edition
GDCh A Journal of the German Chemical Society

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Aims and Scope

Angewandte Chemie is a journal of the German Chemical Society (GDCh). With an excellent Impact Factor of 16.6 (2022 Journal Citation Reports, Clarivate, 2023), the journal is maintaining its leading position among scholarly journals with a focus on general chemistry. It appears weekly in a highly optimized, reader-friendly format; new articles appear online almost every day. Founded in 1887, *Angewandte Chemie* is one of the prime chemistry journals in the world today. Moreover, it is the only journal in the field delivering a stimulating mixture of Review-type articles, Highlights, Communications, and Research Articles weekly.

Review-type articles summarize important recent research on topical subjects across all branches of chemistry, they provide an overview of unresolved problems, and they discuss possible developments. To contribute a Review, Minireview, or Highlight, please contact our editorial office in the first instance so that our team may assess the suitability of the proposal. Unsolicited submissions cannot be considered at this time.

Communications and Research Articles are selected critically and report on the latest research results, making the journal indispensable to chemists who want to stay well informed.

ISSN: 1433-7851 (print). 1521-3773 (online). CODEN: ACIEF5.

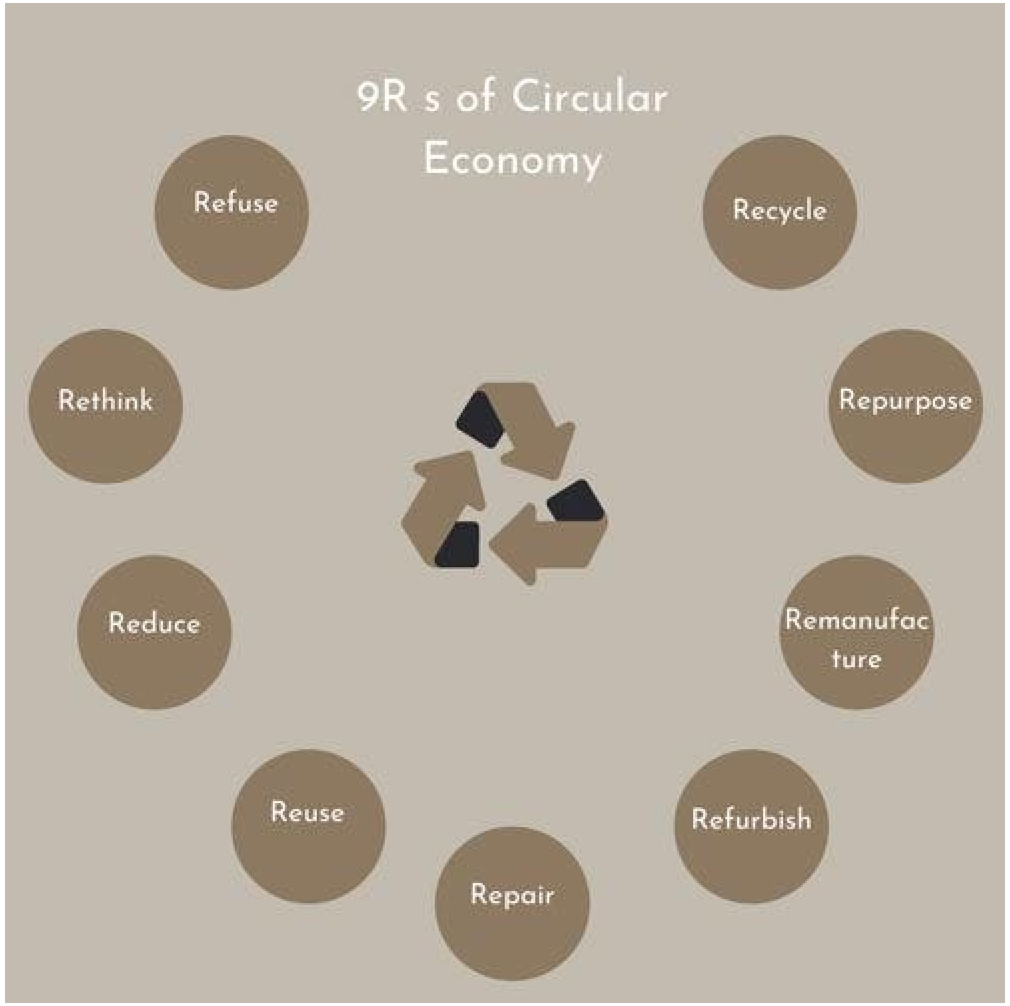
Currently 52 issues per year.

- IF = 16.6
- Founded in 1887
- Chemistry scope

OK, back to it, so what should we actually do?

- Anything better going on?

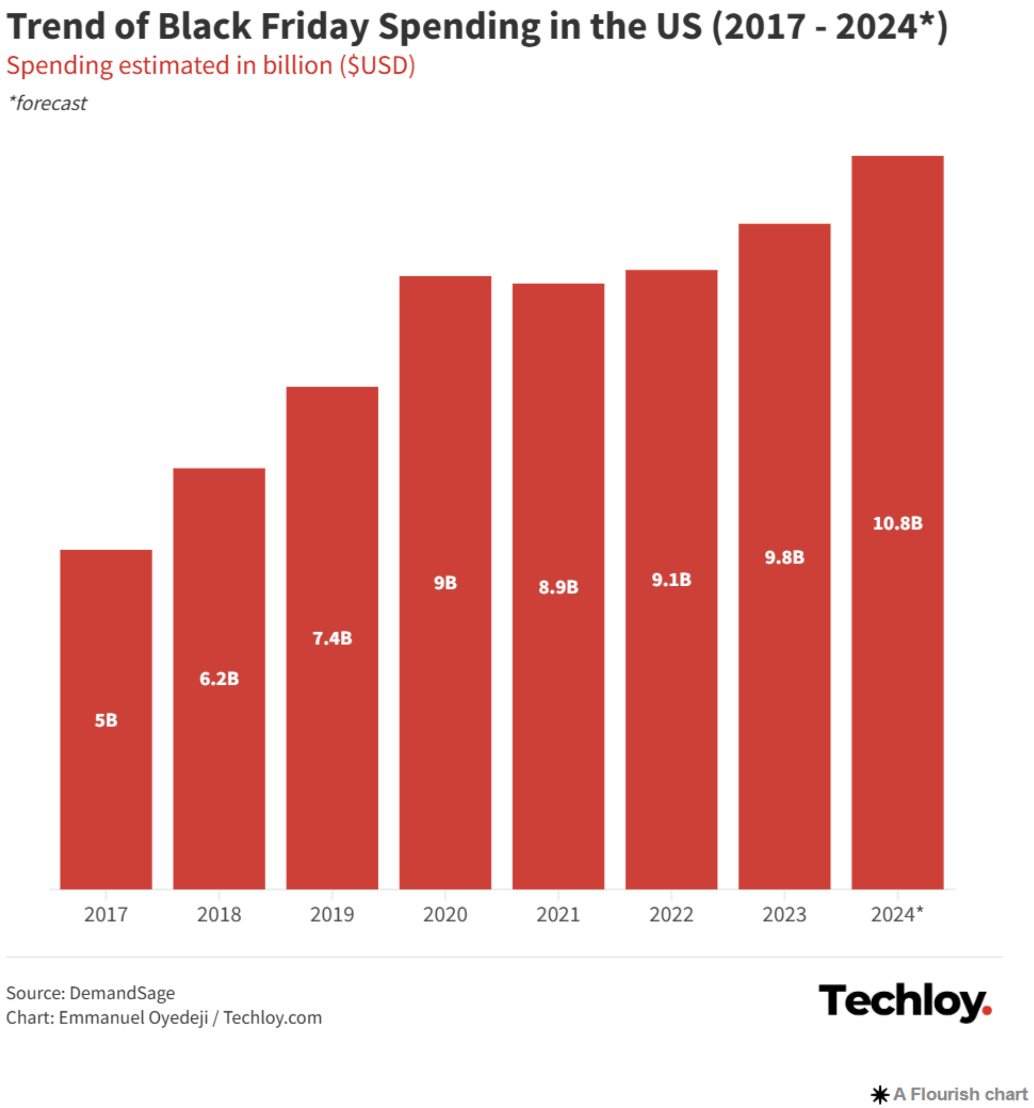
The 9R's



- No direct mention of material alternatives?
- Maybe under "Rethink"? – creating products following a sustainability criteria

[The 9R's of the Circular Economy]

Black Friday? So much for Refuse.



INSIGHTS BLACK FRIDAY

CHART: US Black Friday 2024 Spending Forecasted to Surpass $10 Billion

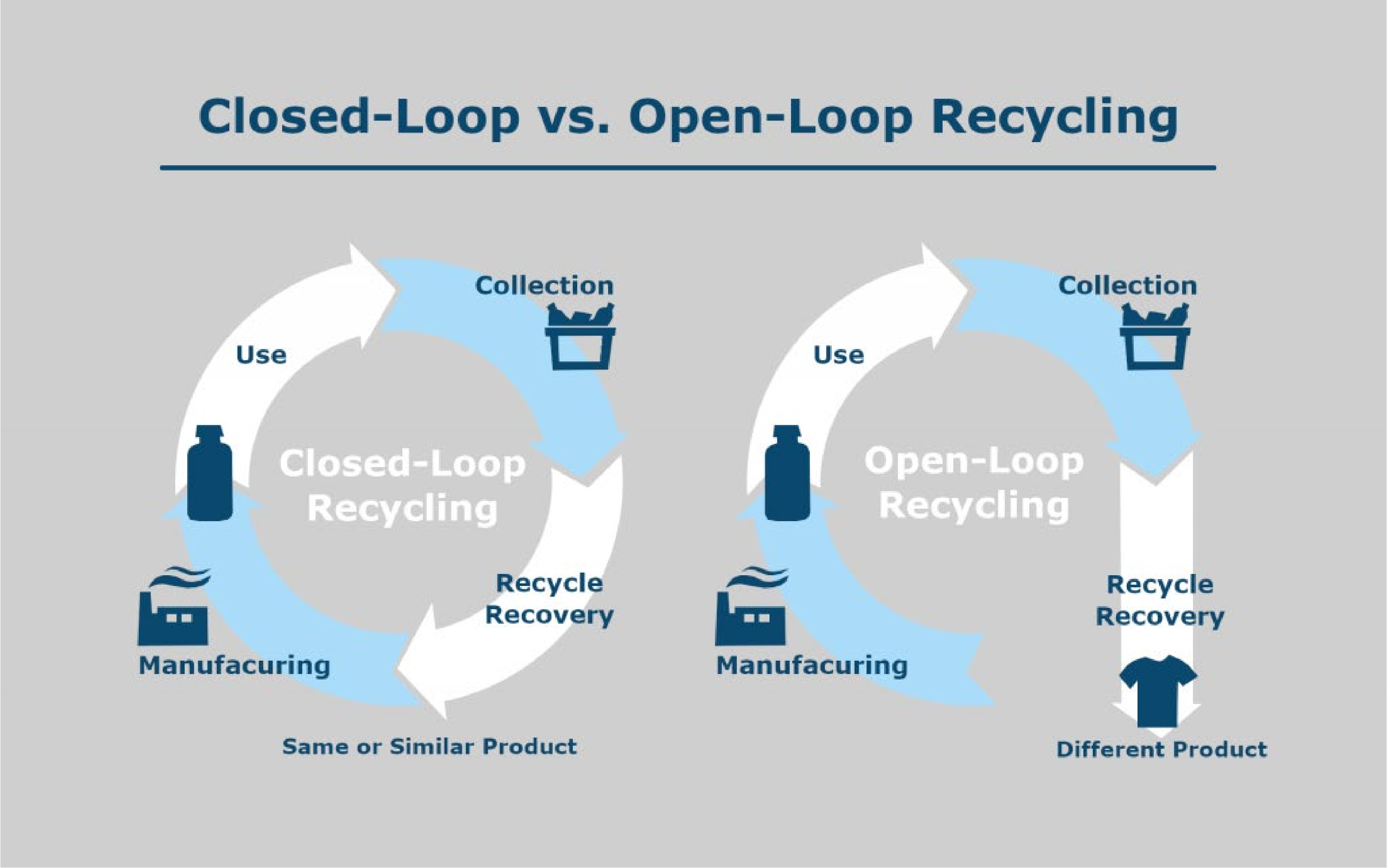
Online shopping is expected to remain the key growth driver.

[2024 Black Friday]

Closed loop, open loop?

[Closed and open loops]

- Usually thought to maintain quality
- Better environmental benefits, since less virgin material needed
- Requires pure recycling streams



- Usually thought to degrade quality/down cycle
- Usually lower value products
- May need more virgin inputs to maintain quality

Upcycling? Is this good?

Turning waste into something of higher value and keeping the materials circulated longer

May have a place but there is some critique:

- Delays waste (not preventative)
- Often needs more material input
- Open loop – bottle to yoga pants can't go back to bottle – can't we just recycle the bottle?
- Many of these products, while creative do not address a core need

Upcycling with ELM's

nature communications

Article https://doi.org/10.1038/s41467-023-40777-x

Engineering microbial division of labor for plastic upcycling

Received: 15 December 2022

Accepted: 9 August 2023

Published online: 26 September 2023

Check for updates

Teng Bao[1,2,9], Yuanchao Qian[1,2,9], Yongping Xin[1,2,9], James J. Collins[3,4,5] & Ting Lu[1,2,6,7,8]

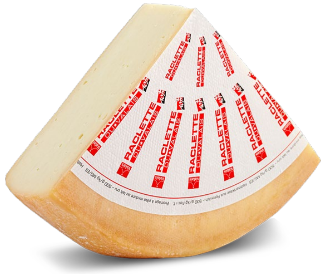
Plastic pollution is rapidly increasing worldwide, causing adverse impacts on the environment, wildlife and human health. One tempting solution to this crisis is upcycling plastics into products with engineered microorganisms; however, this remains challenging due to complexity in conversion. Here we present a synthetic microbial consortium that efficiently degrades polyethylene terephthalate hydrolysate and subsequently produces desired chemicals through division of labor. The consortium involves two *Pseudomonas putida* strains, specializing in terephthalic acid and ethylene glycol utilization respectively, to achieve complete substrate assimilation. Compared with its monoculture counterpart, the consortium exhibits reduced catabolic crosstalk and faster deconstruction, particularly when substrate concentrations are high or crude hydrolysate is used. It also outperforms monoculture when polyhydroxyalkanoates serves as a target product and confers flexible tuning through population modulation for *cis-cis* muconate synthesis. This work demonstrates engineered consortia as a promising, effective platform that may facilitate polymer upcycling and environmental sustainability.

https://www.nature.com/articles/s41467-023-40777-x

- Consortium of microorganisms proposed to break down PET hydrosylate
- Produces chemicals and polymers (PHA) through the microbial degradation
- (PET is fully recyclable by closed loop approach – still using microbes to degrade plastics is important! Using microbes to produce plastics?)

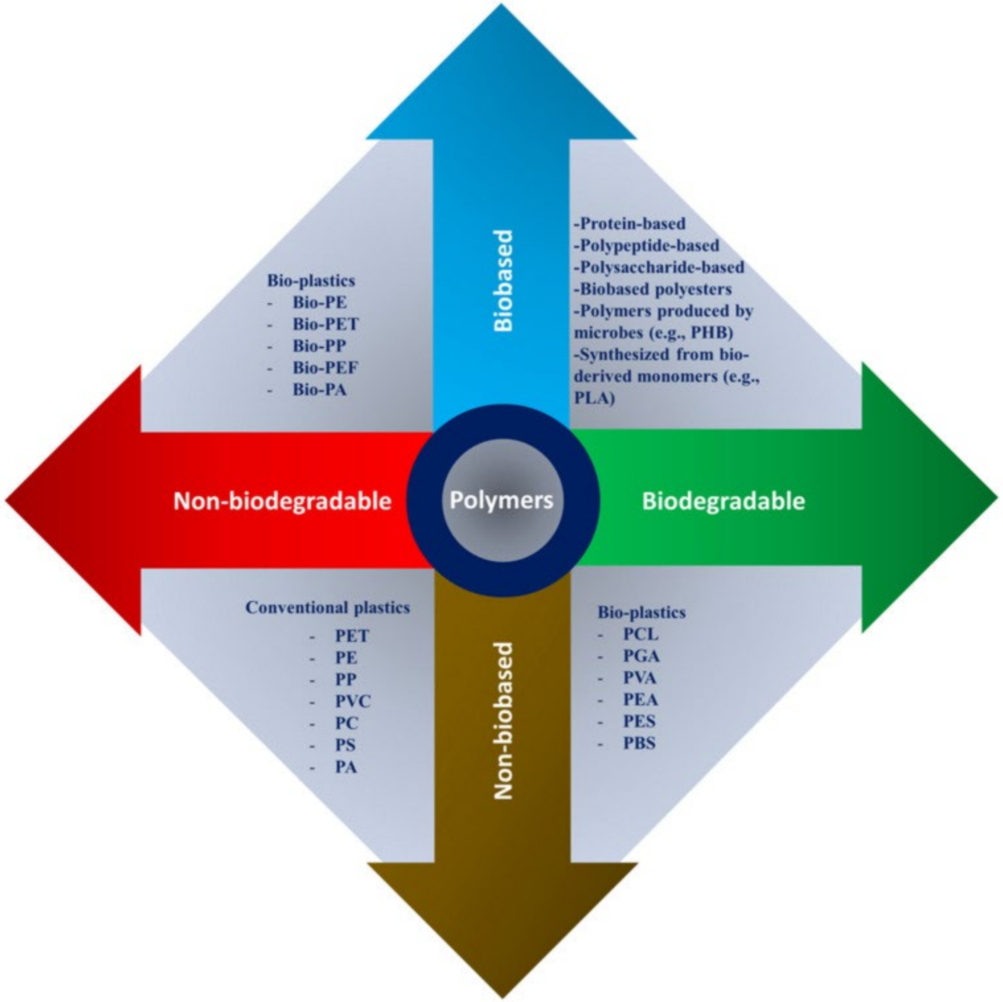
Recycled content by mass balance

- Imagine a large raclette pot filled with 1 kg of cheese - 20% Valais cheese and 80% Kraft singles
- It's all melted together at the molecular level so we don't know which "cheese molecule" is which
- Now the restaurant can say that 20% of it's cheese is Valais and 80% is Kraft singles
- Here's the fun part: they can claim that 0.2 kg of their cheese is 100% Valais, and the other 0.8 kg is Kraft
- They will of course charge you more for the "Valais" cheese
- Now imagine Valais is recycled content and Kraft is virgin plastic



[Mass balance]

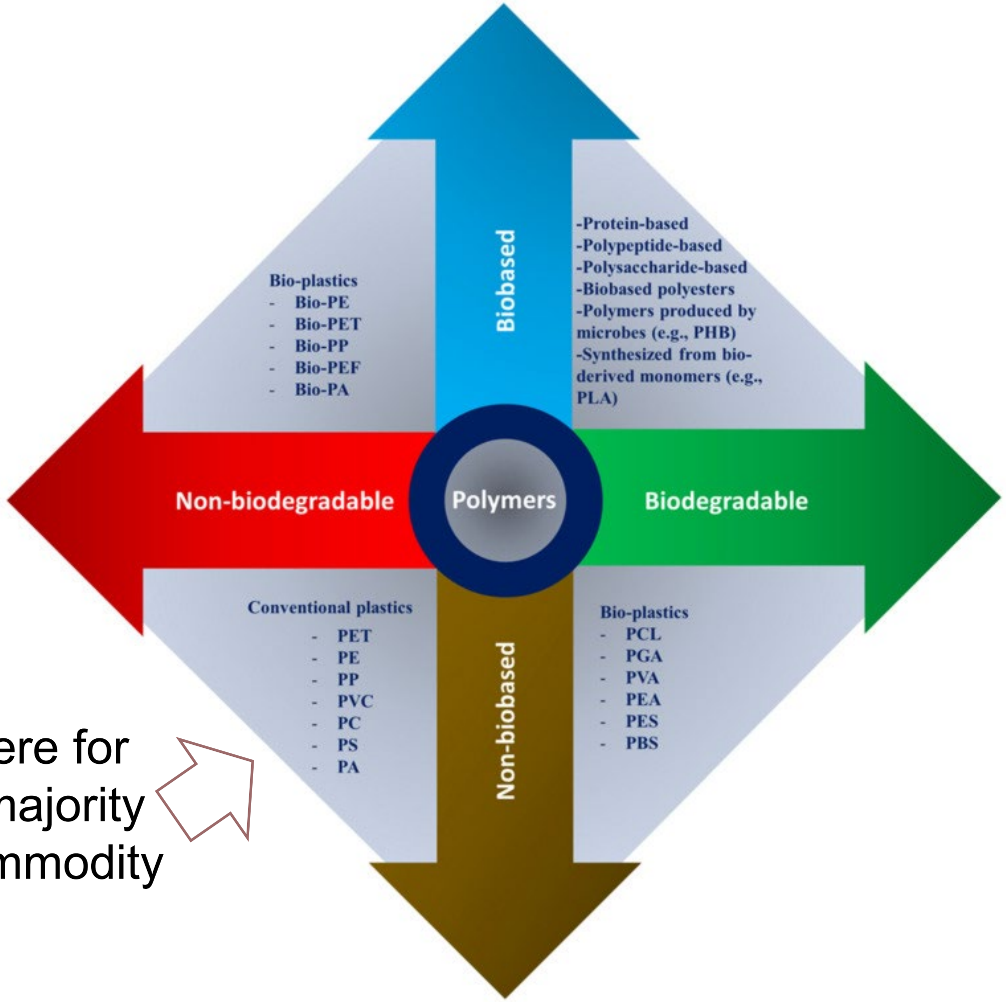
Plastics: By source and end of life



- Lots of options
- Bio-based and non-biodegradable – indistinguishable from petroleum-based plastics
- Bio-based and biodegradable - usually sourced somehow from nature, like microbes
- Non-biobased but biodegradable – usually has cleavable links
- Non-biodegradable and non-biobased – our conventional materials

Image from: Polymers 2021, 13(7):1105. doi: 10.3390/polym13071105.

Plastics: By source and end of life



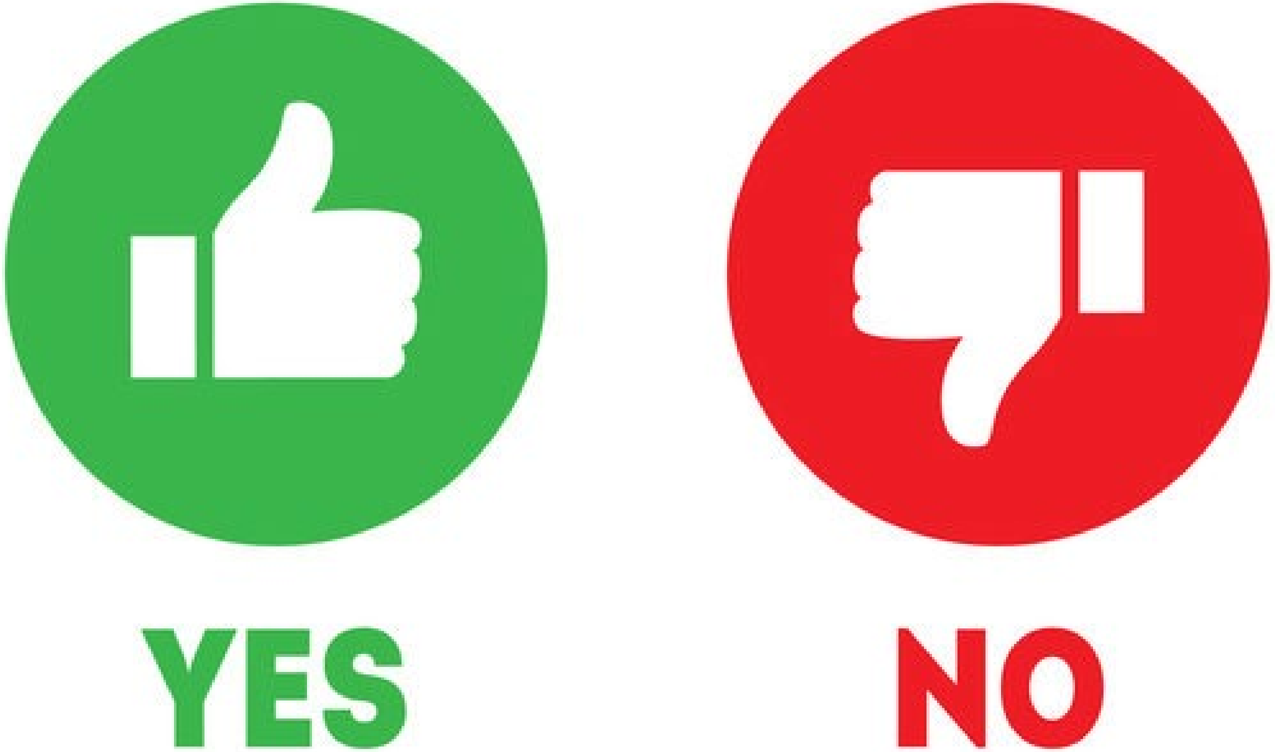
We are here for the vast majority of our commodity plastics

What's are the challenges?

- Scalability
- Are more options better? Need more recycling streams, possibility for contamination of streams is greater
- Economics/cost
- Properties – balancing function and stability with biodegradation
- Competing with food resources and land use for biobased plastic production

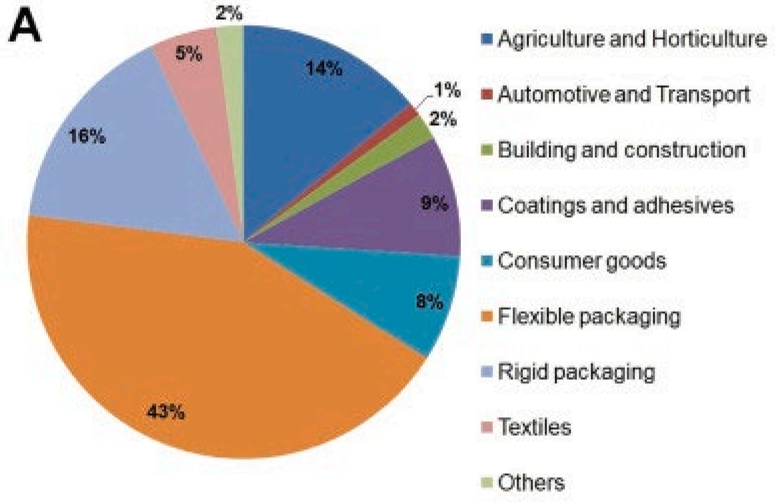
Image from: Polymers 2021, 13(7):1105. doi: 10.3390/polym13071105.

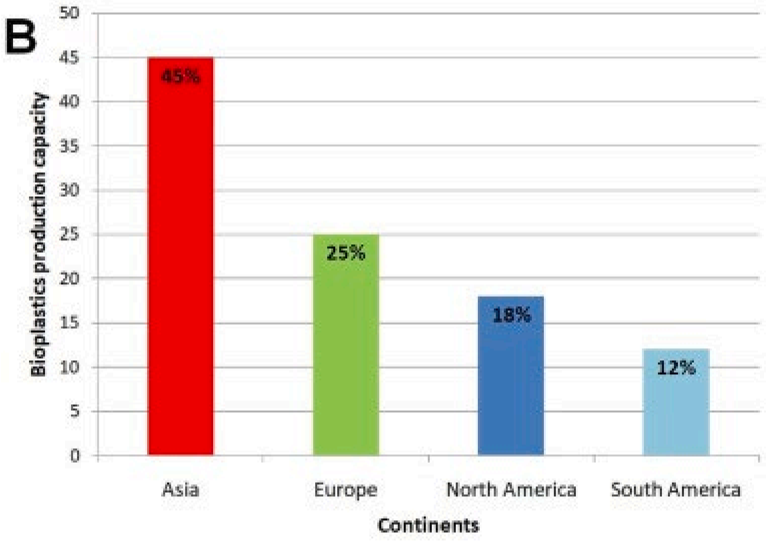
Side note: Do you think making more biodegradable and/or recyclable plastics is the answer to our plastics problem?



Bioplastics? Let's add more to the mix?

- No standard definition
- Most widely accepted: a polymer that is biobased or biodegradable or both
- Not all bioplastics are biodegradable (and some non-biobased ones are, e.g., PBAT)



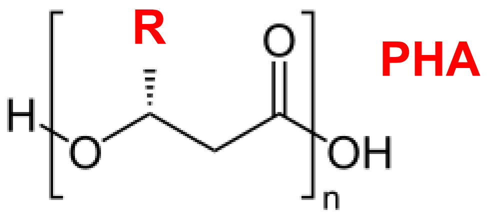


[Bioplastics: A boon or a bane?]

PHA’s

- PHA’s are produced via bacterial fermentation of sugars and fatty acids, under growth limited conditions

- Thermoplastic



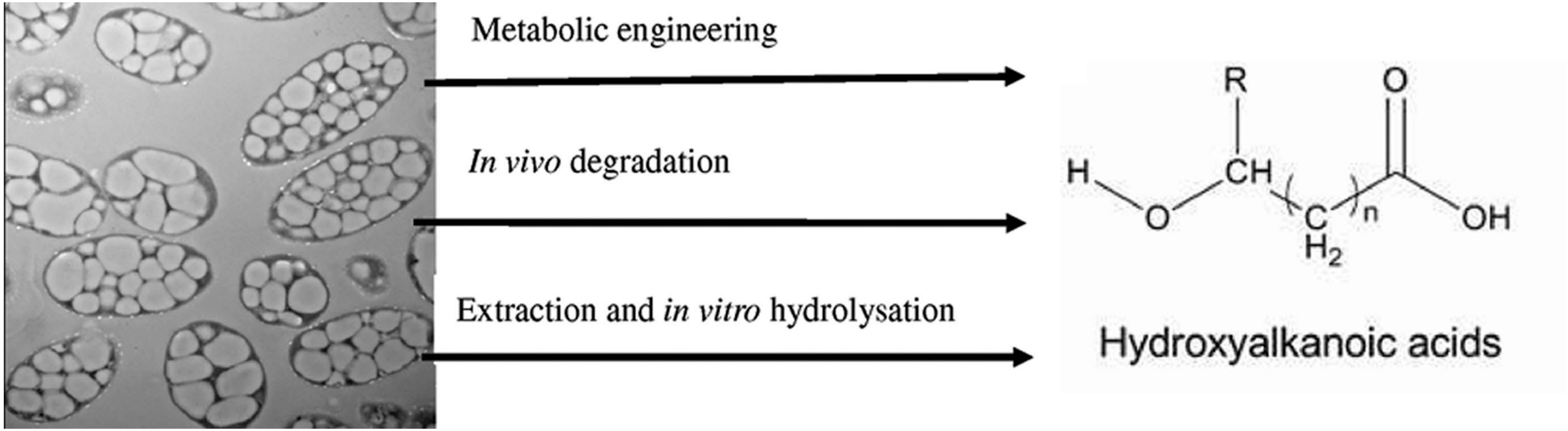
- Biodegradable (no microplastics)

- Bottleneck = high cost, 3-12× more expensive than traditional plastics (other bottleneck is insufficient mechanical properties)

- 50% of cost arises from fermentation substrate (possibility to reduce cost with low or no-cost substrates) – lignocellulose biomass waste

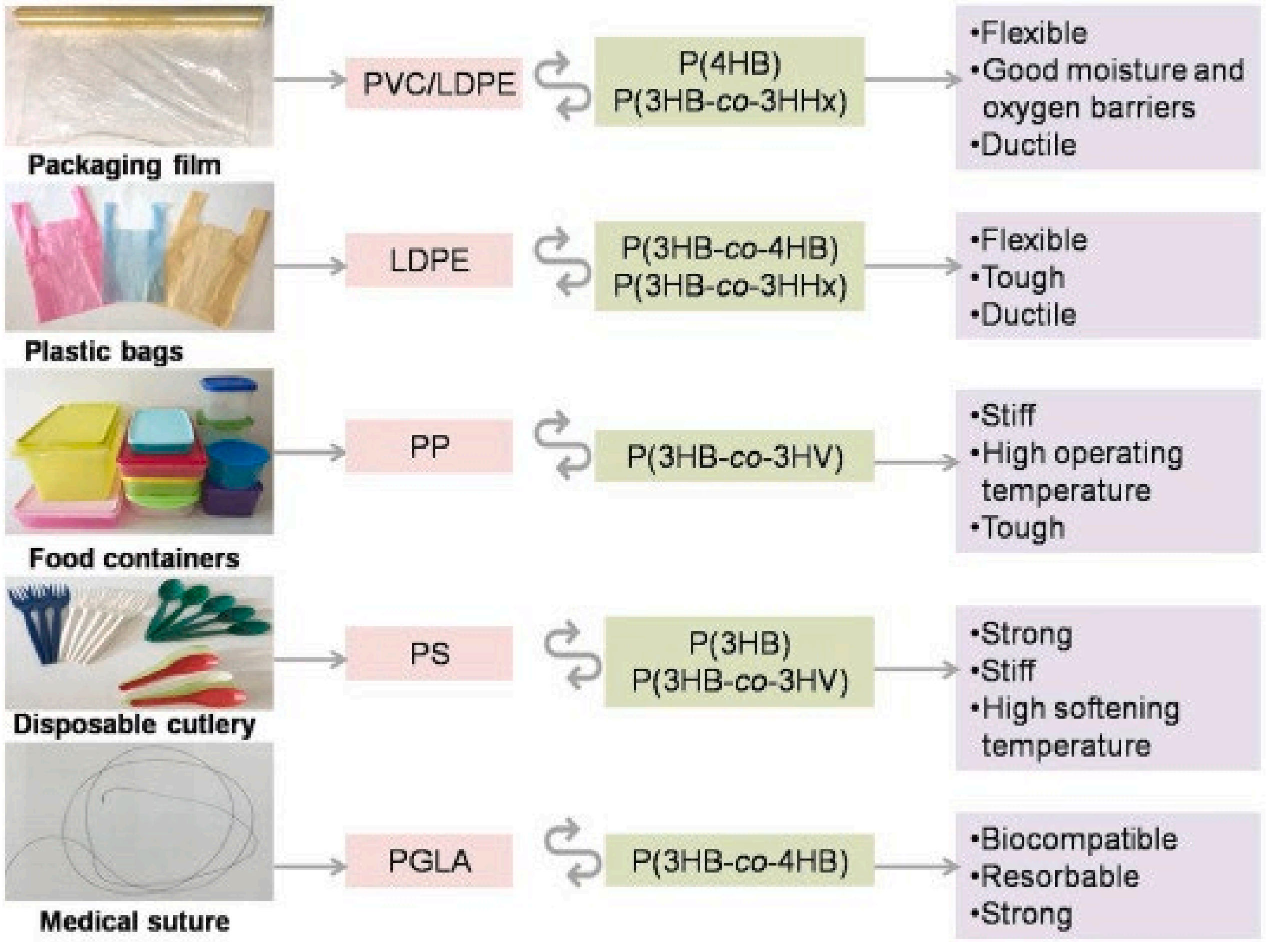
DOI: 10.1039/D3SU00126A

PHA's



https://pubs.acs.org/doi/full/10.1021/cr200162d

PHA and PHA co-polymers



- Can be used as a biodegradable packaging material
- Non-toxic, no severe immune response (used in medical applications)
- Figure on left shows how PHA copolymers can be used in different plastic applications, replacing petroleum-based plastics - variety of PHA's with different properties
- Depends on: substrate, microorganism, and normal things like processing conditions

[Bioplastics: A boon or a bane?](#)

Lignocellulose substrates

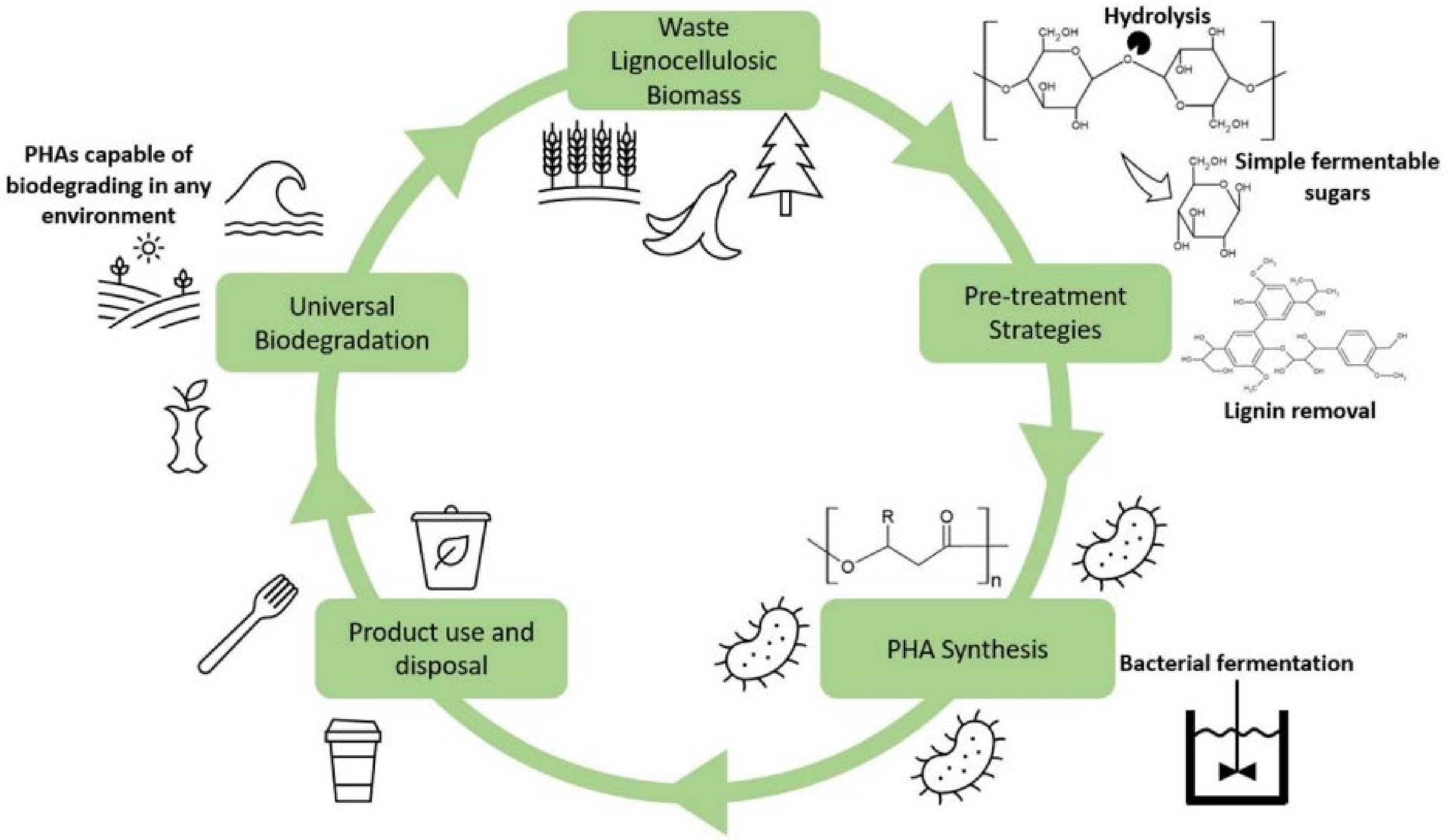


Fig. 2 Potential lifecycle of PHAs through utilization of lignocellulosic waste as feedstock.

DOI: 10.1039/D3SU00126A

Pretreatments to improve fermentation efficiency

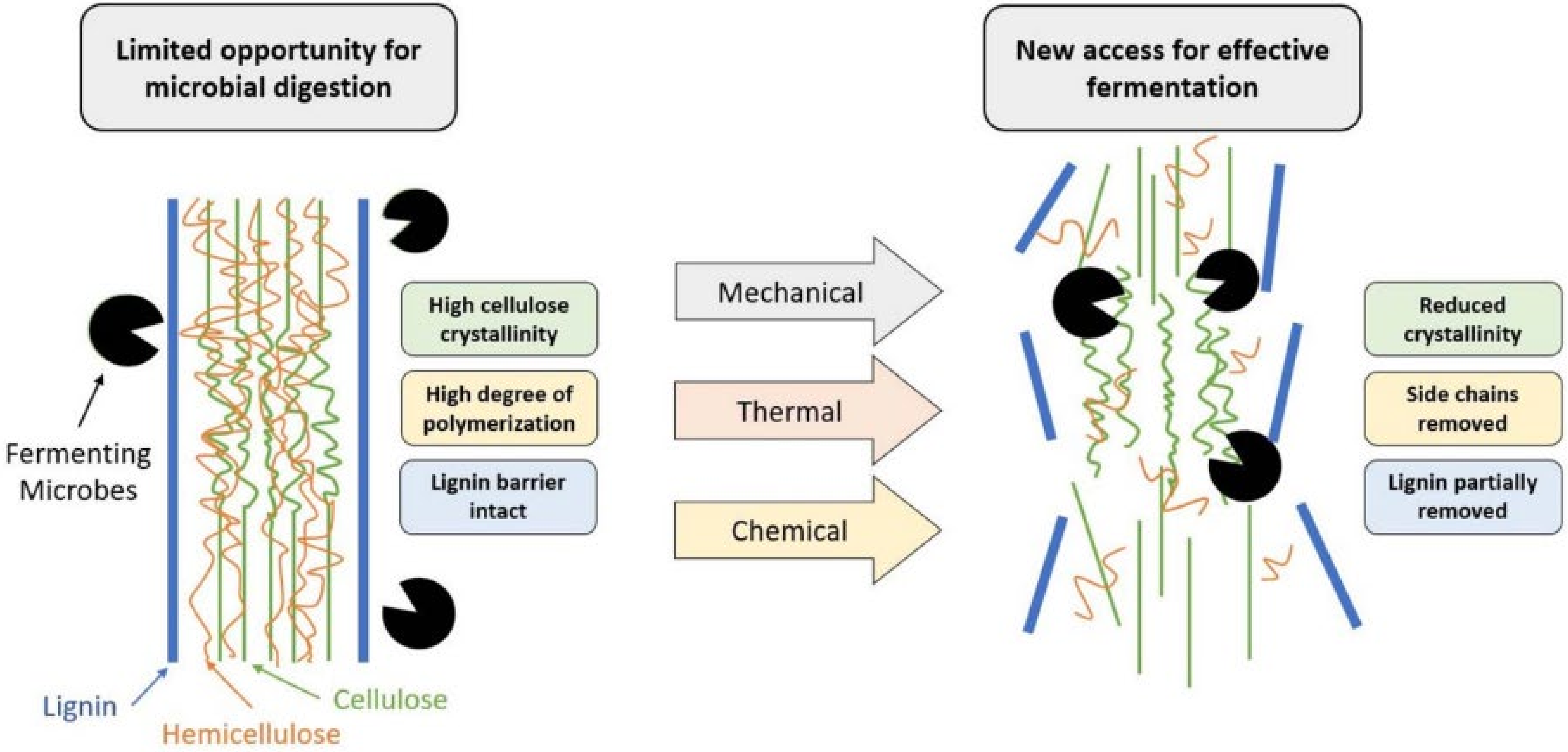


Fig. 4 Depiction of the role that pre-treatment methods have in improving fermentation efficiency.

DOI: 10.1039/D3SU00126A

Bio-On: A PHA unicorn

https://www.bio-on.com/en/

Bio-On: A PHA unicorn

- Italian company that specializes in PHA production
- 2019: Faced legal and financial consequences in 2019 after an investment firm described them as a “house of cards” and a “massive bubble”
- Misrepresented production capabilities, issues with sales and revenue claims, etc.,
- Share value dropped by 50% and trading was suspended
- Declared bankrupt in Dec 2019
- Gruppo Maip, Italian materials company, investing in 2021 to revive Bio-On
- See previous slide, website up and operational

https://bioplasticsnews.com/2020/06/11/bio-on-pha-history-italy-bioplastic/
https://www.gopha.org/news/bio-on-is-back-with-grouppo-maip

EPFL

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SUSTAINABLE MATERIALS LAB

Some more reading

frontiers in Environmental Science

ORIGINAL RESEARCH
published: 24 September 2020
doi: 10.3389/fenvs.2020.562263

Check for updates

The "Plastisphere" of Biodegradable Plastics Is Characterized by Specific Microbial Taxa of Alpine and Arctic Soils

Joel Rüthi[1,2], Damian Bölsterli[1], Lucrezia Pardi-Comensoli[3], Ivano Brunner[1] and Beat Frey[1]*

[1] Forest Soils and Biogeochemistry, Swiss Federal Institute for Forest, Snow and Landscape Research (WSL), Birmensdorf, Switzerland, [2] Institute of Biogeochemistry and Pollutant Dynamics, Swiss Federal Institute of Technology, ETH Zürich, Zurich, Switzerland, [3] Laboratory for Mechanical Systems Engineering, Swiss Federal Laboratories for Materials Science and Technology (EMPA), Dübendorf, Switzerland

2020
Cited 95 times
Swiss research

Plastic pollution poses a threat to terrestrial ecosystems, even impacting soils from remote alpine and arctic areas. Biodegradable plastics are a promising solution to prevent long-term accumulation of plastic litter. However, little is known about the decomposition of biodegradable plastics in soils from alpine and polar ecosystems or the microorganisms involved in the process. **Plastics in aquatic environments have previously been shown to form a microbial community on the surface of the plastic distinct from that in the surrounding water, constituting the so-called "plastisphere."** Comparable studies in terrestrial environments are scarce. Here, we aimed to characterize the plastisphere microbiome of three types of plastics differing in their biodegradability in soil using DNA metabarcoding. Polylactic acid (PLA), polybutylene adipate terephthalate (PBAT), and polyethylene (PE) were buried in two different soils, from the Swiss Alps and from Northern Greenland, at 15°C for 8 weeks. While physico-chemical characteristics of the polymers only showed minor (PLA, PBAT) or no (PE) changes after incubation, a considerably lower α-diversity was observed on the plastic surfaces and prominent shifts occurred in the bacterial and fungal community structures between the plastisphere and the adjacent bulk soil not affected by the plastic. Effects on the plastisphere microbiome increased with greater biodegradability of the plastics, from PE to PLA. Copiotrophic taxa within the phyla Proteobacteria and Actinobacteria benefitted the most from plastic input. Especially taxa with a known potential to degrade xenobiotics, including Burkholderiales, Caulobacterales, Pseudomonas, Rhodococcus, and Streptomyces, thrived in the plastisphere of the Alpine and Arctic soils. In addition, Saccharimonadales (superphylum Patescibacteria) was identified as a key taxon associated with PLA. The association of Saccharibacteria with plastic has not been reported before, and pursuing this finding further may shed light on the lifestyle of this obscure candidate phylum. Plastic addition affected fungal taxa to a lesser extent since only few fungal genera such as Phlebia and Alternaria were increased on the plastisphere. **Our findings suggest that the soil microbiome can be strongly influenced by plastic pollution in terrestrial cryoenvironments. Further research is required to fully understand microbial colonization on plastic surfaces and the biodegradation of plastic in soils.**

Some reading

ELSEVIER

Environment International

Volume 163, May 2022, 107244

Review article

A review on the occurrence and influence of biodegradable microplastics in soil ecosystems: Are biodegradable plastics substitute or threat?

Ping Fan [a b], Hong Yu [a], Beidou Xi [a b], Wenbing Tan [a]

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https://doi.org/10.1016/j.envint.2022.107244

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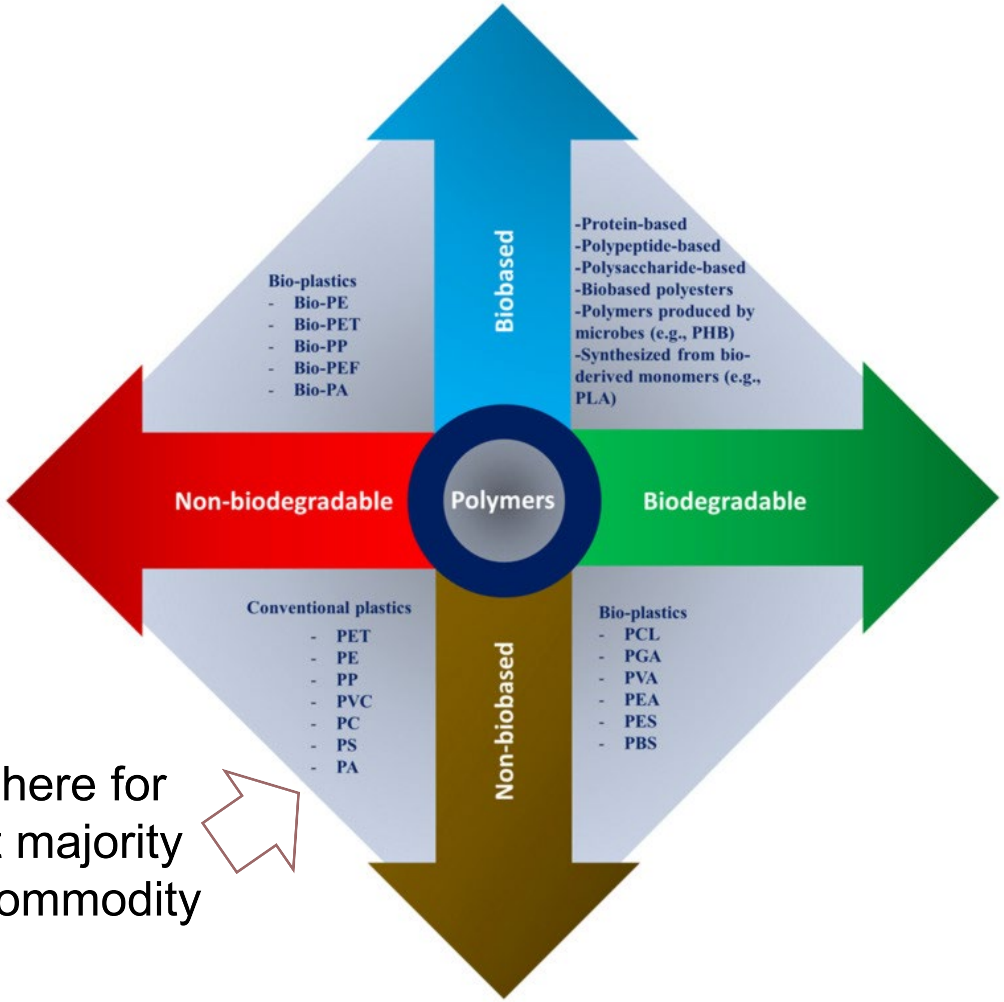
- *2022*
- *Cited 175 times*
- *List of 146 citations on Scopus*

Some entries from the Scopus list

	Document title	Authors	Year	Source
3	Biodegradable microplastics induce profound changes in lettuce (Lactuca sativa) defense mechanisms and to some extent deteriorate growth traits	Adamczyk, S., Zantis, L.J., van Loon, S., (...), Adamczyk, B., Velmala, S.	2024	Environmental Pollution 363,125307
	View abstract Full text at EPFL Library View at Publisher Related documents			
4	Biodegradable plastics – Where to throw? A life cycle assessment of waste collection and management pathways in Austria *Open Access*	Mhaddolkar, N., Lodato, C., Tischberger-Aldrian, A., Vollprecht, D., Fruergaard Astrup, T.	2024	Waste Management 190, pp. 578-592
	View abstract Full text at EPFL Library View at Publisher Related documents			
5	Microbial strategies for effective microplastics biodegradation: Insights and innovations in environmental remediation	Song, Q., Zhang, Y., Ju, C., (...), Meng, Q., Cong, J.	2024	Environmental Research 263,120046
	View abstract Full text at EPFL Library View at Publisher Related documents			
6	Mechanistic insight into interactive effect of microplastics and arsenic on growth of rice (Oryza sativa L.) and soil health indicators	Irshad, M.K., Aqeel, M., Saleem, S., (...), Khalid, N., Lee, S.S.	2024	Science of the Total Environment 955,176875
	View abstract Full text at EPFL Library View at Publisher Related documents			

- *Seems like we are just beginning to study the effects of biodegradable plastics on the soil microbiome*

Are more options better?



We are here for the vast majority of our commodity plastics

My somewhat controversial statement as head of the "Sustainable Materials Lab"

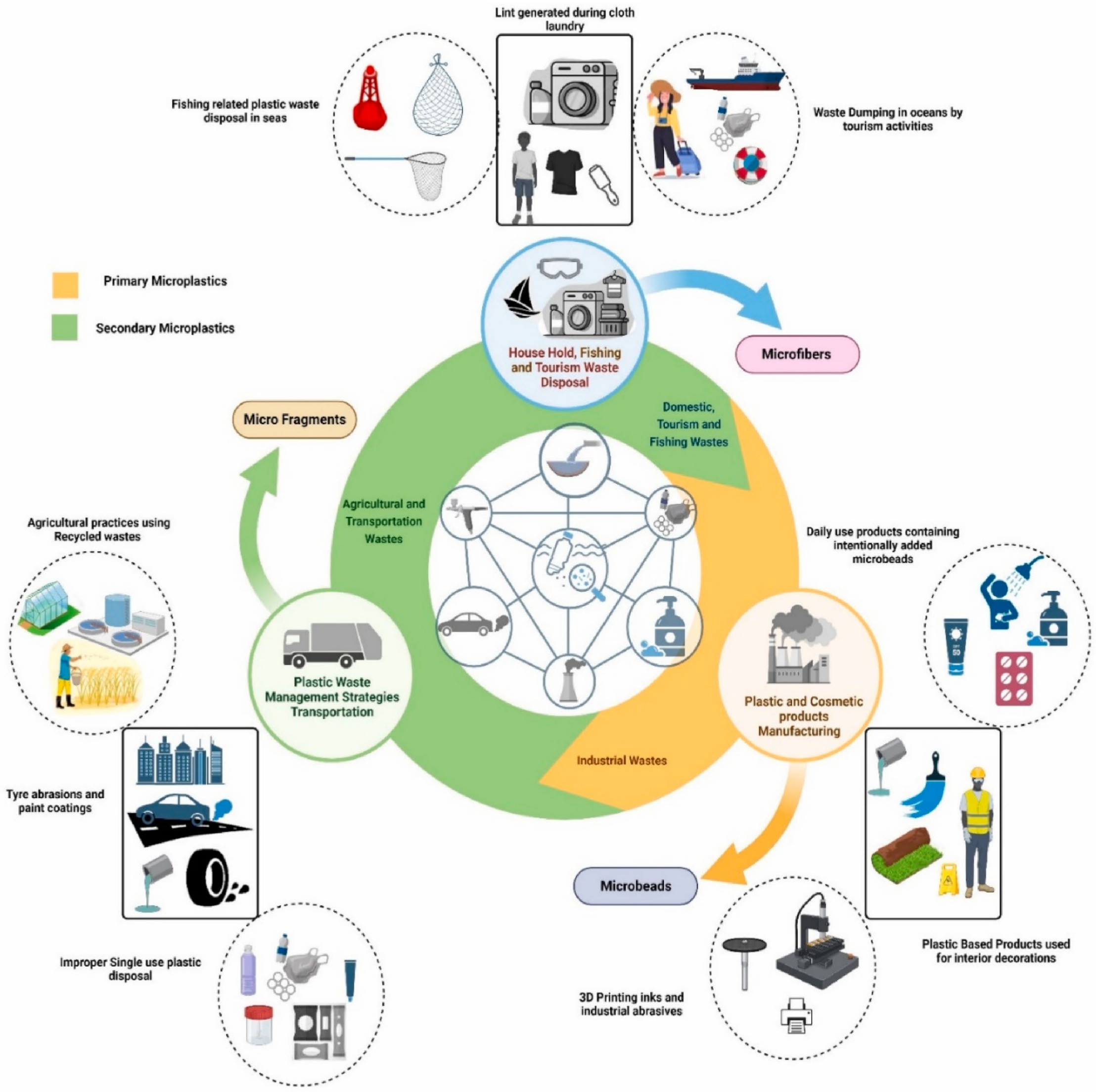
- Less is more?
- Fewer options, select for performance and recyclability (not biobased or biodegradable)
- Closed loop recycling
- Investment in recycling infrastructure
- Changing attitudes around recycling – maybe you return to company for recycling, leaving the design for recycling in their hands
- Incentivizing recycling
- Maybe biobased isn't always better – only makes sense when it gives us a possibility or functionality that was not possible before… just being biobased and biodegradable might not be enough…
- How will huge amount of biodegradable plastics effect our microbial ecosystem?

Image from: Polymers 2021, 13(7):1105. doi: 10.3390/polym13071105.

But this doesn't solve microplastics

https://education.nationalgeographic.org/resource/microplastics/

But this doesn't solve microplastics



https://doi.org/10.1016/j.jenvman.2023.119988

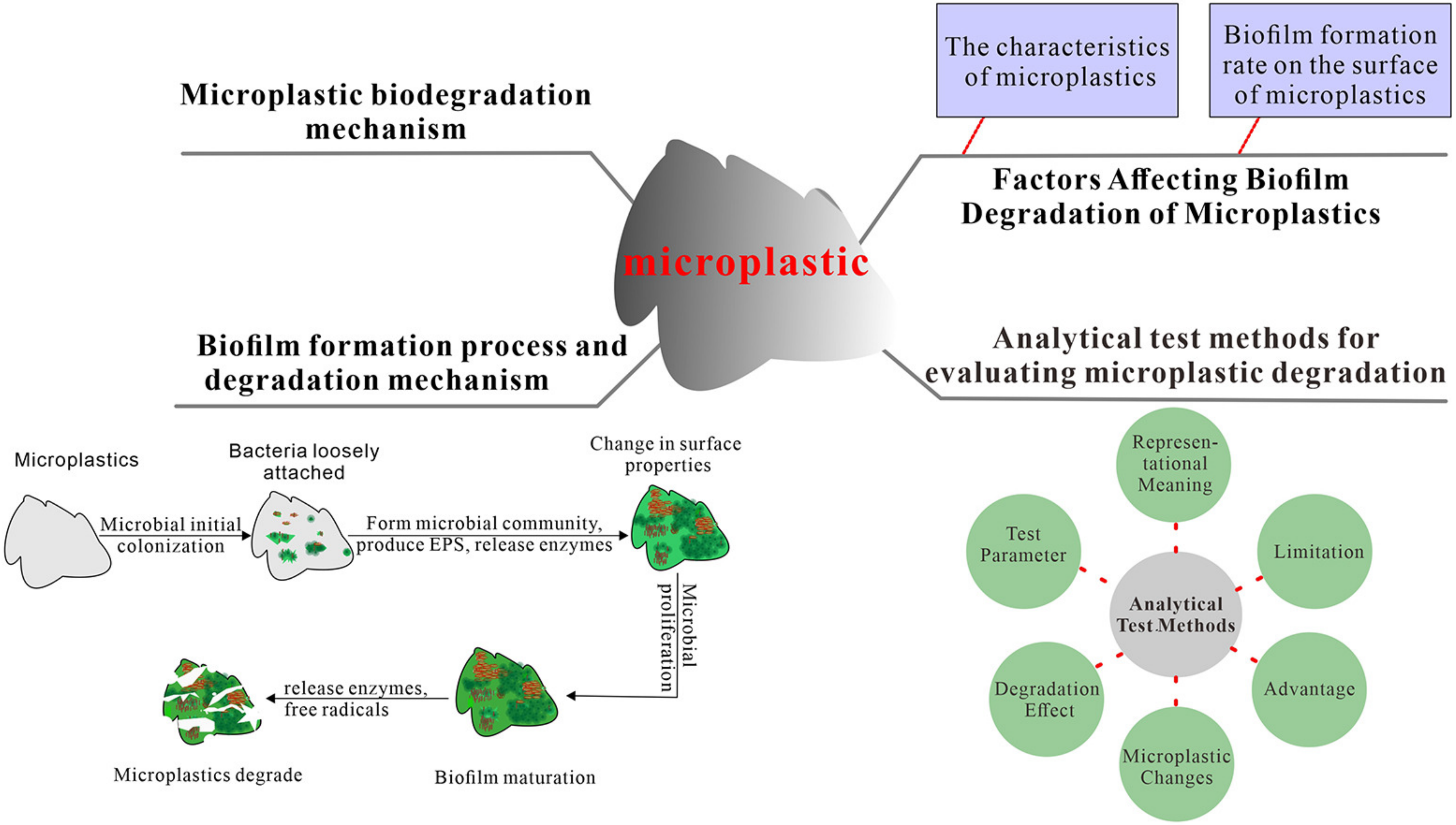
- Discusses the present ecotoxicology, mainly relates to water as the main reservoir and channel
- Technologies for removing plastics from the environment

But this doesn’t solve microplastics

- Discusses managing solutions but also how to convert microplastics into other value added materials (see upcycling ☺)

https://doi.org/10.1016/j.jenvman.2023.119988

Bioremediation of microplastics



https://doi.org/10.1016/j.scitotenv.2022.160953

Takeaways (this was a lot)

- Plastics are so useful (and pretty stable)
- Our best bet – reduce, recycle, new materials?
- In terms of recycling, closed loop is generally preferred (no upcycling or downcycling)
- Mass balance – how companies market and sell recycled or other types of “green” alternatives (it’s considered legit)
- We can find alternatives that are biodegradable, recyclable, and/or bio sourced – but not without challenges, let’s not be naïve
- Research – is being biobased and biodegradable enough?
- Microorganisms can be used to produce biodegradable plastics
- Microorganisms can also be used to bioremediate plastics pollution, especially the problematic microplastics