Module 5 – Green Chemistry in the Real World I

Global Greenchem Innovation & Network Program

UNIDO

Green Chemistry Toolkit

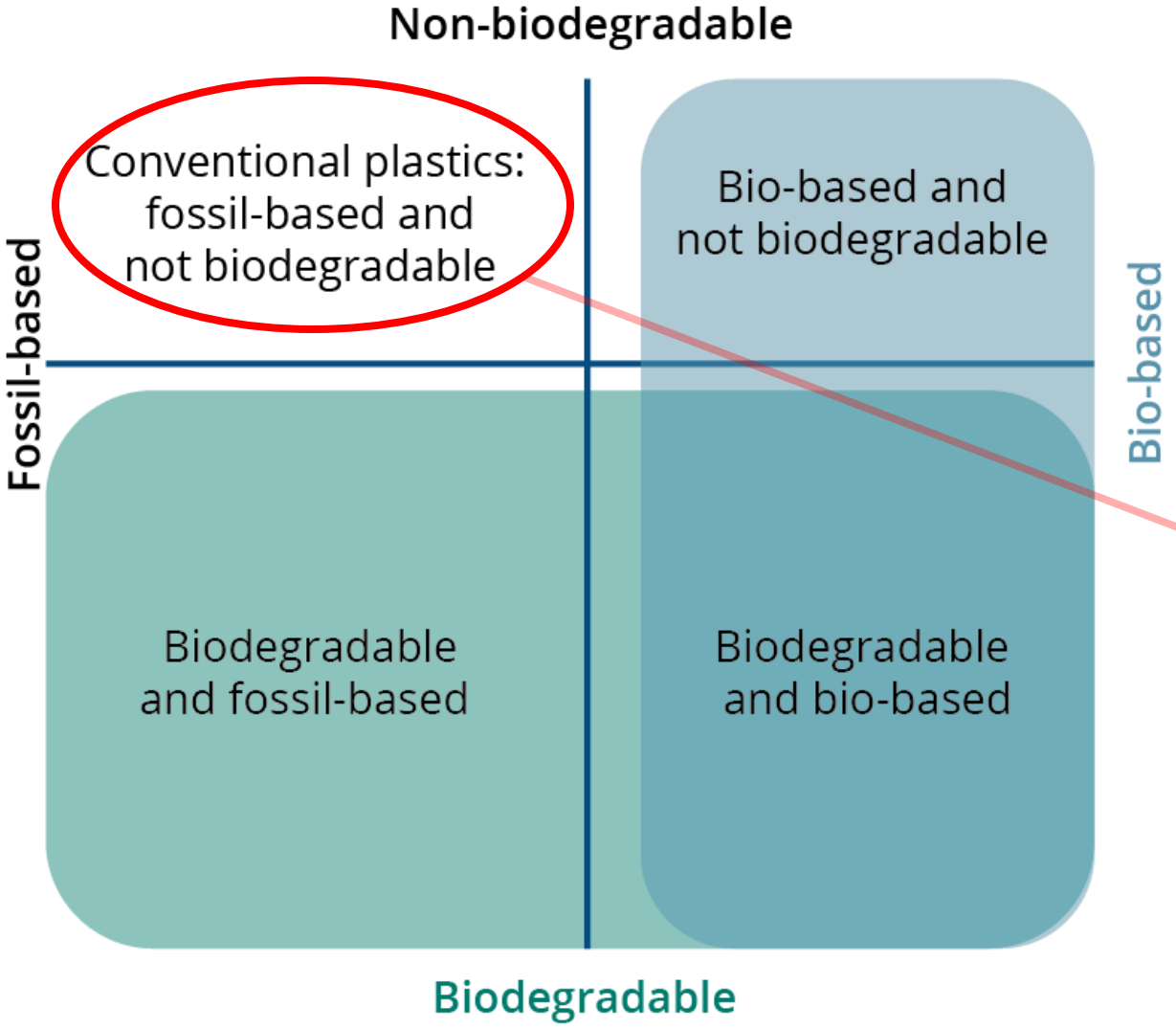
gef

Center for Green Chemistry & Green Engineering at Yale

Companies that do Green Chemistry!

Natureworks & World Centric

Plastics weren't designed for Degradability



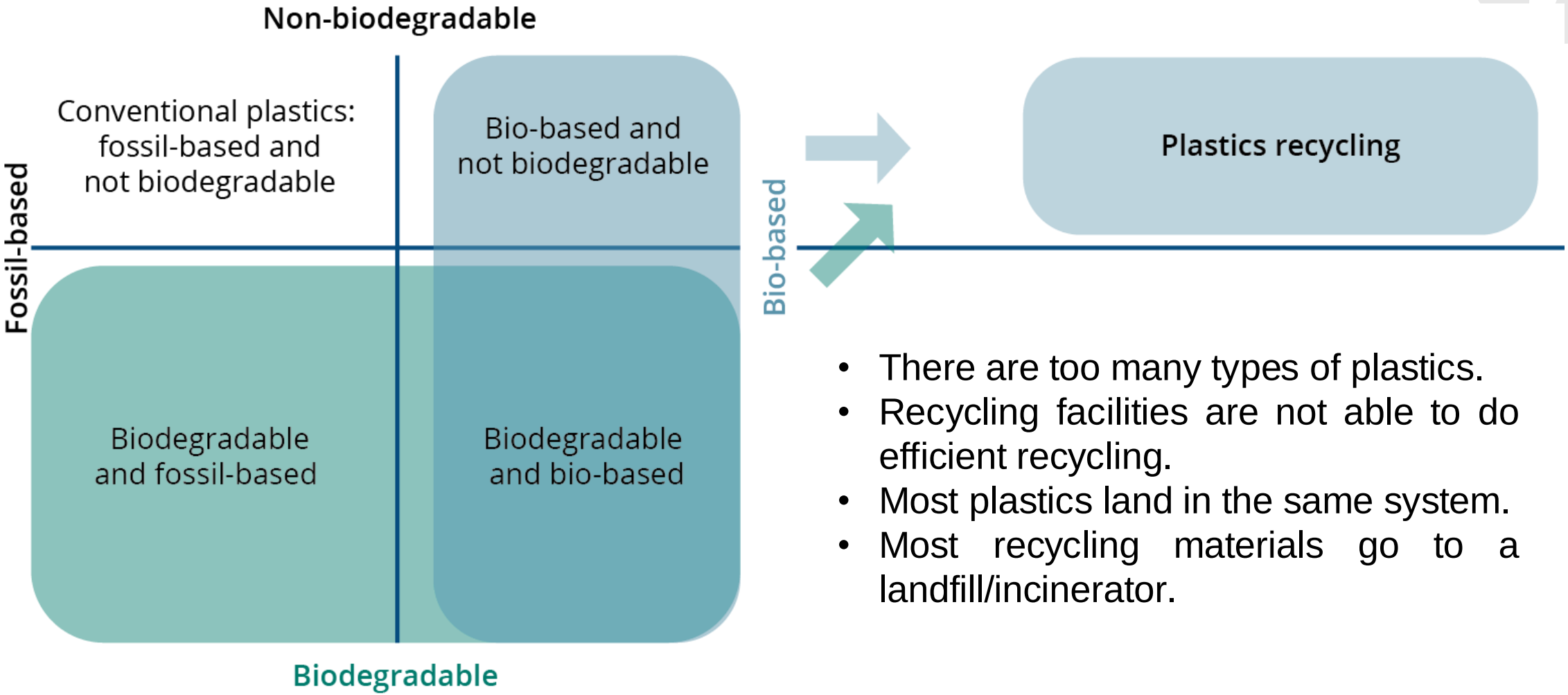
Too many common plastics (PS, PE, PP, PET) are in this area!

Source: ETC/WMGE and EEA.

Plastics weren't designed for Degradability

1 PETE	2 HDPE	3 PVC	4 LDPE	5 PP	6 PS	7 OTHER
Polyethylene Terephthalate	High-Density Polyethylene	Polyvinyl Chloride	Low-Density Polyethylene	Polypropylene	Polystyrene	Other
Common products: soda & water bottles; cups, jars, trays, clamshells	Common products: milk jugs, detergent & shampoo bottles, flower pots, grocery bags	Common products: cleaning supply jugs, pool liners, twine, sheeting, automotive product bottles, sheeting	Common products: bread bags, paper towels & tissue overwrap, squeeze bottles, trash bags, six-pack rings	Common products: yogurt tubs, cups, juice bottles, straws, hangers, sand & shipping bags	Common products: to-go containers & flatware, hot cups, razors, CD cases, shipping cushion, cartons, trays	Common types & products: polycarbonate, nylon, ABS, acrylic, PLA; bottles, safety glasses, CDs, headlight lenses
Recycled products: clothing, carpet, clamshells, soda & water bottles	Recycled products: detergent bottles, flower pots, crates, pipe, decking	Recycled products: pipe, wall siding, binders, carpet backing, flooring	Recycled products: trash bags, plastic lumber, furniture, shipping envelopes, compost bins	Recycled products: paint cans, speed bumps, auto parts, food containers, hangers, plant pots, razor handles	Recycled products: picture frames, crown molding, rulers, flower pots, hangers, toys, tape dispensers	Recycled products: electronic housings, auto parts,
						

Recycling can't keep up

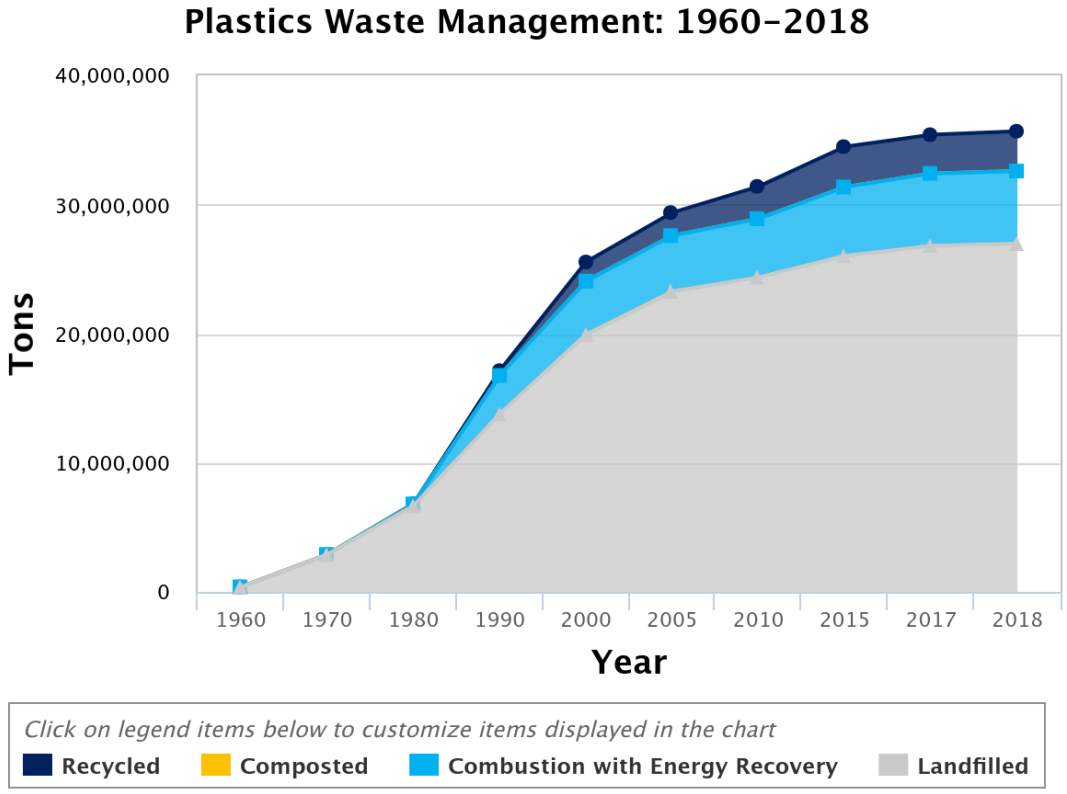


- There are too many types of plastics.
- Recycling facilities are not able to do efficient recycling.
- Most plastics land in the same system.
- Most recycling materials go to a landfill/incinerator.

Single use items are commonplace

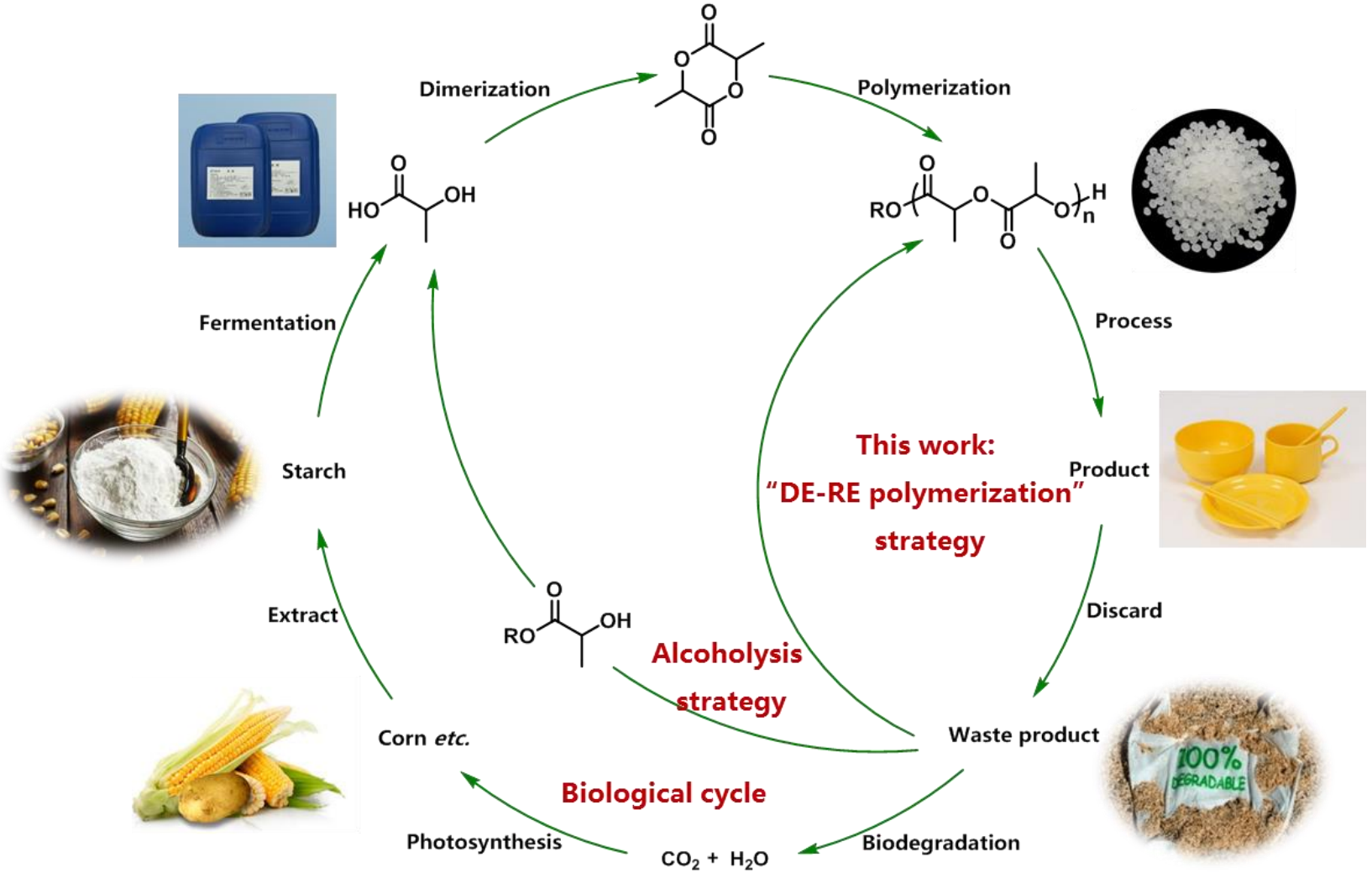
Single use items are commonplace

- Single use plastics are practical and common.
- Alternatives are available, but adoption needs commitment.
- Recycling efficiency is lower than consumers think.
- Governments start banning single plastic items, but movement is slow.



https://www.epa.gov/facts-and-figures-about-materials-waste-and-recycling/plastics-material-specific-data

Compostable plastics to bridge this issue



- Plastics like polylactic acid **(PLA)** allow us to bridge this issue.
- It can potentially be recycled but is also **compostable.**

Image by YANG Rulin and XU Guangqiang

How does Natureworks do business?

Renewable Feedstocks

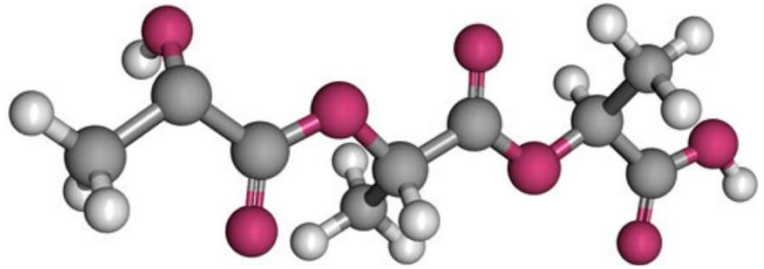
NatureWorks uses corn, cassava, sugar cane or beets as feedstocks, which efficiently capture CO_2 and transform it into long-chain sugar molecules.

Lactic Acid

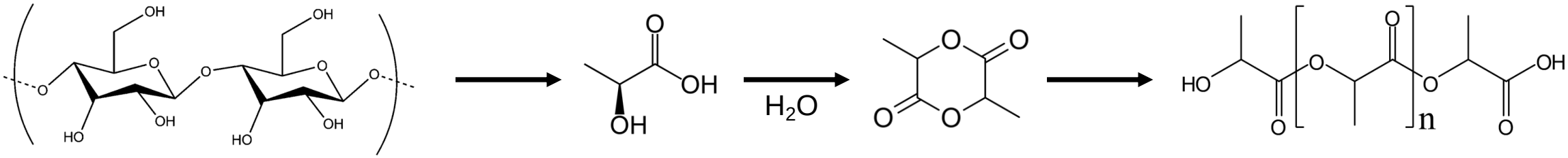
A milling process is used to initiate the extraction of starch from the plants. Enzymes are then added to the starch to convert it to dextrose via hydrolysis. Microorganisms ferment the dextrose into lactic acid, the building block of Ingeo.

Polylactic Acid

A proprietary two-step process transforms the lactic acid into lactide. These lactide rings are opened and linked together to form polylactic acid (PLA), or Ingeo. Ingeo is formed into pellets that can be transformed into everyday consumer products.

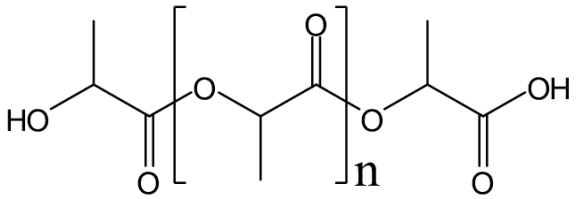


How does Natureworks do business?



Starch → Lactic Acid → Lactide → PLA/Ingeo

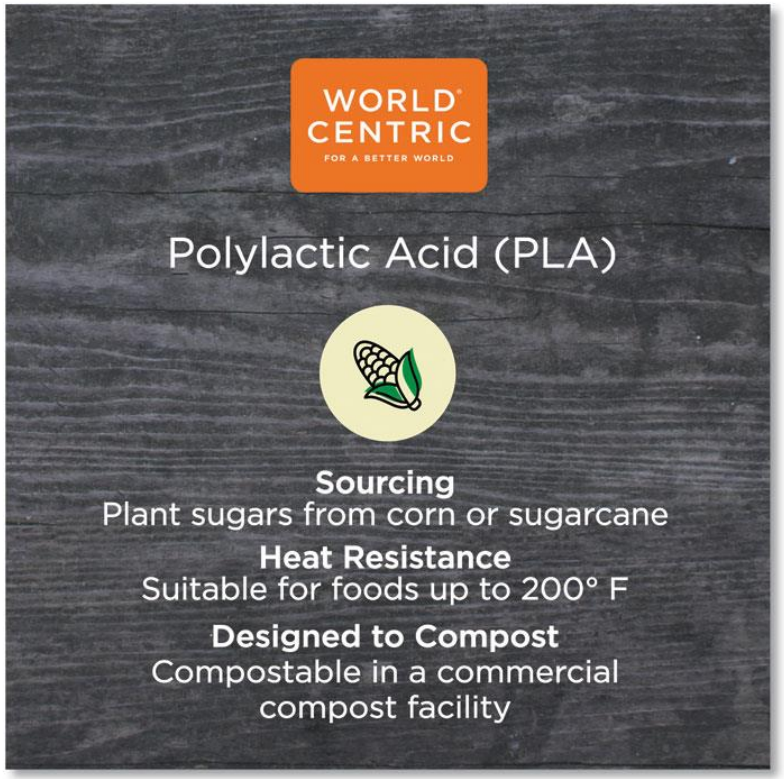
How getting from there to plastic items?



PLA/Ingeo

Single use materials that are **certified** compostable.

That is Worldcentric's business



IMPORTANT!

Disposal systems need to adapt too

Industrial

Composting

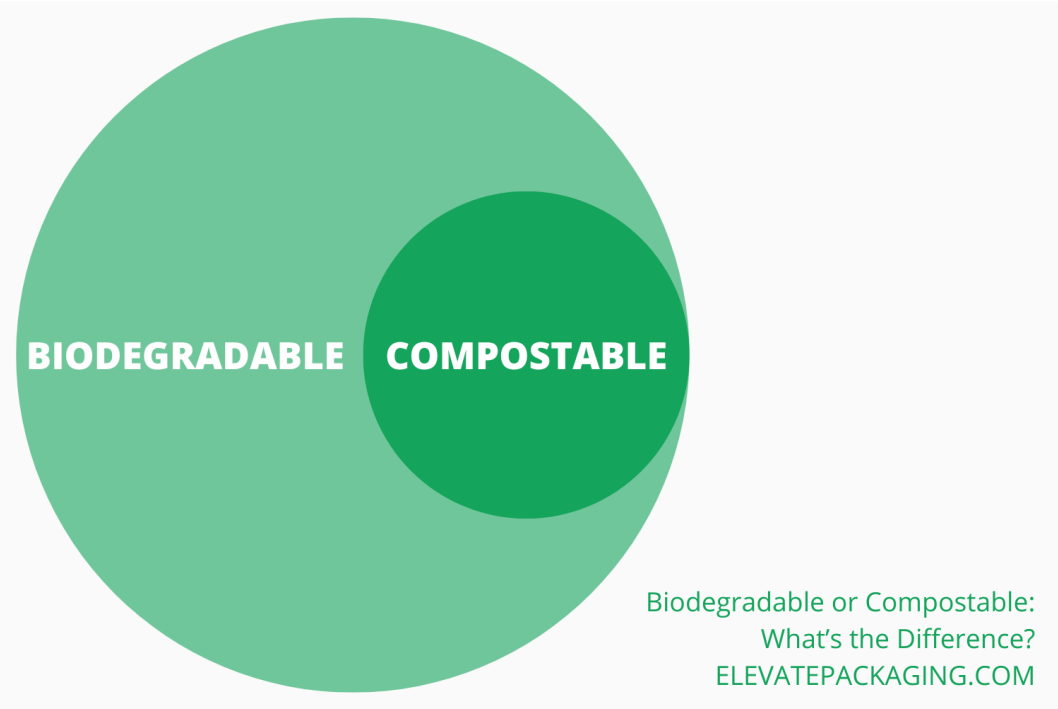
PLA doesn't readily biodegrade, only **industrial composting** conditions will close the loop (55-70°C, controlled humidity).

We don't only have to redesign products, but also behaviors.

Biodegradable or compostable?

- **Biodegradable** simply means that a polymer can degrade, this can potentially be negative, often leaving smaller fragments (micro-/nanoplastics) and other potentially harmful residues.
- A polymer that is (certified) **compostable** will degrade into water and CO_2 via biodegradation under composting conditions (55-70°C, controlled humidity).

Bottom line: Degradability is a great feature, but alone it is not enough in the context of polymers.



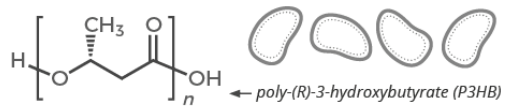
THE CHEMISTRY OF BIODEGRADABLE PLASTICS

COMMON BIOPOLYMERS & SOURCES

POLYLACTIC ACID (PLA)

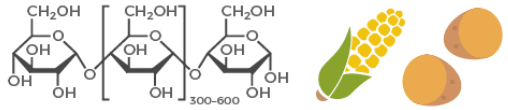
Obtained from fermented plant starch from corn, cassava, sugar cane or sugar beet.

POLYHYDROXYALKANOATES (PHAs)



Extracted from bacteria, which produce it via the fermentation of sugar or lipids.

THERMOPLASTIC STARCHES (TPS)



Starches from plant materials are heated with water, then mixed with plasticisers or other polymers.

EVERYDAY USES OF BIOPOLYMERS

Biodegradable coffee cups are paper cups with a PLA lining to make the paper waterproof.

PLA has the second largest production volume of any biopolymer (behind TPS). It is also used in plastic films, bottles, and food containers.

PLA and TPS both find use in the manufacture of plastic cutlery that's biodegradable.

TPS is also used in food waste bags and some magazine wrappers. PHAs have fewer uses, but have medical uses such as in surgical sutures.

ADVANTAGES AND DISADVANTAGES

GLOBAL PLASTIC PRODUCTION

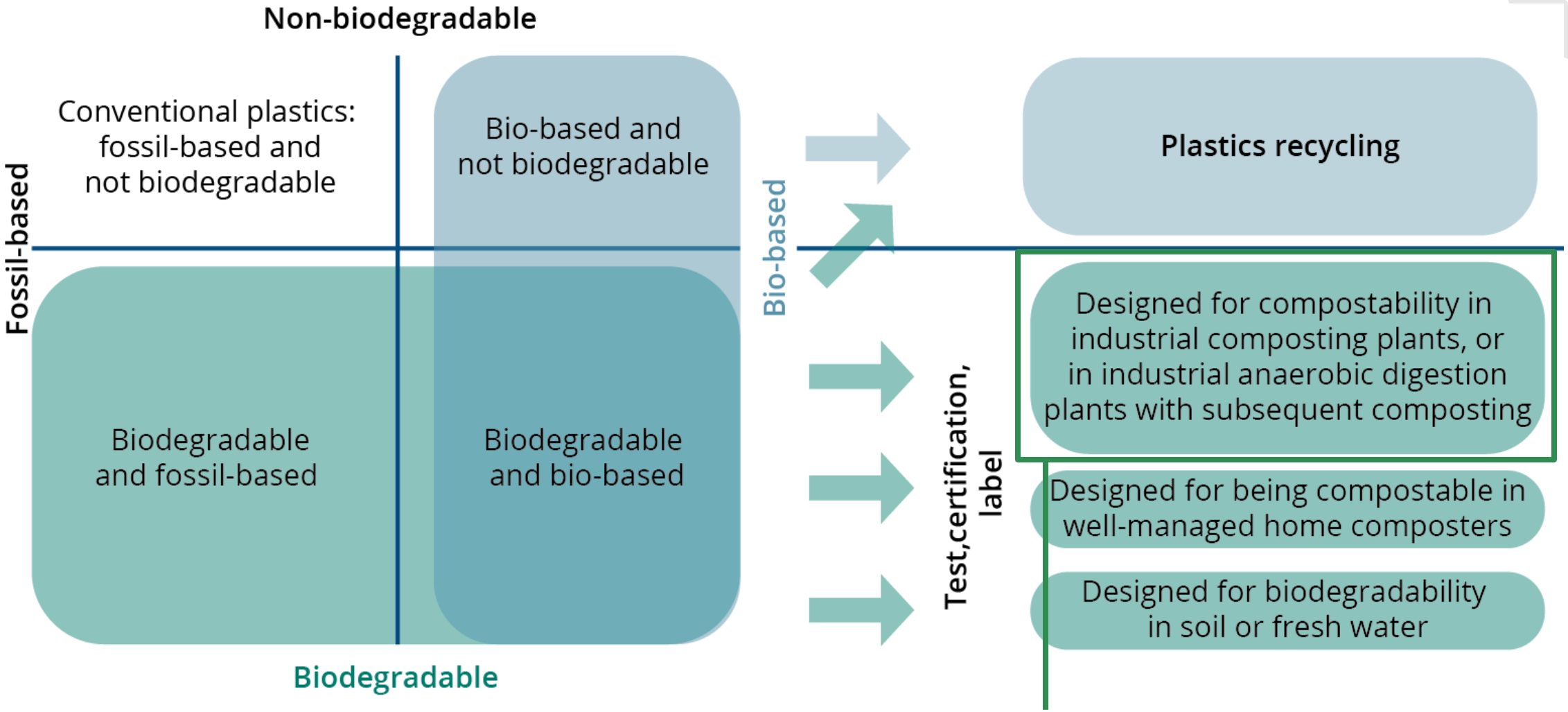
Use of bioplastics is increasing, but they still account for less than 1% of the global plastics market (as of 2018).

CONDITIONS FOR BIODEGRADING

Compostable plastics need specific conditions to break down – and take much longer to do so completely if they go to landfill instead of being recycled. However, they still break down faster than conventional plastics.

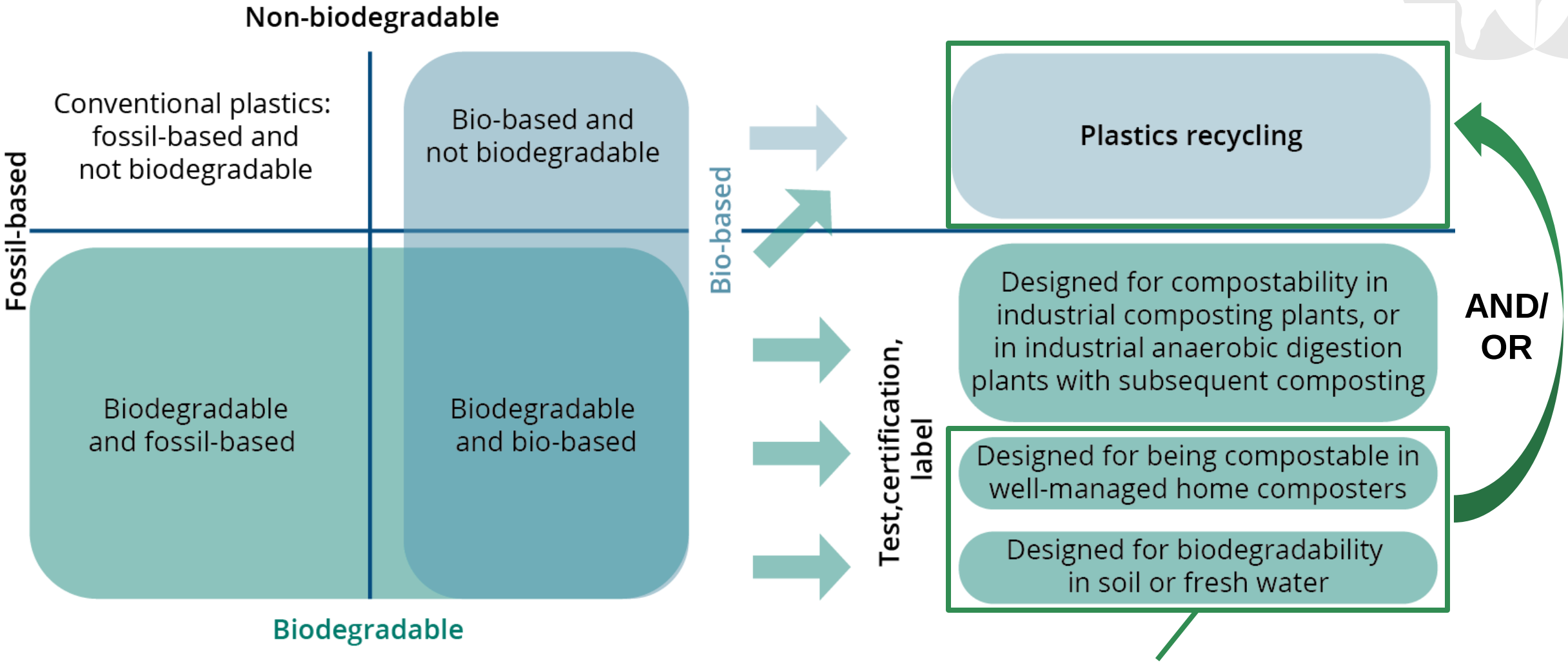
Biodegradable plastics are more expensive than plastics derived from fossil fuels on weight basis, and require land to grow raw materials. However, the greenhouse gas emissions associated with their production are lower.

What is next?



We have this in the moment.

What needs to be improved?



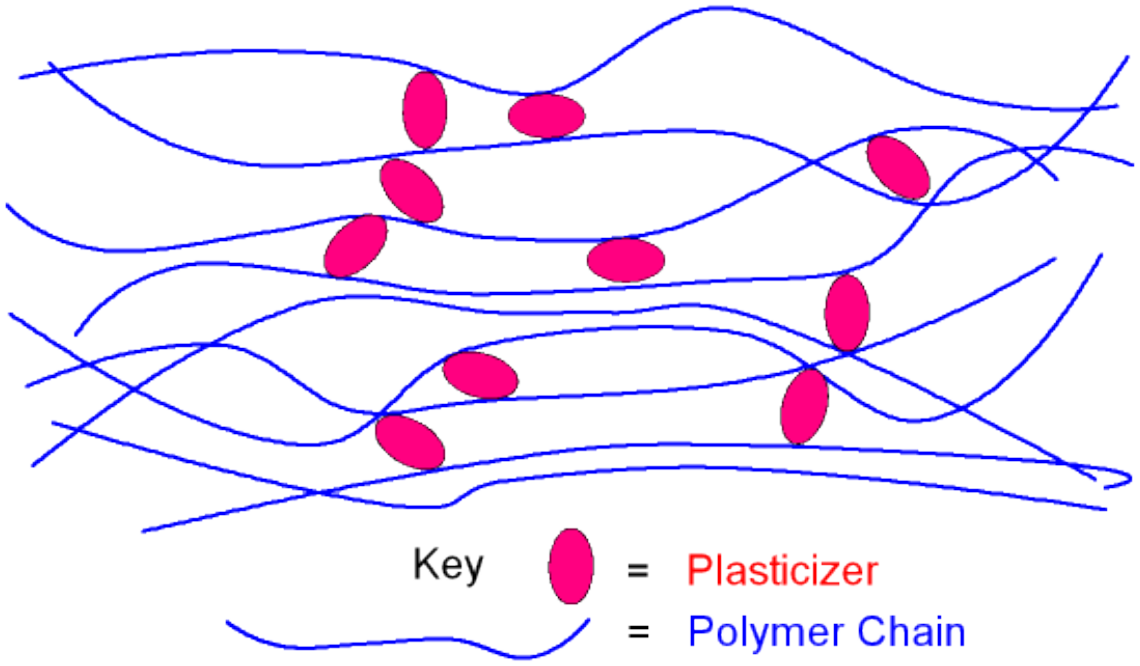
Composting under 'non-industrial' conditions; better recycling performance.

Discussion

- Where do you see the future of plastics going?
- How to address the challenges?
- How important is consumer acceptance?
- How important might regulations or policies be?

Perstorp

What is a plasticizer?



https://www.gcsescience.com/o59.htm

Plasticizers give a plastic the mechanical properties we require. Without a plasticizer, materials will be very stiff, brittle and break easily.

There are:

- internal plasticizers covalently bound to the material (co-polymers)
- external plasticizers only formulated in the material without binding to them

Why are they a problem?

What might have happened here?

Why are they a problem?

This is a very soft plastic, which contains a large amount of external plasticizer (up to 80% and more).

This is a hard plastic, containing rather small amounts of external plasticizers (0-5%).

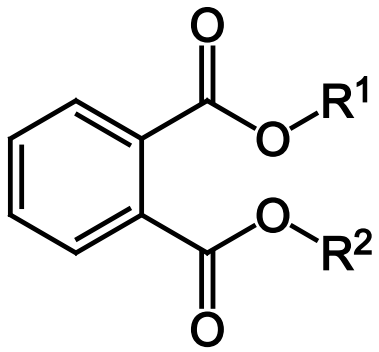
Why are they a problem?

By simply putting these two materials adjacent to each other, the plasticizer from the softer polymer can migrate into the harder polymer and change its structural properties!!!
This process is called **leaching** or **migration**.

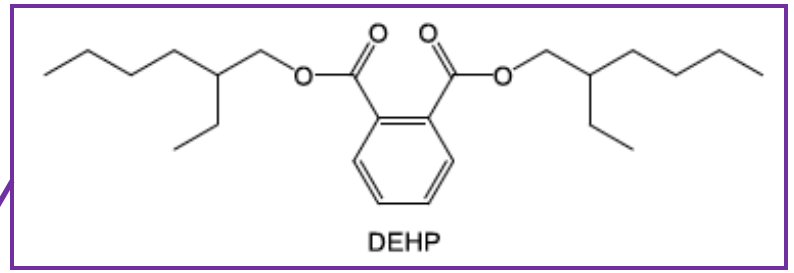
Many of these molecules, especially in PVC are **phthalates**.

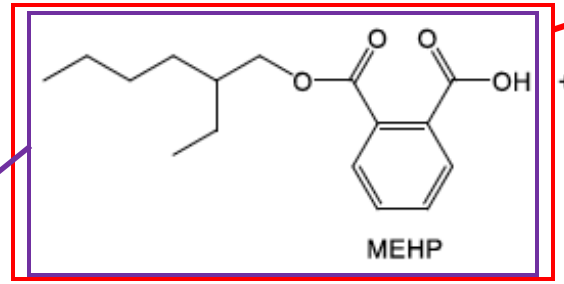
Migration/Leaching processes can also ocurr when plastics are in contact with water, saliva, or other liquid matrices that come into contact with humans or the environment.

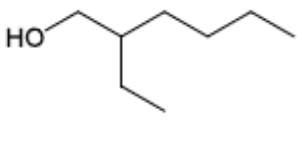
The chemistry of phthalates

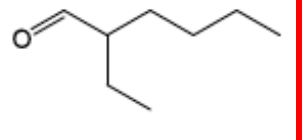


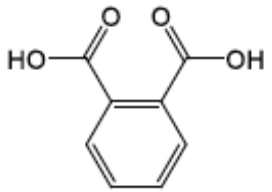
General chemical structure of Phthalates

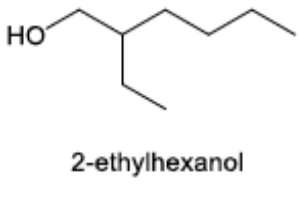


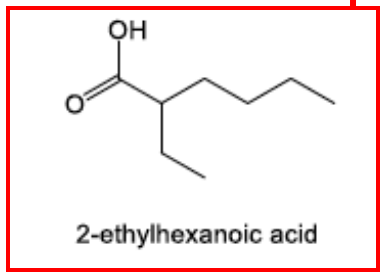












Persistencet in the Environment

Endocrine-disrupting activity

Phtalates are metabolized into problematic products!

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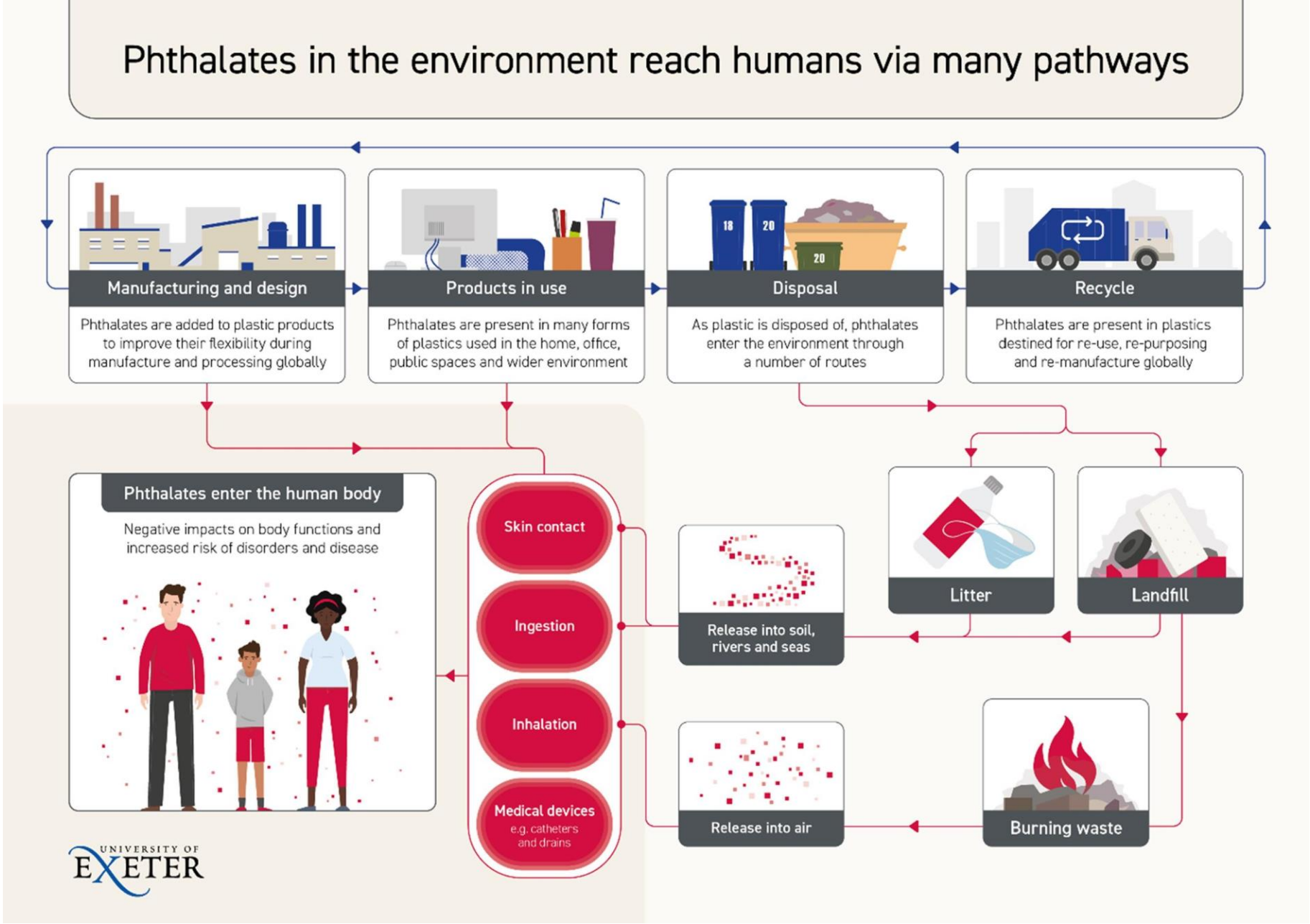
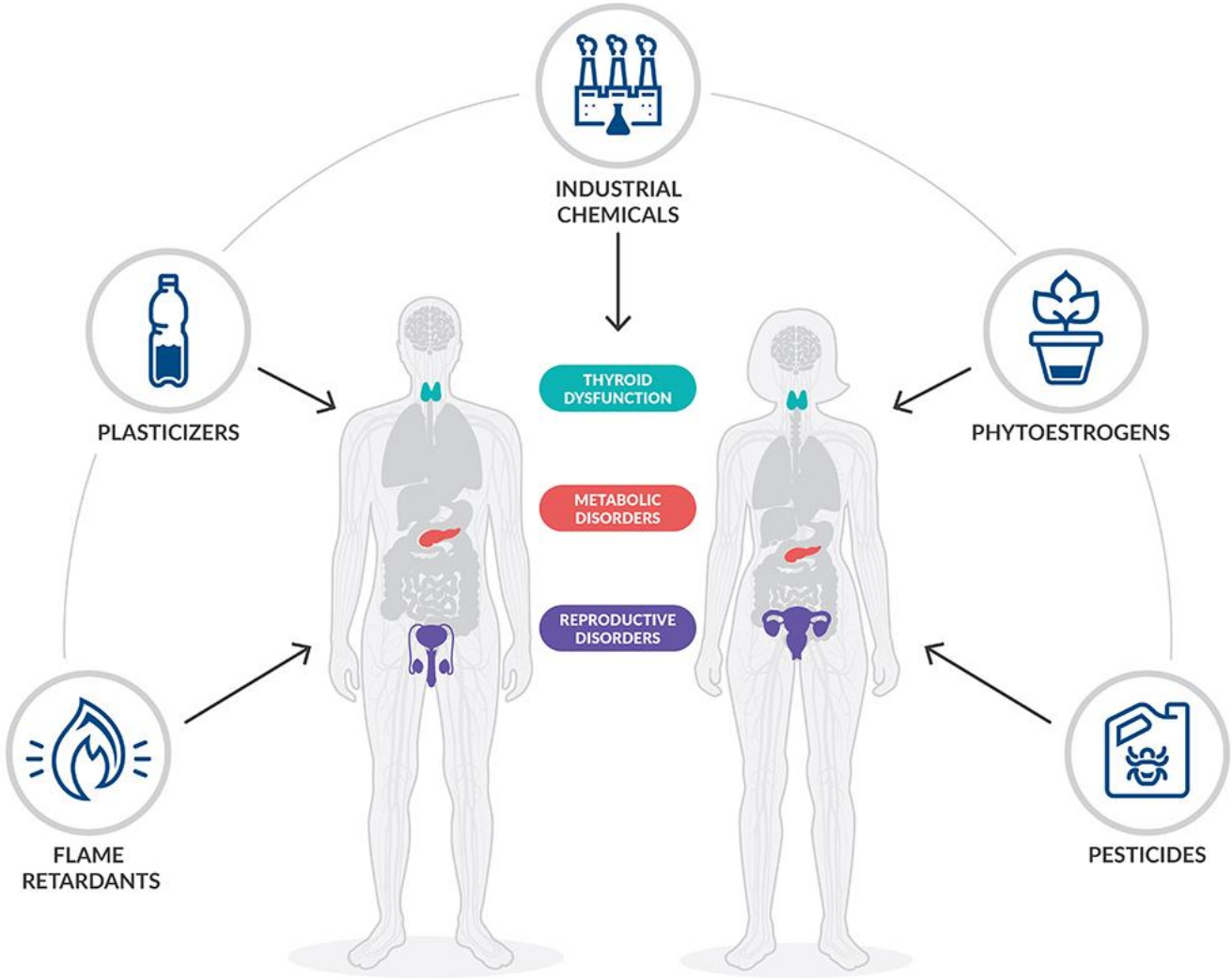

Phthalates in the environment reach humans via many pathways
Manufacturing and design
Phthalates are added to plastic products to improve their flexibility during manufacture and processing globally
Products in use
Phthalates are present in many forms of plastics used in the home, office, public spaces and wider environment
Disposal
As plastic is disposed of, phthalates enter the environment through a number of routes
Recycle
Phthalates are present in plastics destined for re-use, re-purposing and re-manufacture globally
Phthalates enter the human body
Negative impacts on body functions and increased risk of disorders and disease
Skin contact
Ingestion
Inhalation
Medical devices
e.g. catheters and drains
Release into soil, rivers and seas
Release into air
Litter
Landfill
Burning waste
UNIVERSITY OF EXETER

Endocrine disrupting Chemicals



From: https://www.caymanchem.com/news/endocrine-disrupting-chemicals-present-human-and-environmental-health-risks

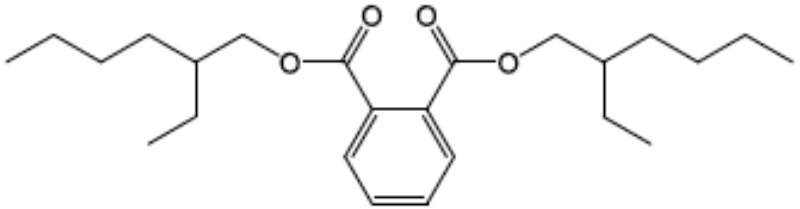
Endocrine disrupting Chemicals

- Plasticizers like phtalates are powerful **endocrine disruptors**.
- However, several other compound classes can also fall into this classification (e.g. PFAS, Dioxins, DDT, etc.)

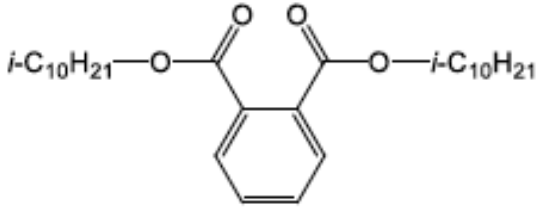
High demand for Plasticizers

- Despite proven harmful effects, phtalates are still among the most commonly used plasticizers, and demand high.

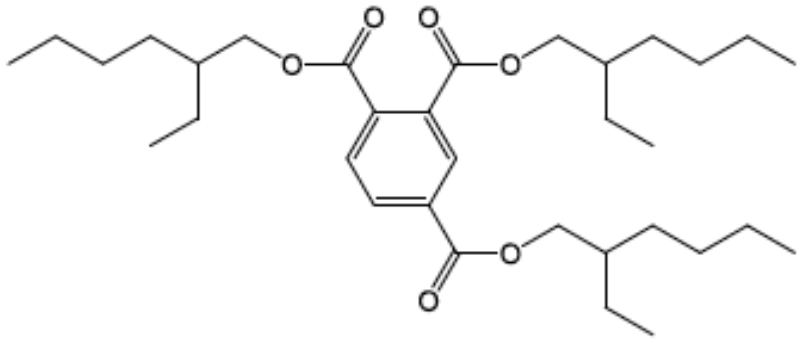
Regrettable substitution



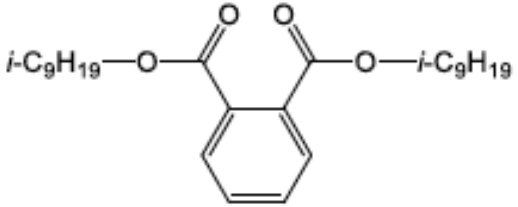
Di (2-ethylhexyl) phthalate (DEHP)



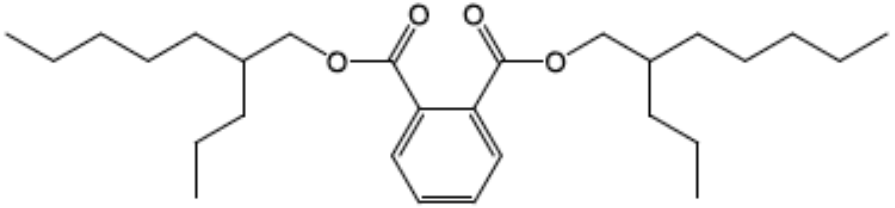
Diisodecyl phthalate (DIDP)



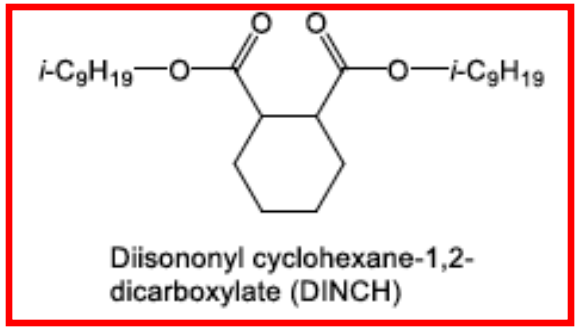
Tri (2-ethylhexyl) trimellitate (TEHTM or TOTM)



Diisononyl phthalate (DINP)



Di (2-propylheptyl) phthalate (DPHP)



Diisononyl cyclohexane-1,2-dicarboxylate (DINCH)

- A substitution of phtalates by cyclohexane-derivatives (e.g. DINCH) has been done by industry, but due to similar adverse biological effects, it appears to be a regrettable substitution with similar dangerous health effects: research is ongoing…

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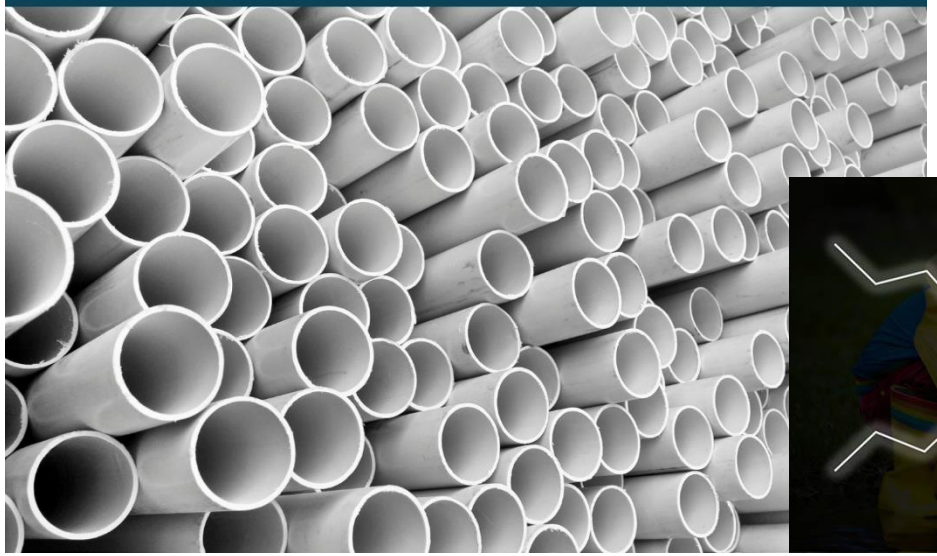
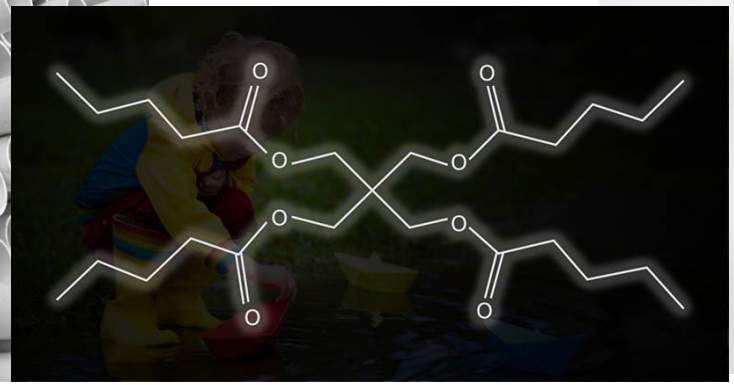
Perstorp's different approach

Pevalen™ Pro 36

Perstorp develops Pevalen™ Pro 36 (or Pentaerythritol tetravalerate/PETV), a renewable, phthalate-free plasticizer that improves the sustainability of flexible PVC.





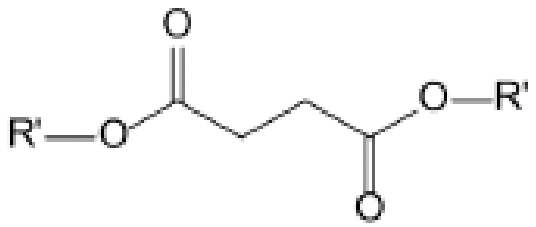
Benefits

Since Pevalen™ Pro does not consist of phthalate, it is a great choice for PVC products that come in direct human contact, such as apparel and accessories, sports products, automotive interiors, and other indoor applications. The FDA also approved for the use of Pevalen™ Pro in products that contact food. It can simply be used as a drop in for existing formulations.

Pentaerythritoltetravalerate (PETV) has much more benign hydrolysis products: **Pentaerythrol and valeric acid.**

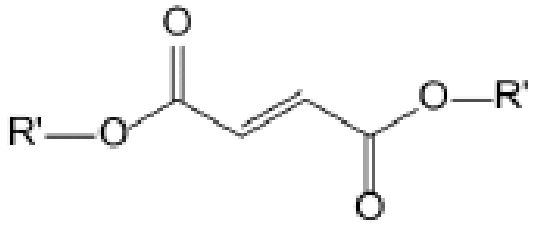
Other benign plasticizer candidates

Succinates:



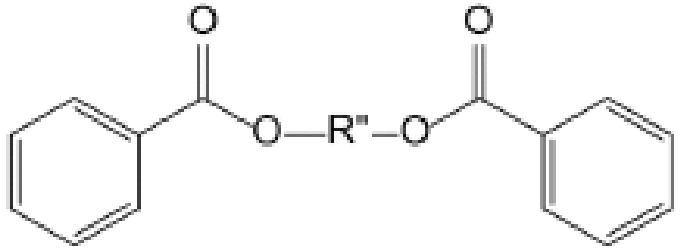
Maleates:

Fumarates:



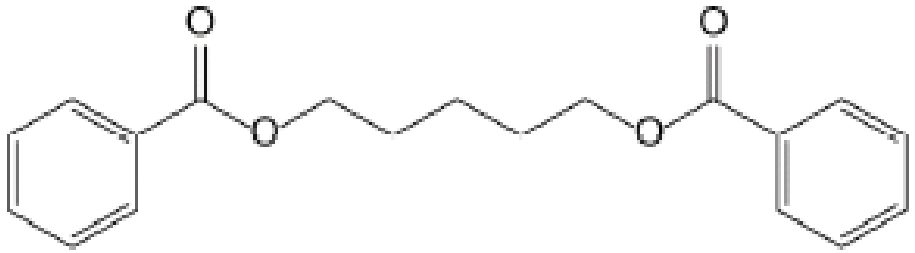
R' = C_2H_5, C_4H_9, C_6H_{13}, C_8H_{17}

Alkyl dibenzoates:

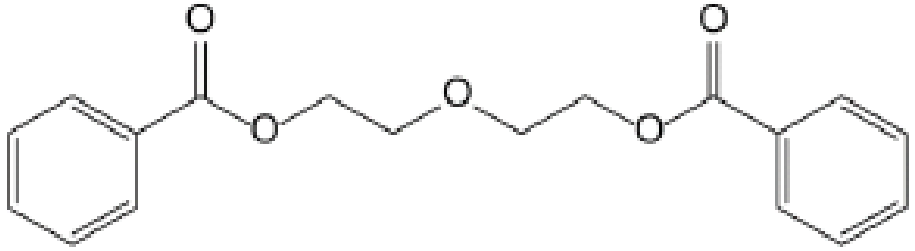


R" = C_3H_6, C_4H_8, C_5H_{10}, C_6H_{12}

1,5-PDB:



DEGDB:



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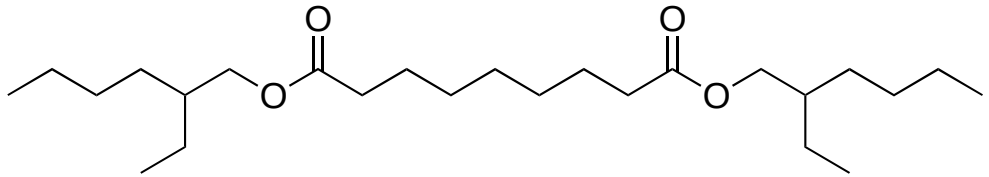
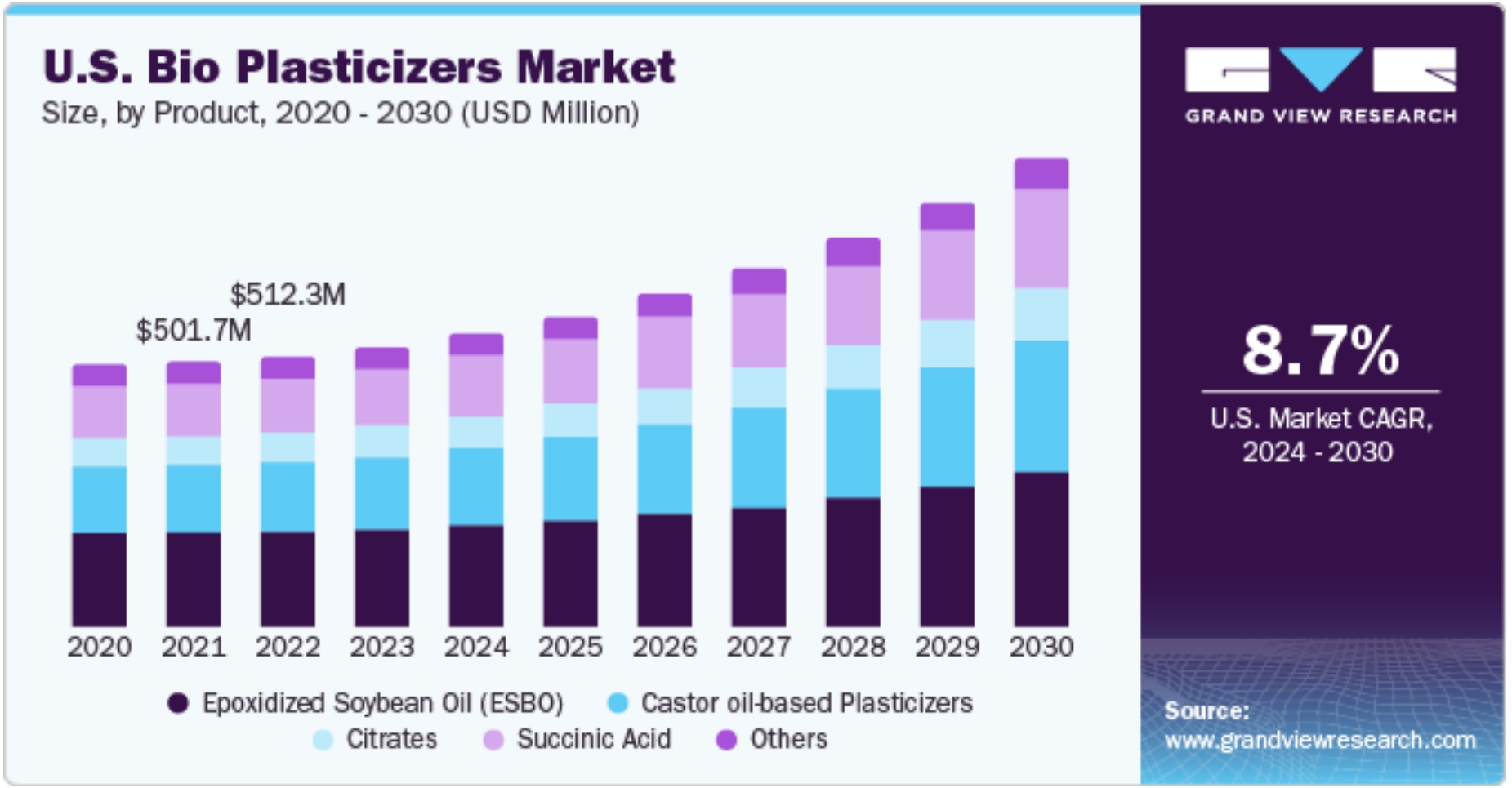
And even more, somealready commercial



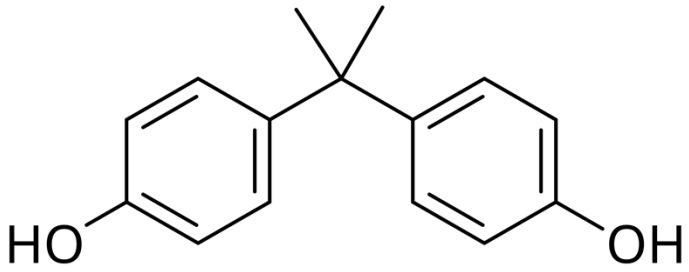
Emery Oleochemicals

The company Emery Oleochemicals develops plasticizers based on naturally occurring acids. Azelaic acid is abundant in plants. **Observations?** One of the potential hydrolysis products is 2-ethylhexanoic acid, which is potentially problematic. More work is needed.

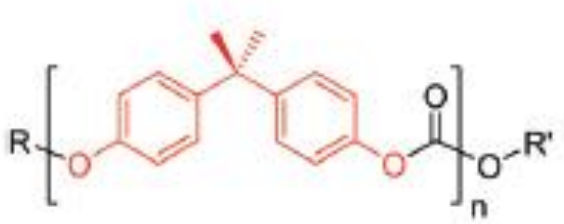
Bioplasticizers are on the rise



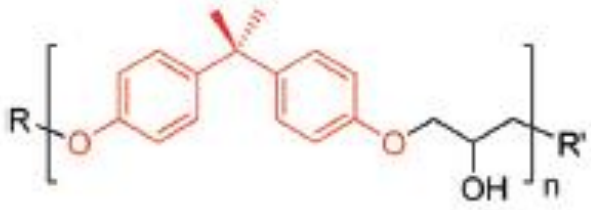
An example for problematic co-polymers



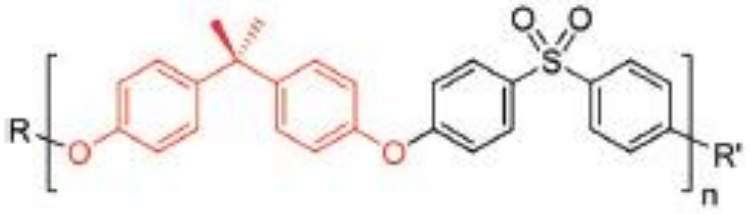
- Bisphenol A (BPA) is among the most commonly used co-monomers. Sometimes it is called an internal plasticizer, which it is not, but the problems are similar



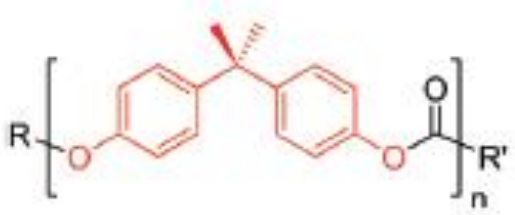
polycarbonates



epoxy resins

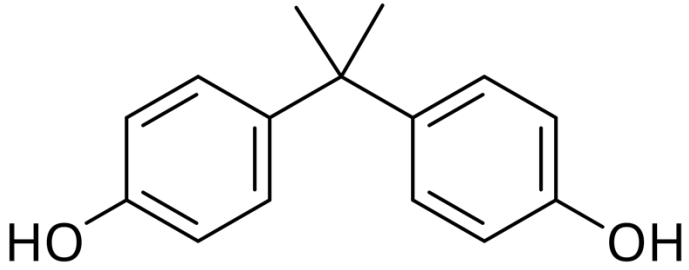


polyethersulphones



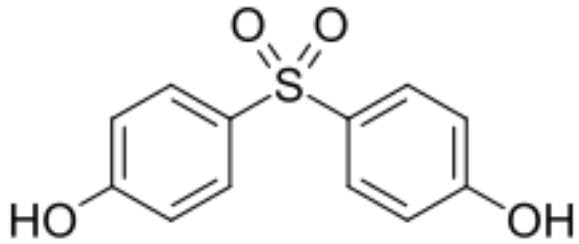
polyesters

An example for problematic co-polymers

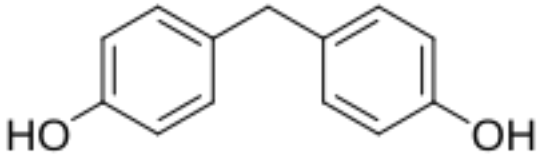


- It acts as a xenestrogen, a hormone disruptor, and many people have tried to substitute it.

Bisphenol A substitutes:



Bisphenol S



Bisphenol F

And guess what... These substitutes are regrettable, since they have basically the same effects as Bisphenol A.

Discussion

- Is there a way to avoid plasticizers completely?
- Which challenges might be posed by these approaches?
- How would the perfect plasticizer look like?
- How important might regulations or policies be?

Yale School of the Environment

Center for Green Chemistry & Green Engineering at Yale

- Advance Science
- Catalyze Implementation
- Prepare the next generation
- Raise Awareness

Thank You!

For questions, please reach out:

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