

# Science of recycling: the chemistry, challenges, and outlook

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FEBRUARY 20, 2020

LASAN RECYCLING MARKETS SYMPOSIUM

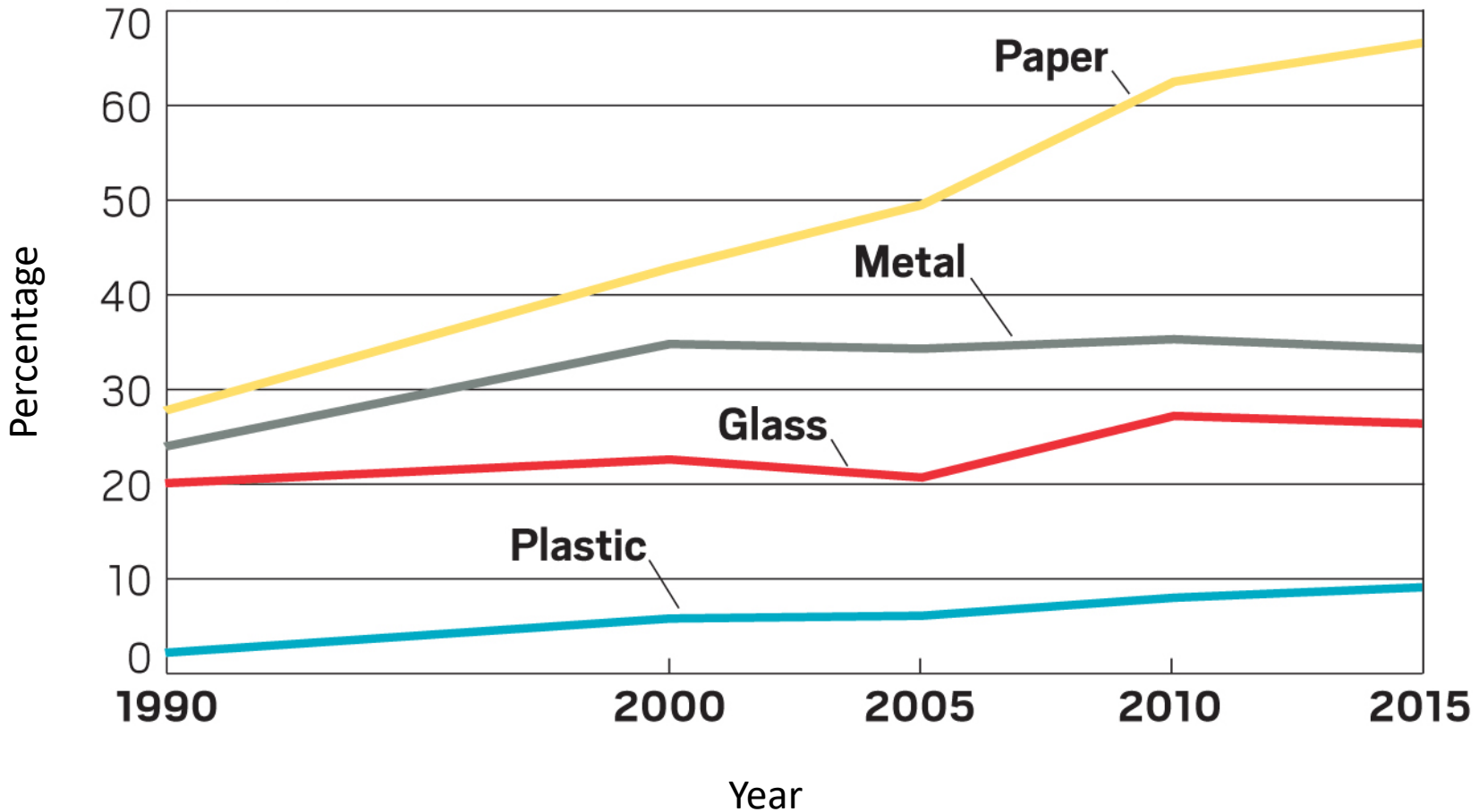
# Outline

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- Current recycling methods
  - Paper
  - Aluminum
  - Plastics
- Alternative methods/materials
  - Upcycling
  - New plastics
- Future outlook
  - How can we help?



# Recycling rate of materials in the US



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- Current recycling methods**

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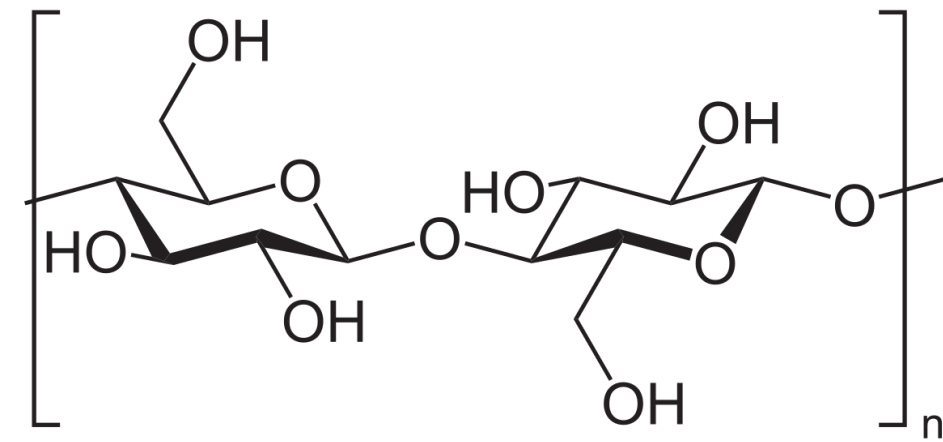
- Future outlook**

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# Paper is derived from a biomolecule: cellulose fibers

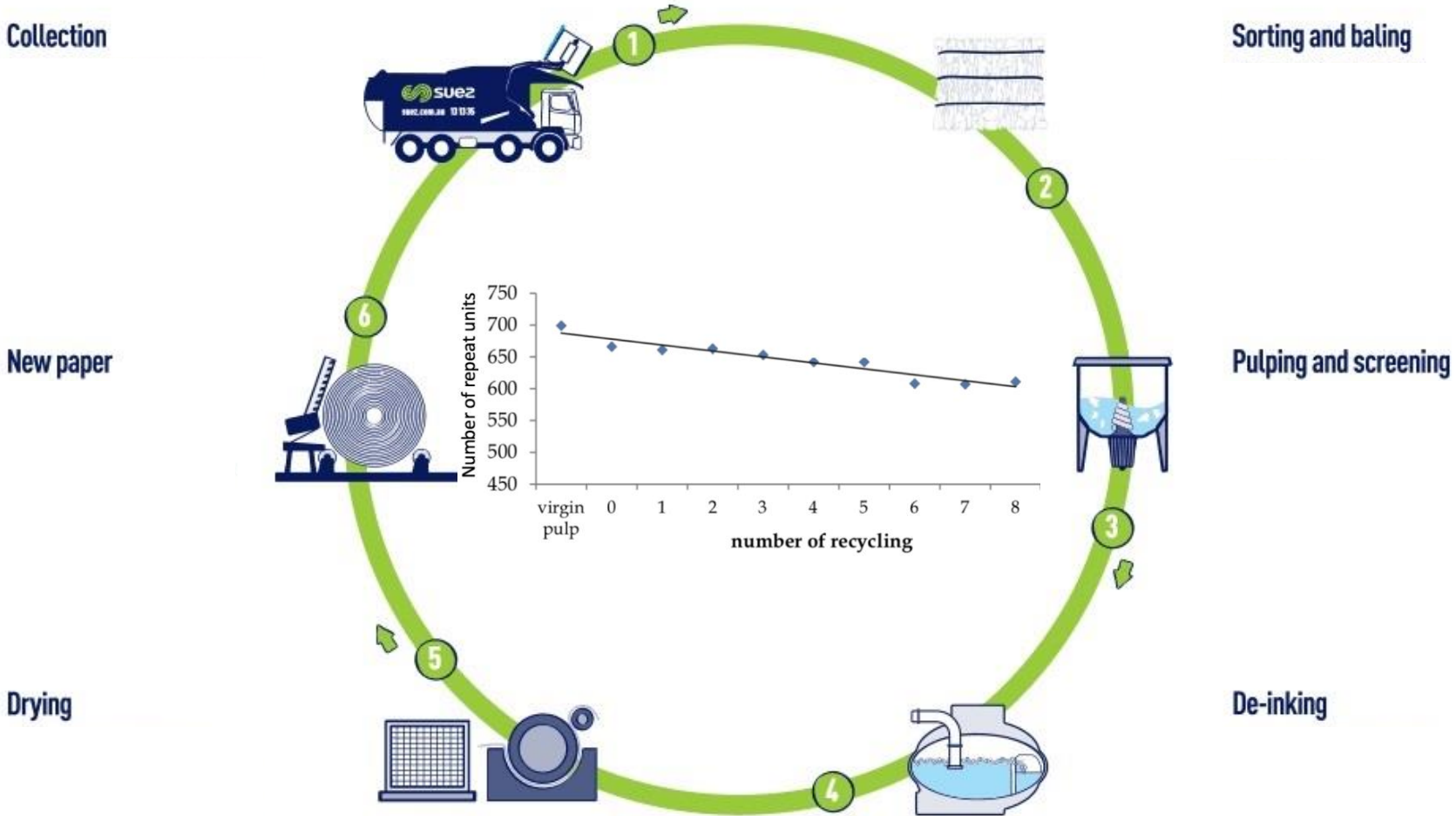
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Cellulose is a biopolymer composed of repeating glucose units

Mechanical properties of paper are dependent on  $n$ , the number of repeat units

# Paper recycling is a closed loop process

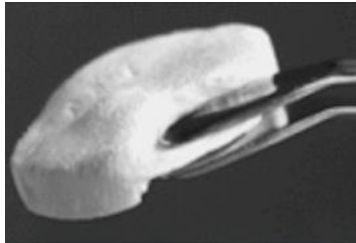


EPA states maximum number of recycles for virgin material to be five to seven cycles

# Waste paper can be downcycled or used in nanocomposites

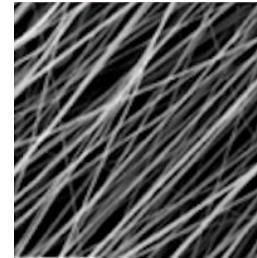
## Foams

- Acoustic
- Structural
- Thermal
- Absorption



## Fibers & Films

- Reinforcement
- Textiles
- Woven
- Films



## Tissue Engineering

- Scaffolds
- Bandages
- Drug delivery



## Adhesives & Additives

- Paints
- Cosmetics
- Food



# Outline

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## **Current recycling methods**

Paper

**Aluminum**

Plastics

## **Alternative methods/materials**

Upcycling

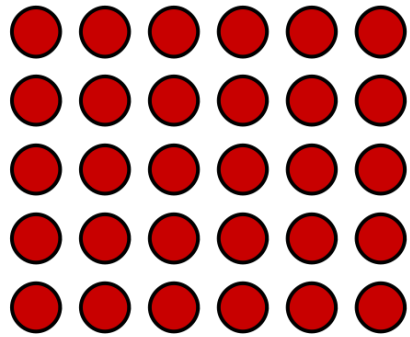
New plastics

## **Future outlook**

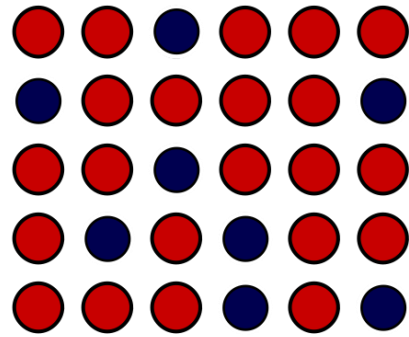
How can we help?



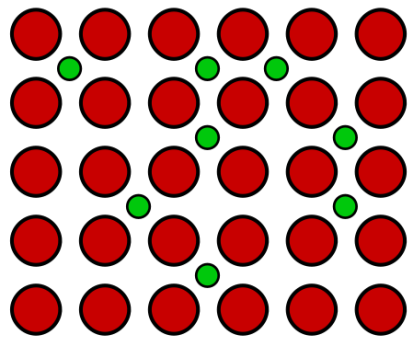
# Metals and alloys are more robust than molecules



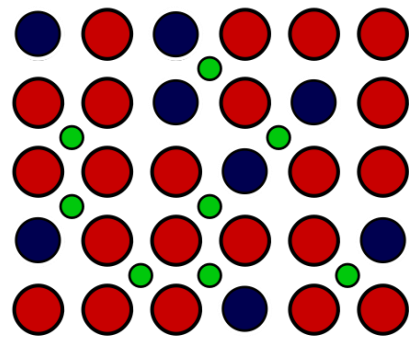
Pure metal



Substitutional alloy



Interstitial alloy



Substitutional / interstitial alloy

- Alloys and metals exhibit different bonding than polymers/ plastics
- This different bonding allows for infinite melting and cooling cycles without compromising its properties

# Different aluminum alloys have different applications and properties

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<b>Alloy series</b>	<b>Alloy</b>	<b>Properties</b>	<b>Applications</b>
1XXX	Pure	Low strength, excellent thermal/electrical conductivity, and corrosion resistance	Fuel filters, electrical conductors, lighting reflectors
2XXX	Copper	High strength, relatively low corrosion resistance	Aircraft fittings, ballistic armor
3XXX	Manganese	Medium strength, good corrosion resistance	Storage tanks, beverage cans, home appliances
4XXX	Silicon	High castability, high machinability, low ductility	Variety of castings, filler metals

# Aluminum sorting technology makes aluminum recycling easier

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<b>Separator type</b>	<b>Physical parameter</b>	<b>Desired separation</b>	<b>Technology</b>
Elemental composition	Vapor phase, x-ray energy	Alloy type	LIBS, XRF, PGNAA
Imagine analysis	Color and shape	Alloy type	Color, etch, 3D shape
Transmission	Atomic number	Alloy type	XRT

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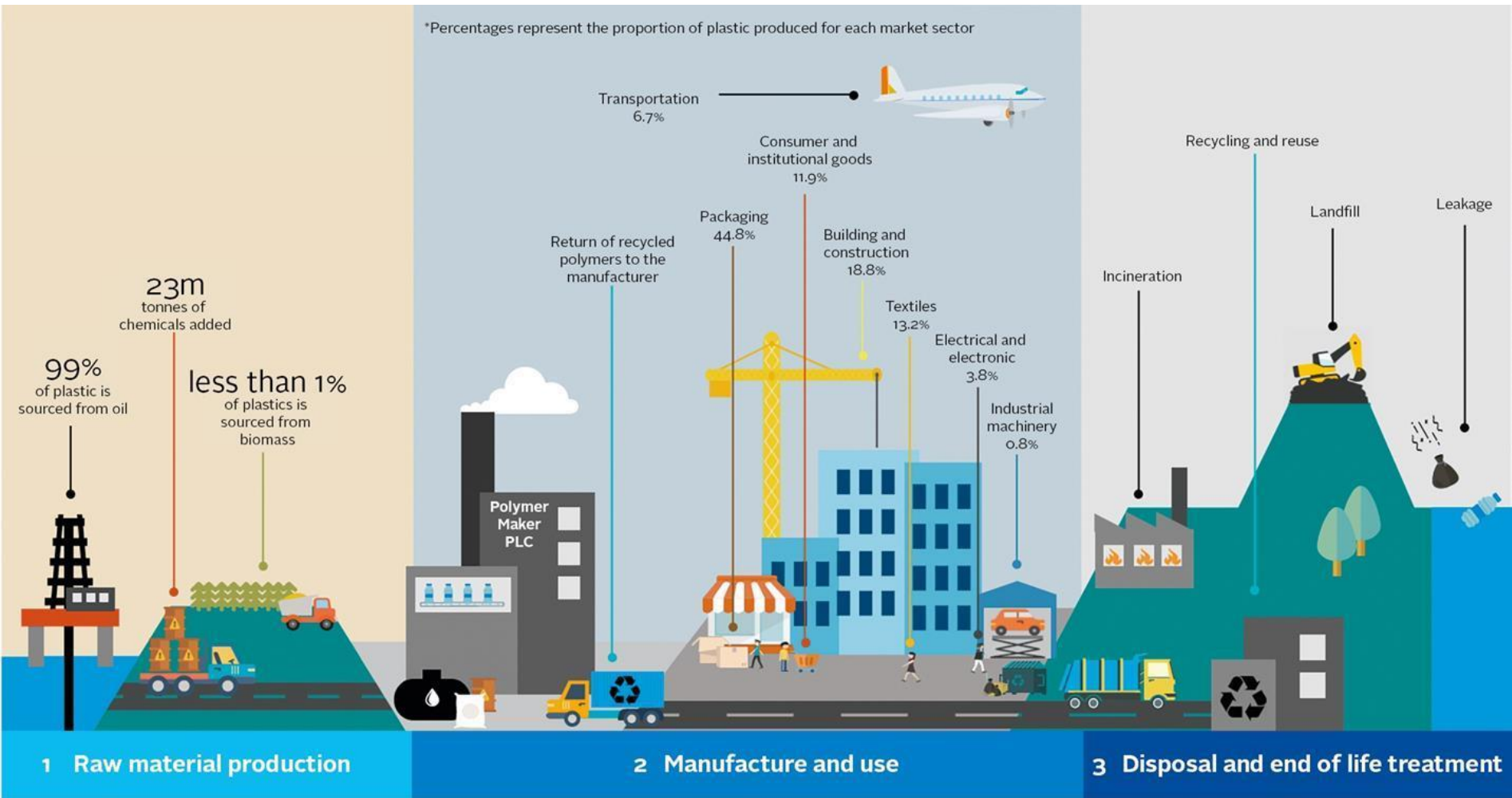
- New plastics

- Future outlook**

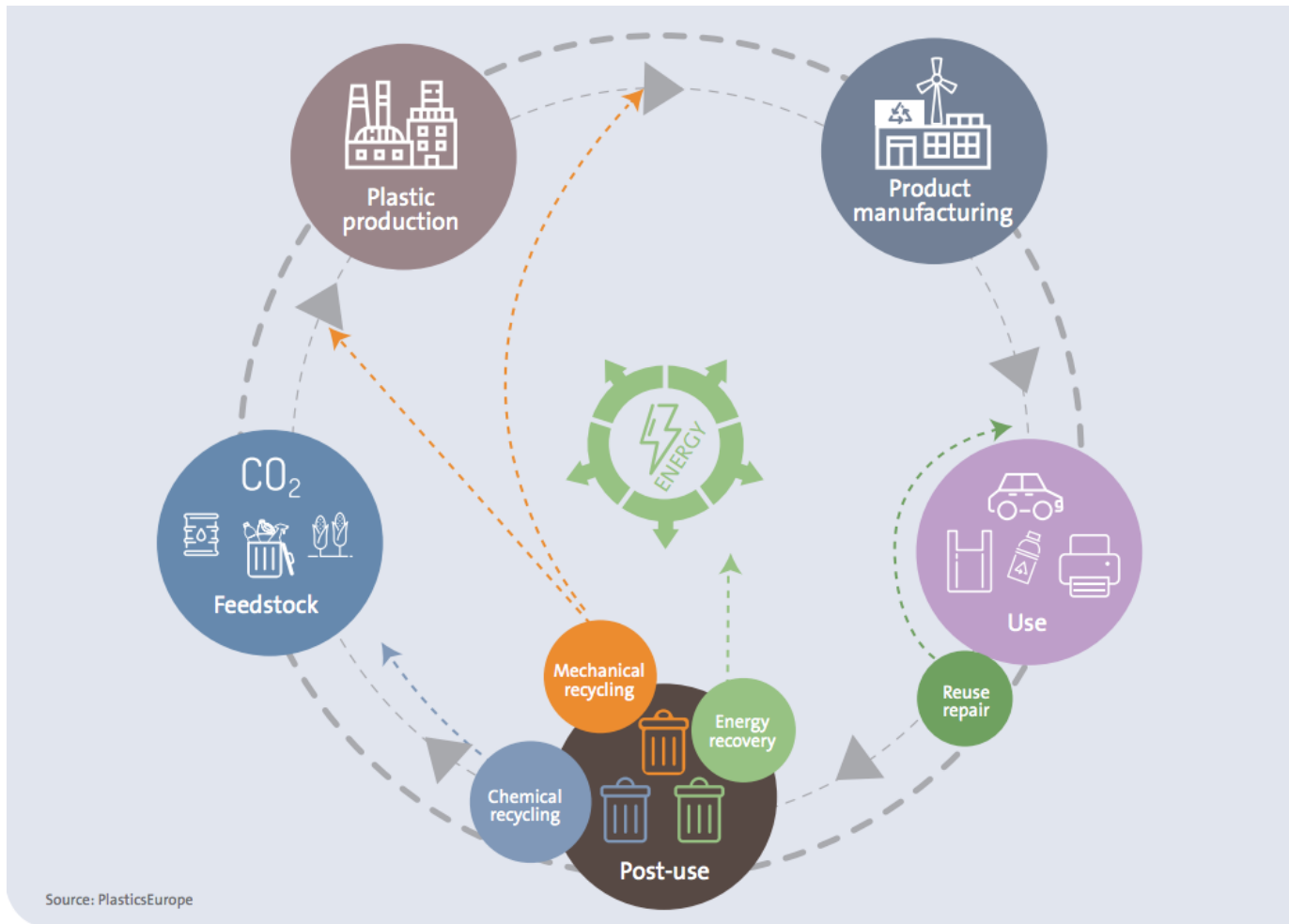
- How can we help?



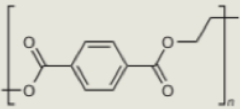





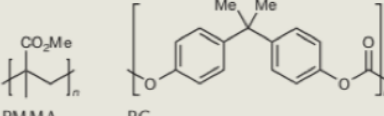
# The plastics problem

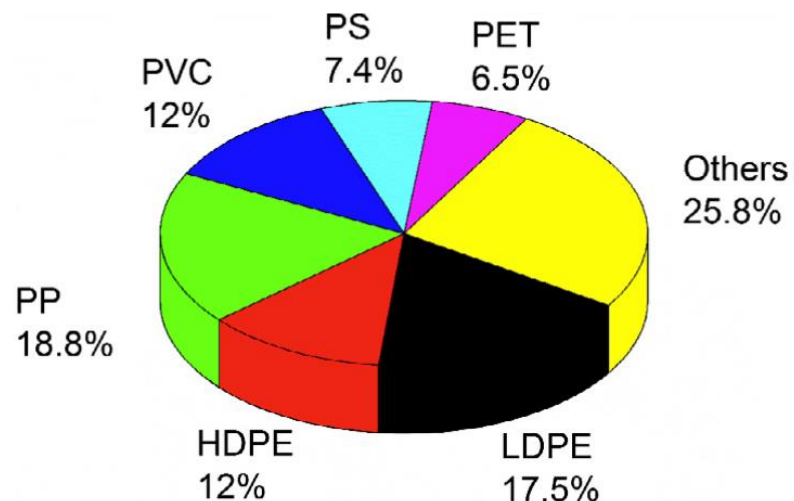


# The current plastic “cycle” is not closed



# Current plastic recyclability has less than 20% recovery rates

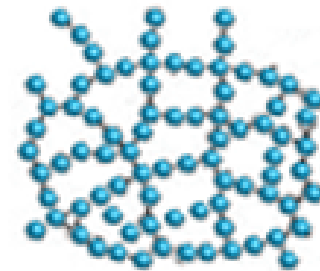
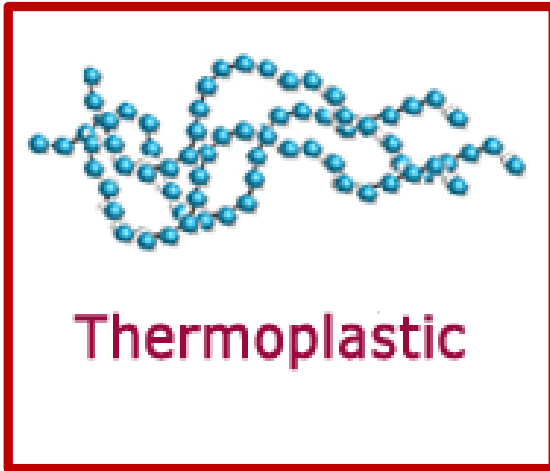
SPI number	Full name	Chemical structure	Currently recyclable?	Recovery Rate (%)
1	Polyethylene terephthalate	 PETE/PET	Yes	19.5
2	High-density polyethylene	 HDPE	Yes	10
3	Polyvinyl chloride	 PVC	No	0
4	Low-density polyethylene	 LDPE	Mostly no	5
5	Polypropylene	 PP	Sometimes	1
6	Polystyrene	 PS	Sometimes	1
7	Other: for example, polycarbonate and polymethyl methacrylate	 PMMA PC	No	varies



Plastic demand by resin type

# Chemistry dictates recyclability

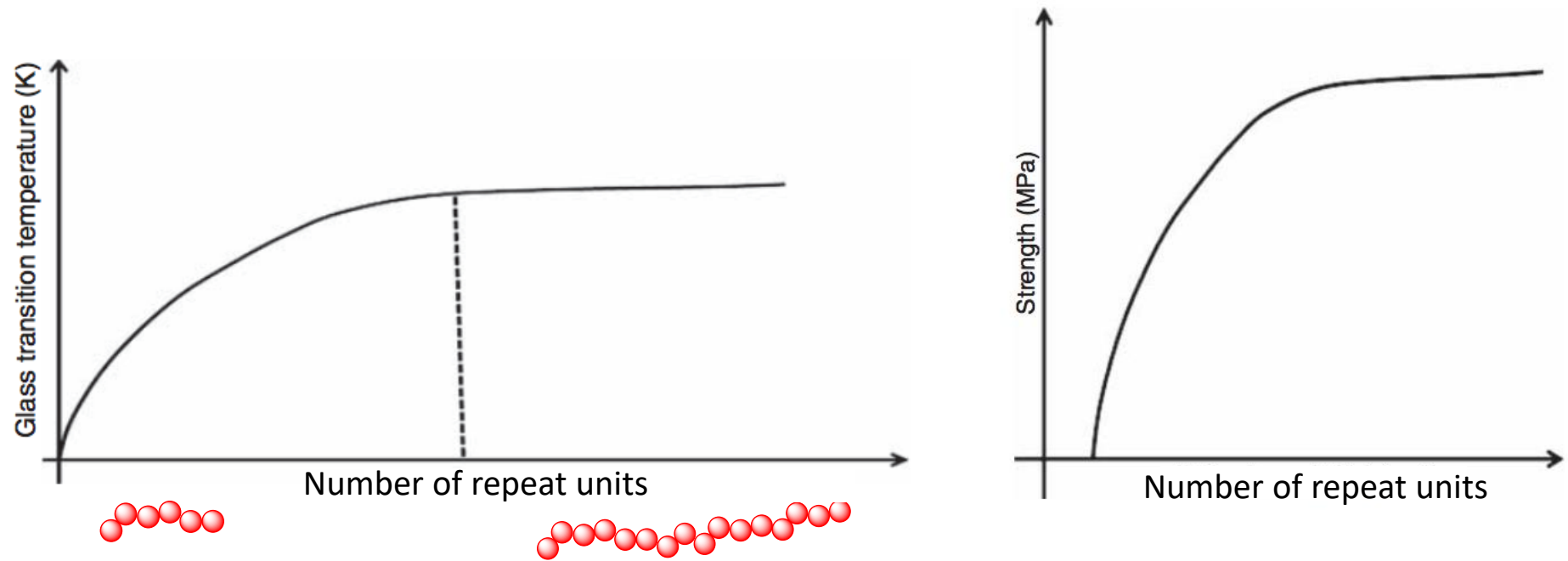
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Thermoplastics have accessible temperature ranges at which a plastic material transitions from a hard “glassy” state into a viscous or rubbery state (known as glass transition temperature)

# Molecular weight affects physical and mechanical properties

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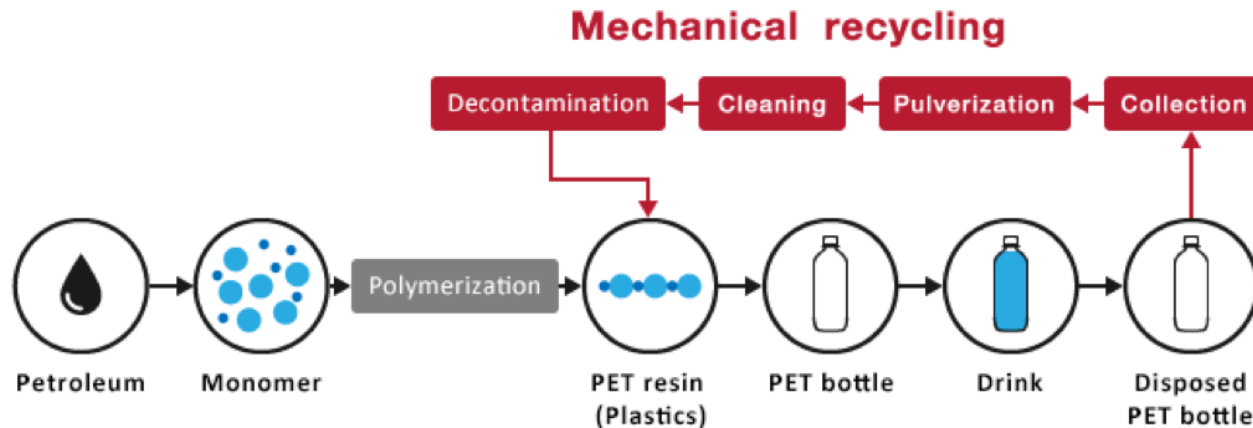


Both glass transition temperature and strength are a function of the number of repeat units

# Primary and secondary mechanical recycling

Primary mechanical recycling requires the direct reuse of uncontaminated plastics into new products (coined closed-loop recycling)

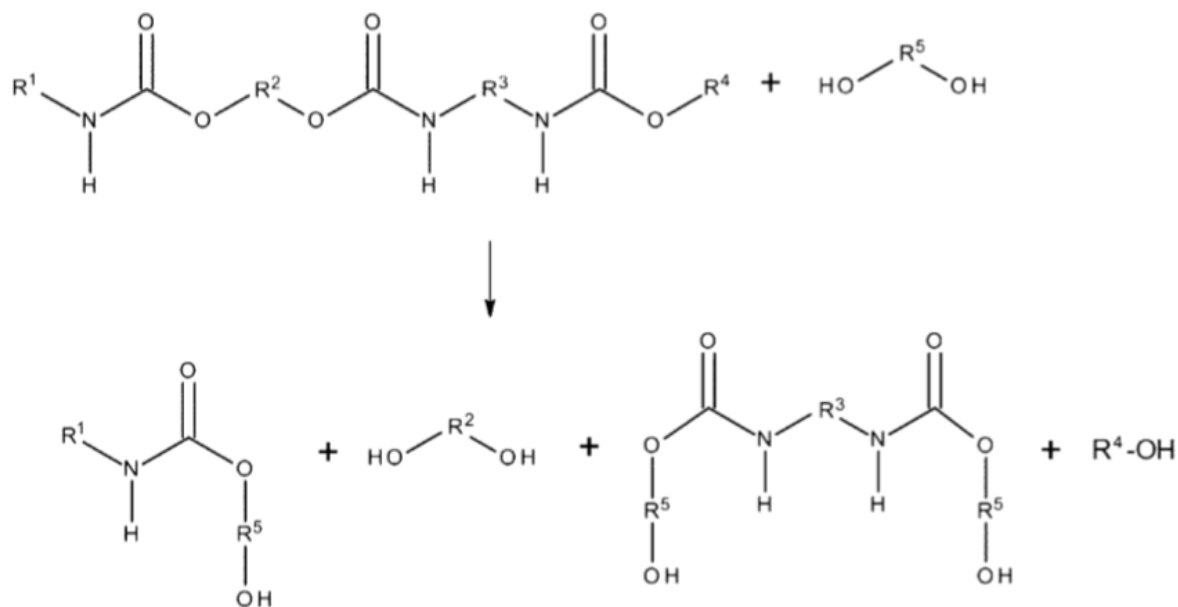
Content and purity of end-of-life and post-consumer-streams are difficult to know which leads to secondary mechanical recycling—requires sorting, separation/purification



# Tertiary recycling (feedstock recycling) aims to recover starting material

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Processes include, hydrolysis, pyrolysis, hydrocracking, catalytic depolymerization and gasification



Polyurethanes can be depolymerized by hydrolysis or glycolysis

# Quaternary recycling involves incineration/combustion for energy recovery

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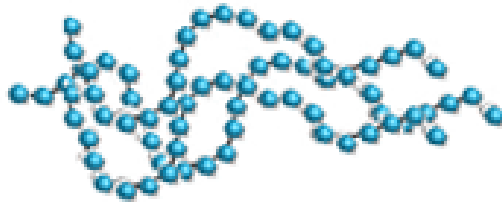
Plastics have high energy content and incineration leads to waste volume reduction

Item	Calorific value (MJ kg <sup>-1</sup> )
Polyethylene	43.3–46.5
Polypropylene	46.50
Polystyrene	41.90
Kerosene	46.50
Gas oil	45.20
Heavy oil	42.50
Petroleum	42.3
Household PSW mixture	31.8

- Quaternary recycling common for mixed- and heavily-contaminated plastics
- Sequestration of polycyclic aromatic hydrocarbons and dioxins poses a challenge

# Thermosets differ chemically from thermoplastics

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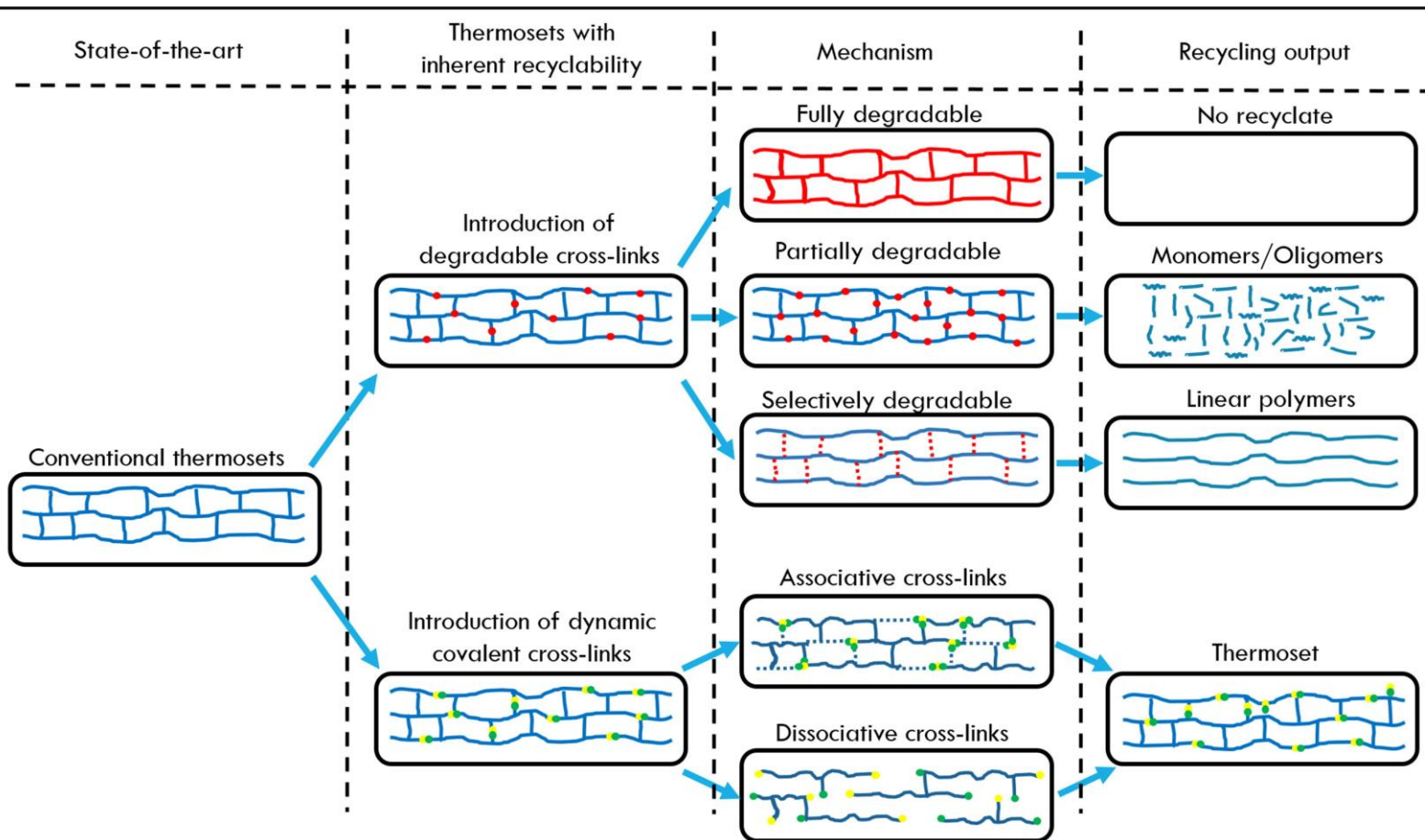
Thermoplastic



Thermoset

- Thermosets are extensively cross-linking upon heating
- A strong network of covalently bonded polymer chains leads to unchangeable mold

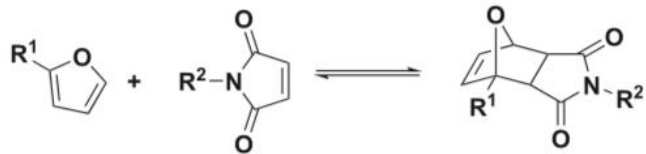
# Specific cross-linking modes determine degradation and recyclability



# Reversible cross-linking offers a path towards more recyclable thermosets

## A Dynamic covalent reactions forming new bonds

### Diels-Alder reaction



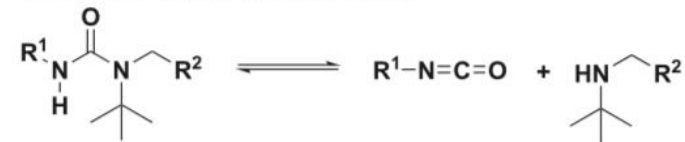
### Imine condensation



### Boronic ester condensation



### Urethane bond dissociation



## B Dynamic exchange reactions

### Transesterification



### Boroxine exchange reactions



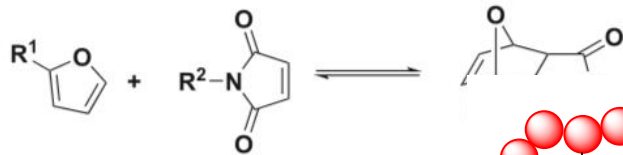
### Vinylogous urethane exchange



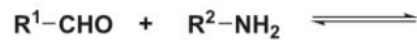
# Reversible cross-linking offers a path towards more recyclable thermosets

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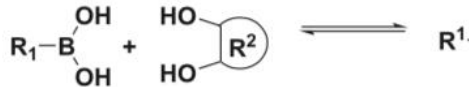
### Diels-Alder reaction



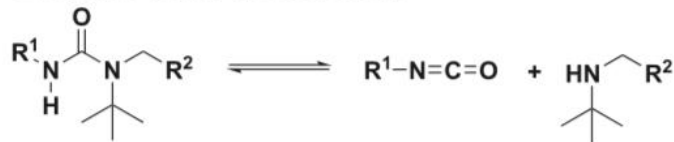
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### Boronic ester condensation

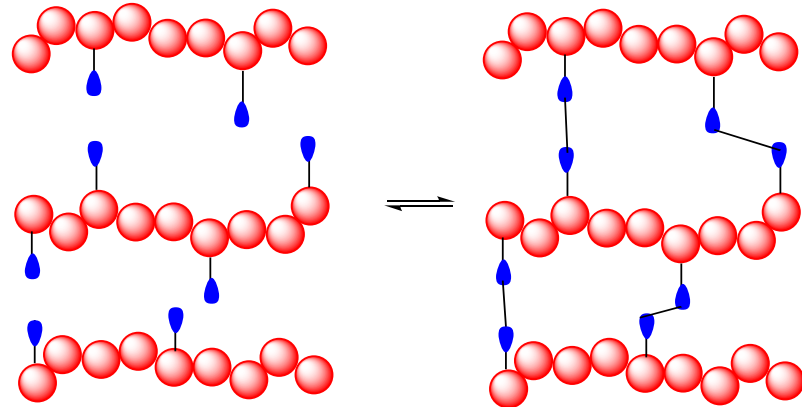
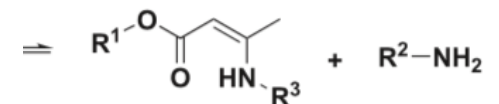
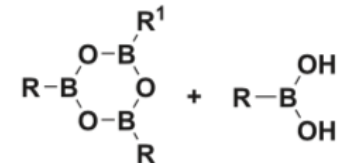
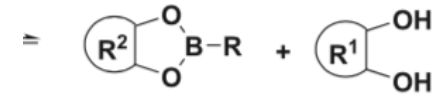


### Urethane bond dissociation



## B Dynamic exchange reactions

### Transesterification



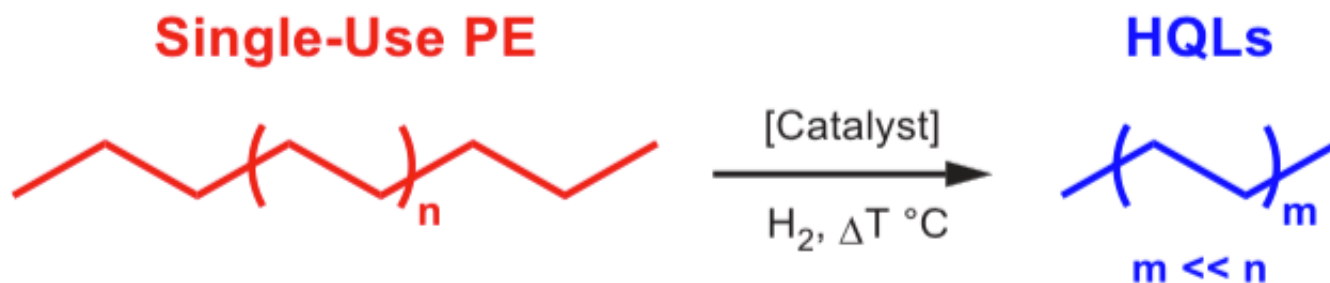
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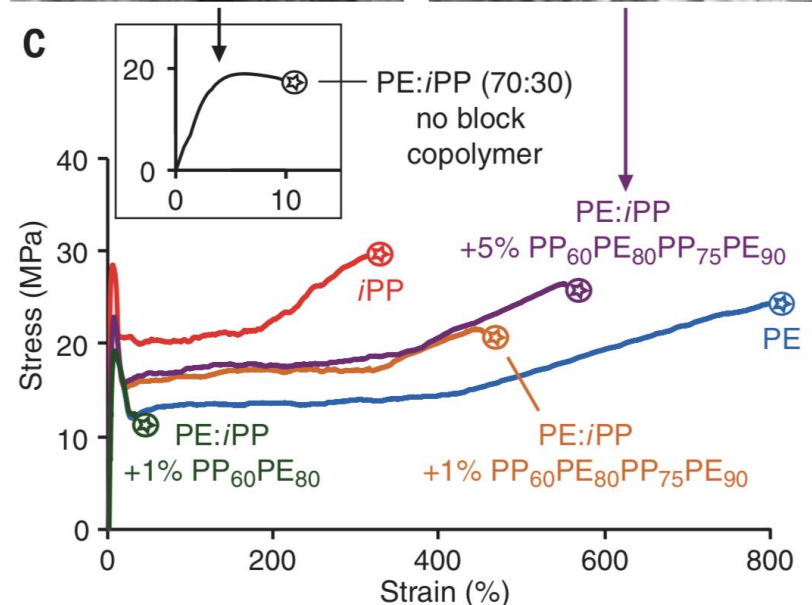
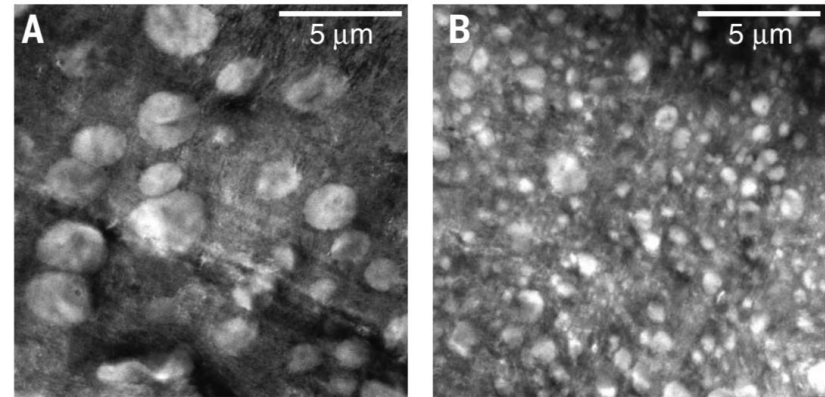
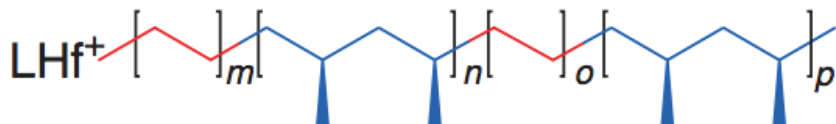
# Upcycling plastics offers a new route for value added recycling products



Achieved 99% conversion with new catalyst, producing no light hydrocarbons, in contrast to commercially available catalysts

# Interfacial compatibilization: an upcycling technique for improving blend properties

- Blending PP and PE with a PP-*b*-PE copolymer increases tensile strength



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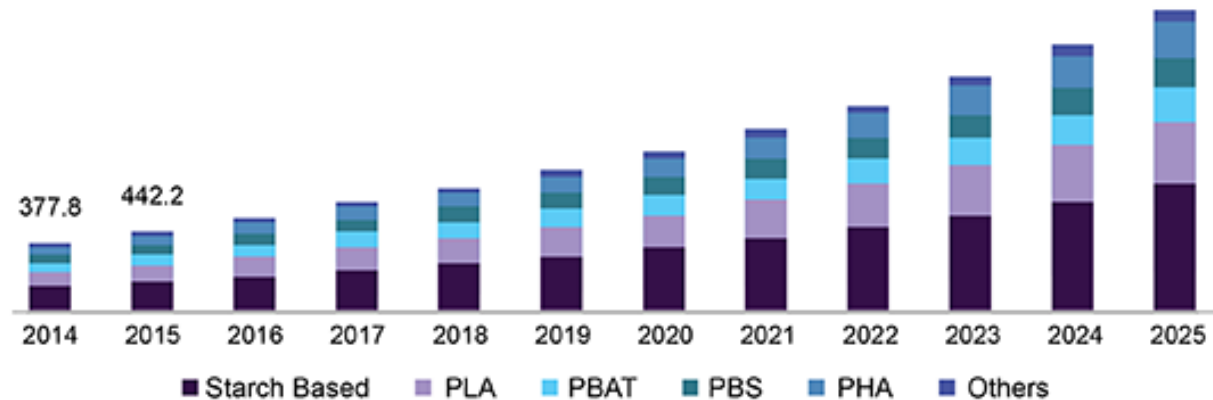
# The market for biodegradable plastics is increasing

Global biodegradable plastic market share, by end of use, 2017 (%)



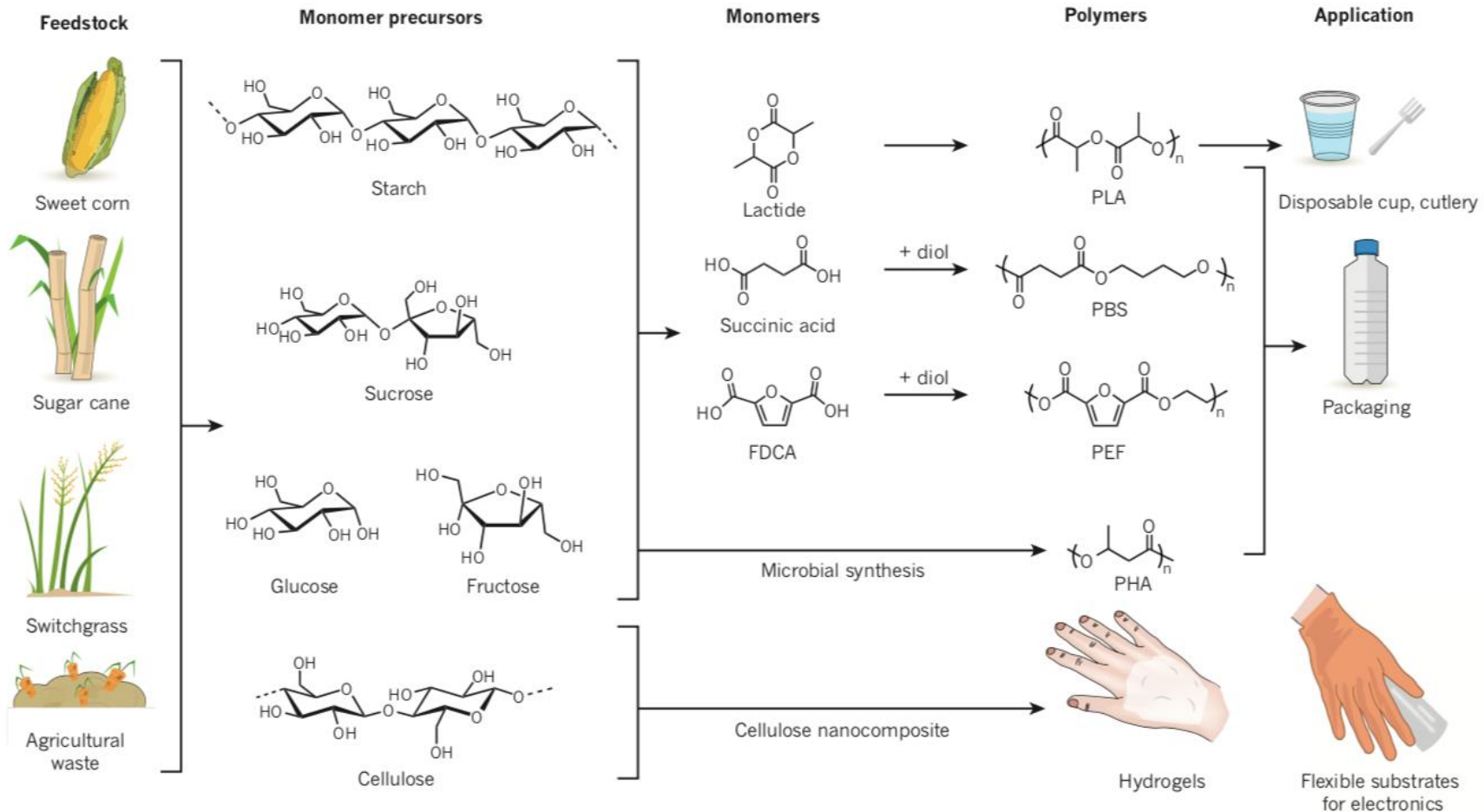
- Packaging
- Agriculture
- Consumer Goods
- Others

US biodegradable plastic market size, by type, (USD Millions)

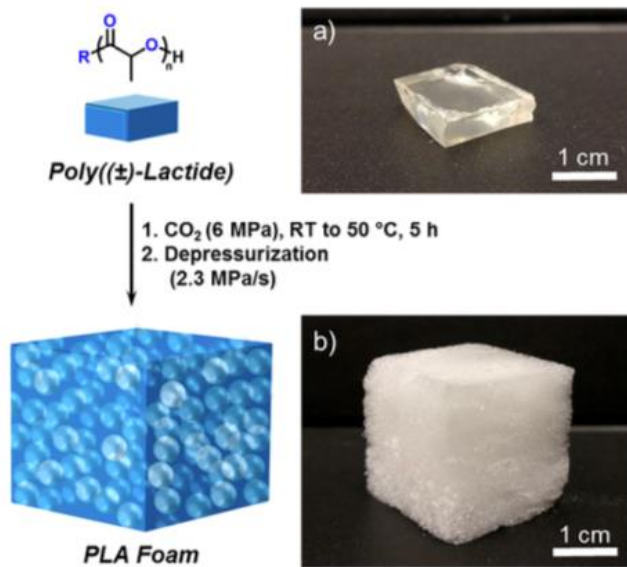


- Starch Based
- PLA
- PBAT
- PBS
- PHA
- Others

# Options for replacing petrochemicals as raw materials in polymer manufacturing



# Starch based and polylactide constitute the majority of biodegradable plastic production



PLA based foams offer an alternative to traditional non-recyclable foams

# Outline

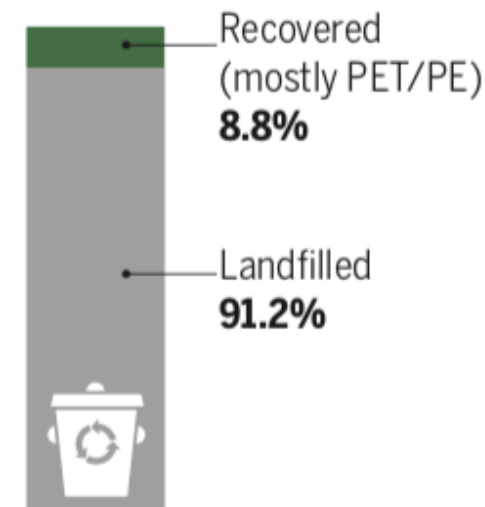
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# The future of plastic recycling requires research & capital investment

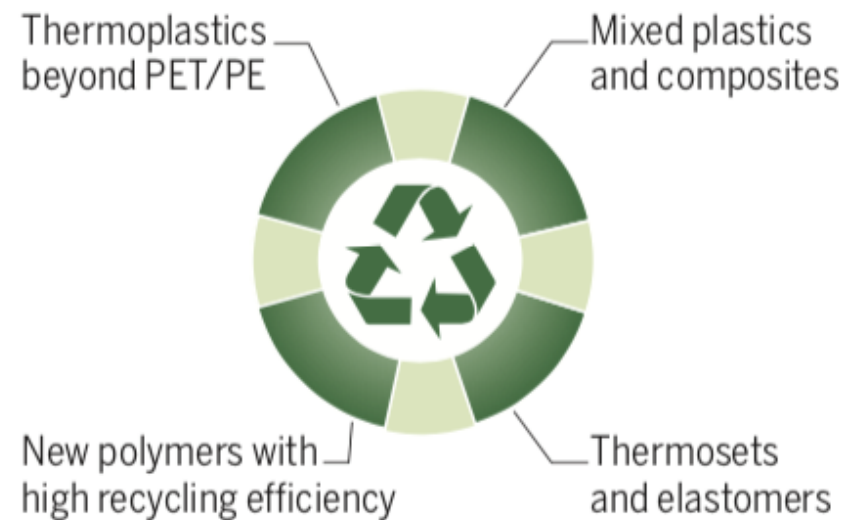
## Current plastic waste treatment



### Research advances

- New polymers
- Compatibilizers
- More efficient catalysts
- Advanced sorting

## Recycling of diverse polymers

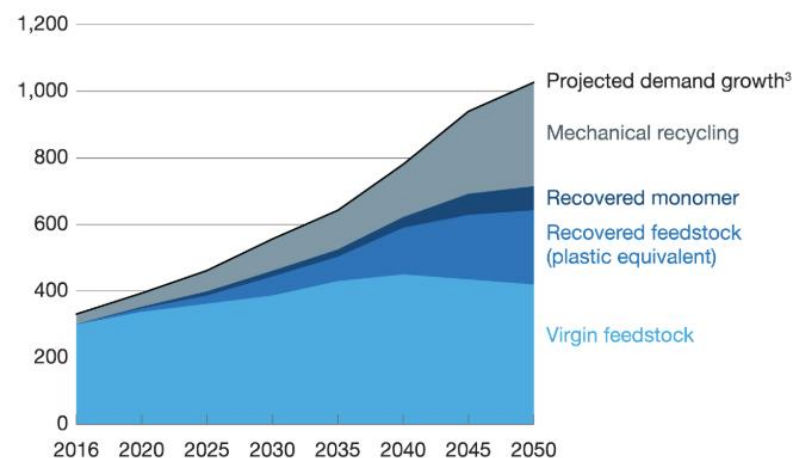


# The future of plastic recycling requires research & capital investment

To achieve a 50 % recovery rate by 2030, the modeling suggests that waste-recovery capital investment of about \$15 billion to \$20 billion/year would be required (global petrochemical and plastics industry has invested, on average, about \$80 billion to \$100 billion/year over the past decade)

By 2050, nearly 60 percent of plastics production could be based on plastics reuse and recycling.

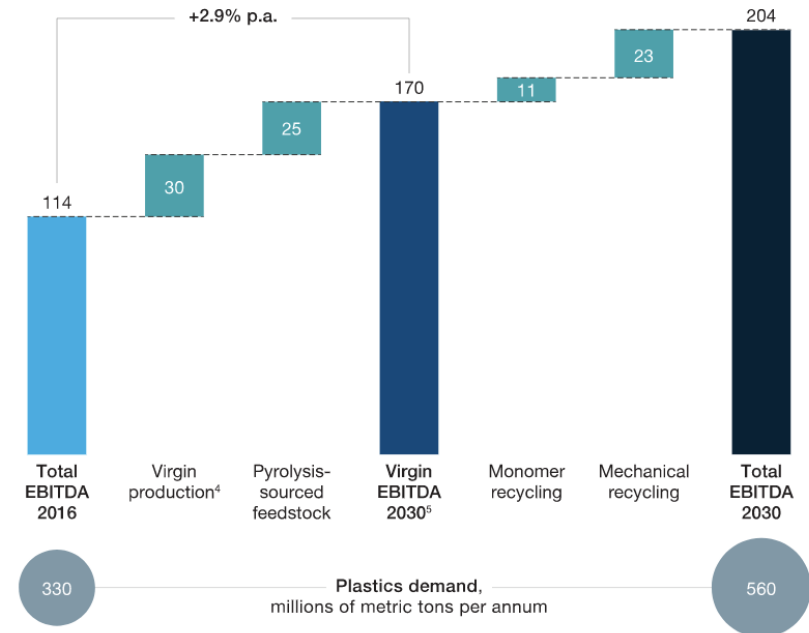
Global polymer demand 2016–50 and how it could be covered, millions of metric tons<sup>1</sup>



CAGR 2016–50,<sup>2</sup> %



Total integrated EBITDA<sup>1</sup> margin of petrochemical industry,<sup>2</sup> \$ billion<sup>3</sup>



Thanks for listening!

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Questions?

# Common recycling methods for various plastic waste

**Table 1.** Most common polymer recycling methods.

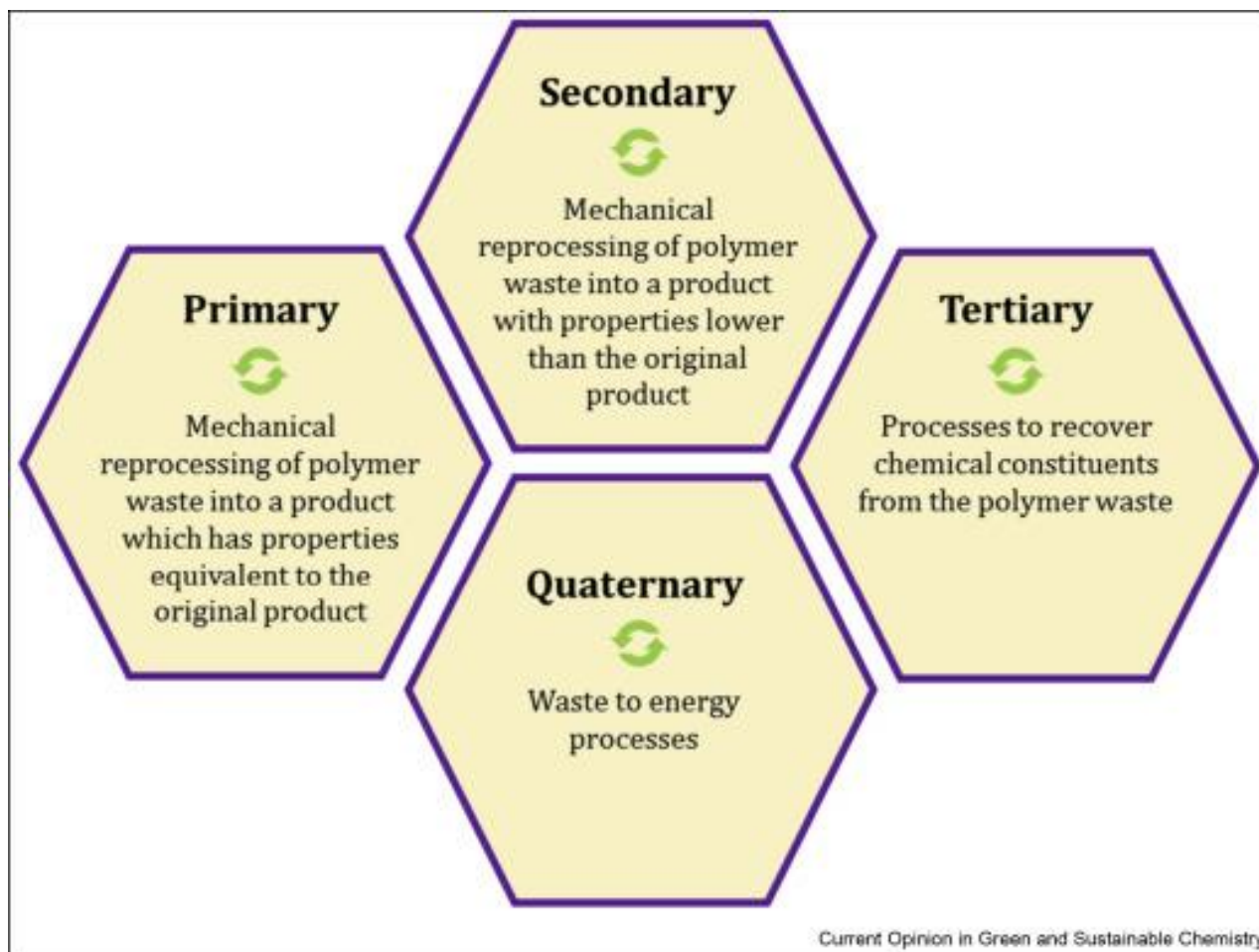
Input	Option	Process	Output
EOW/EOL/PC	preparation for recycling	collection and preparation	input for recycling, recovery of material and energy
EOW	material recovery	primary mechanical recycling	recyclate or (semi) ready product
EOL/PC	material recovery	secondary mechanical recycling	recyclate or (semi) ready product
EOW/EOL/PC	material recovery	tertiary or feedstock recycling	chemicals (mono- and oligomers, other substances/ reaction mixtures in form of gas, liquid, or solid)
EOW/EOL/PC	energy recovery	direct or controlled combustion (quaternary recycling)	heat, steam, or electricity

EOW: end-of-waste

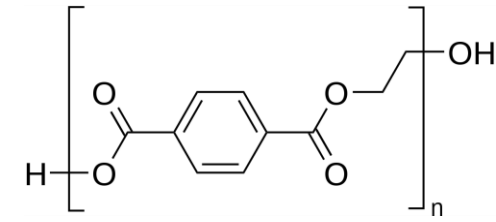
EOL: end-of-life

PC: post-consumer

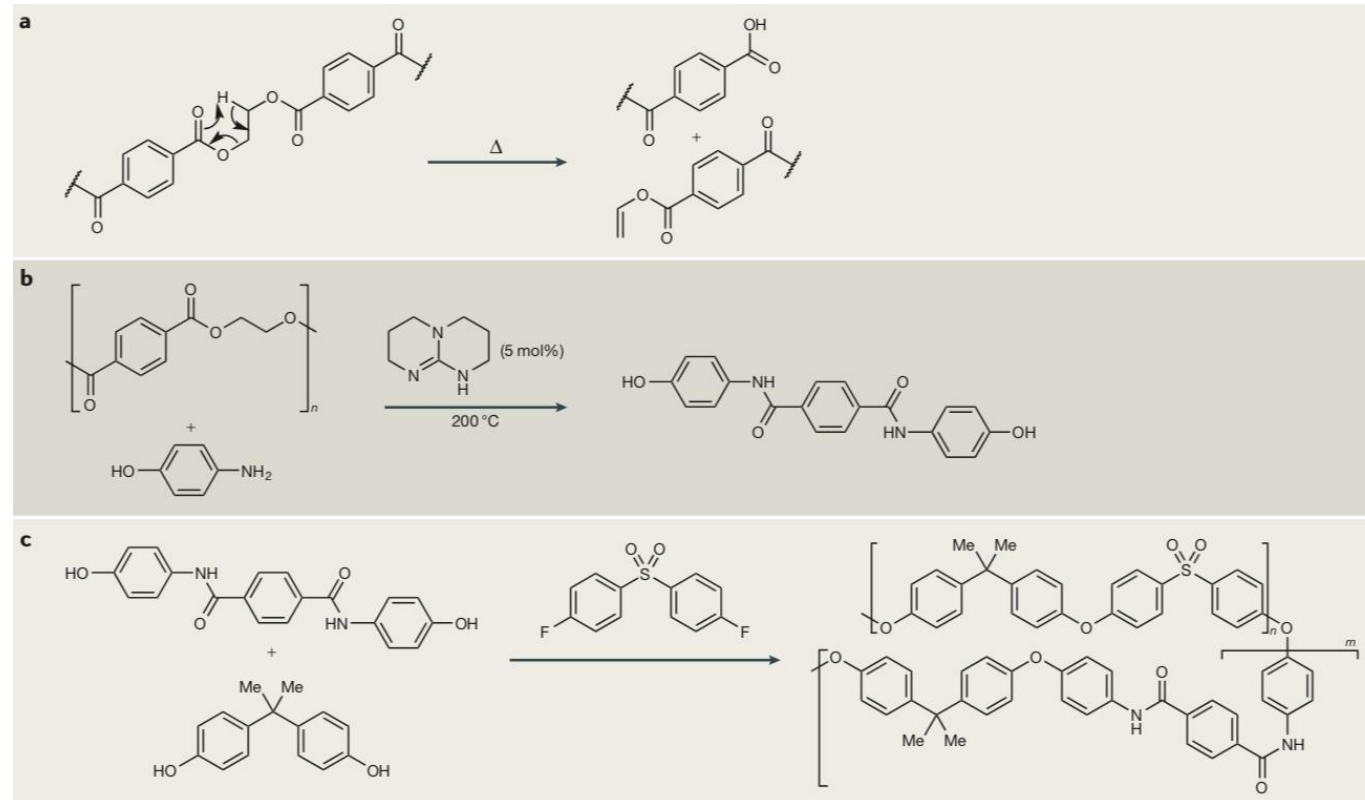
# Four modes of recycling include mechanical, chemical, and combustion



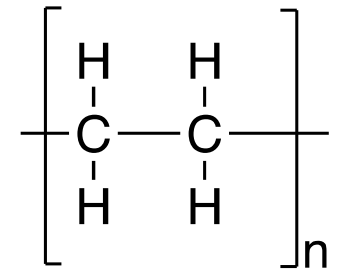
# Chemical recyclability of polyethylene terephthalate (PET)



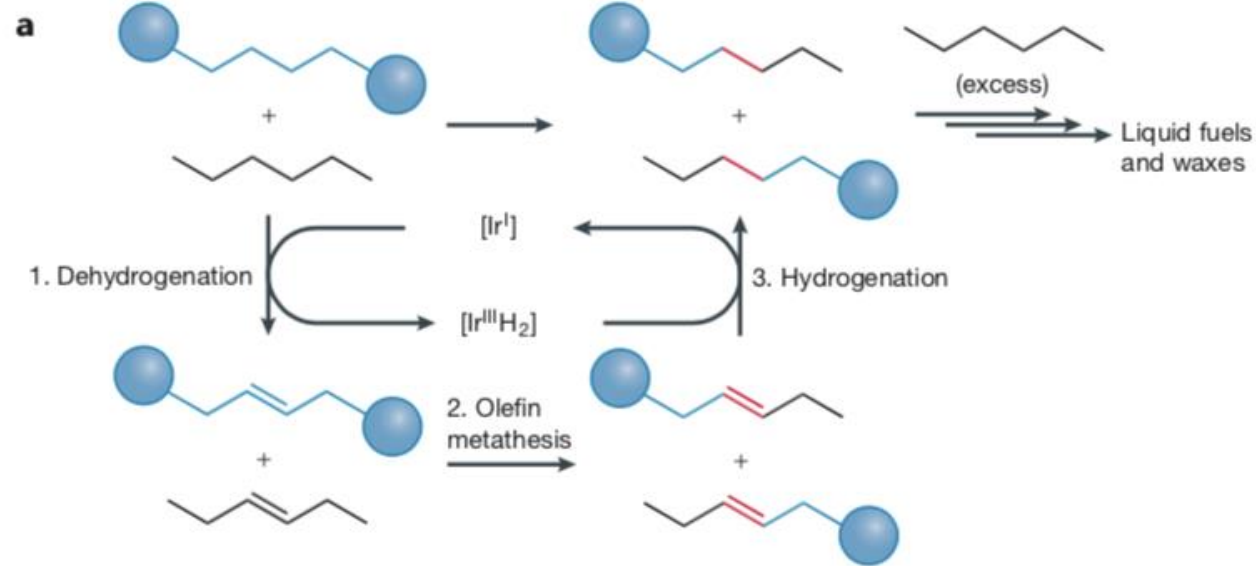
- Uses: disposable bottles for drinks and medicines
- Ductility drastically decreases during recycling of PET
- Thermal depolymerization above 300 °C can recover some starting materials



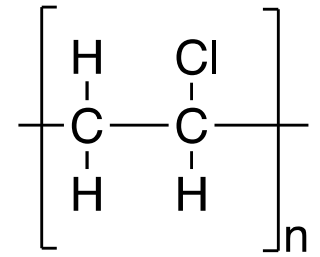
# Chemical recyclability of polyethylene (PE)



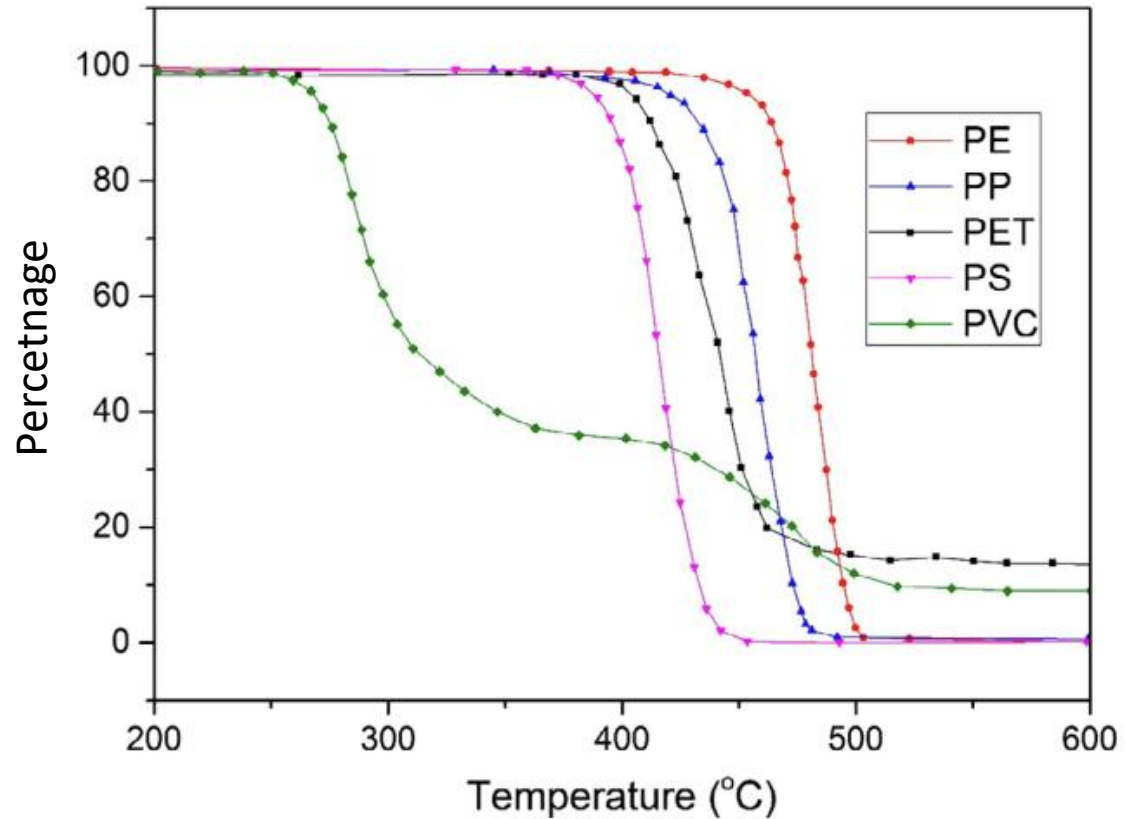
- Uses: shampoo containers & detergent bottles (HDPE); plastic bags, wrapping films (LDPE)
- Thermal depolymerization above 400 °C via random chain scission produces inseparable mixture of products and waxes
- Controlled catalytic depolymerization can produce liquid fuels such as gasoline



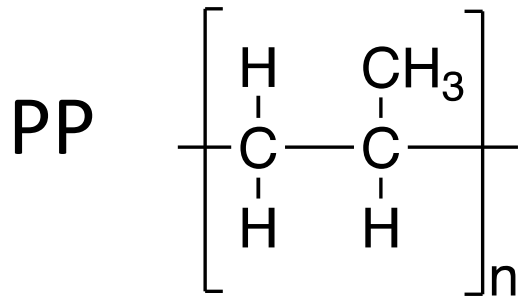
# Recyclability of polyvinylchloride (PVC)



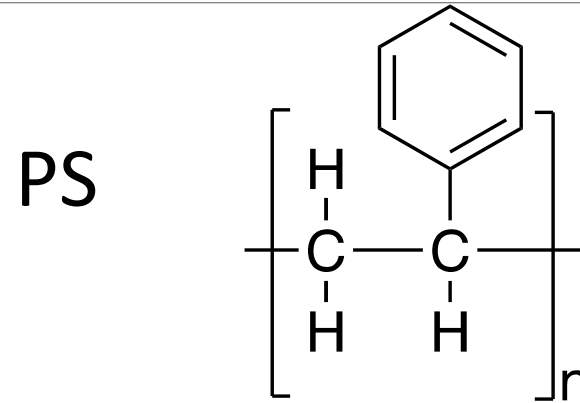
- Uses: piping, cables, garden furniture, fencing, carpet backing
- Pyrolysis most promising method to recycle PVC
- Release of HCl problematic—neutralization/inhibition required to prevent corrosion; PVC additives (phthalates, dyes) pose contamination problem
- Better HCl inhibitors and depolymerization catalysts are needed



# Low recyclability of polypropylene (PP) and polystyrene (PS)

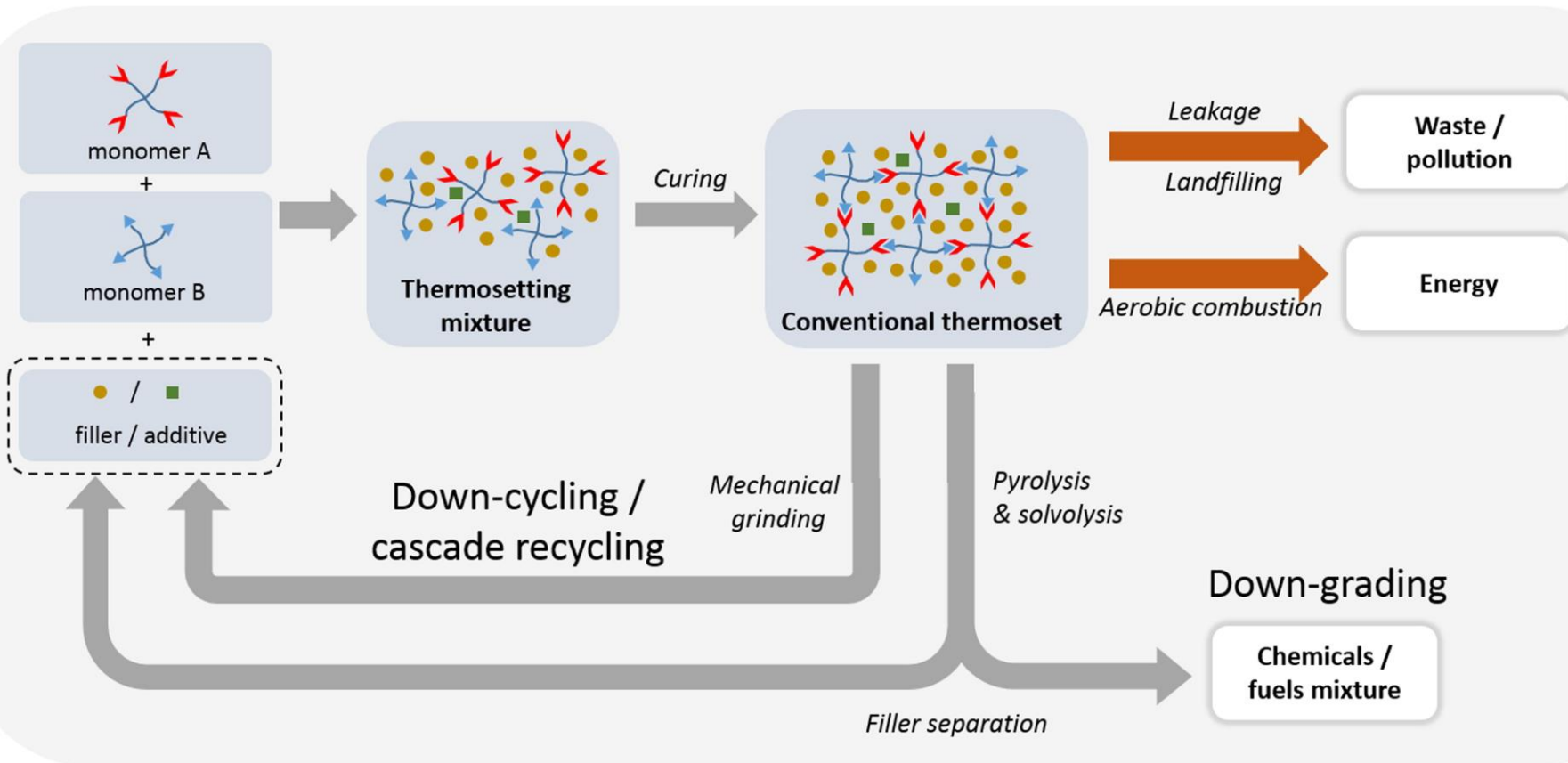


- Uses: bottle caps, reusable food containers, car parts
- Much more susceptible to chain scission (shortening) during mechanical recycling
- Tertiary and quaternary recycling methods most common



- Uses: plastic utensil, packing peanuts, Styrofoam
- Lowest recovery rates of SPI 1-6 due to difficulty of recovery (~ 50% PS blended with other materials)
- Tertiary and quaternary recycling methods most common
- Mealworm recycling being explored as an alternative

# Thermoset recycling technology does not regenerate original materials



# Options for replacing petrochemicals as raw materials in polymer manufacturing

