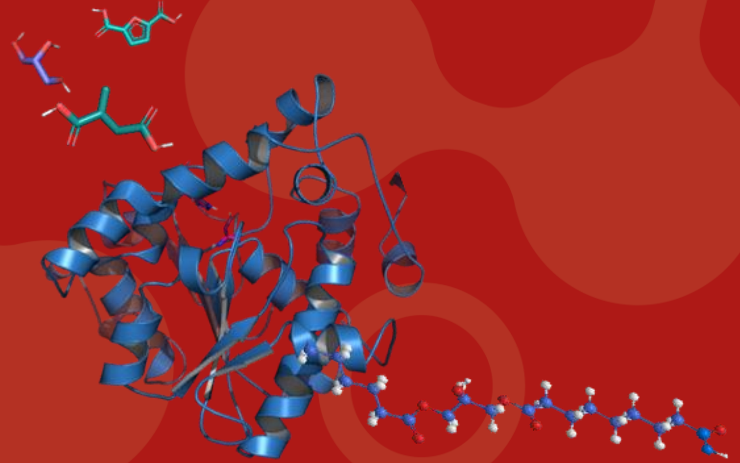
Ecodesign di polimeri e fibre sostenibili e circolari



Lucia Gardossi

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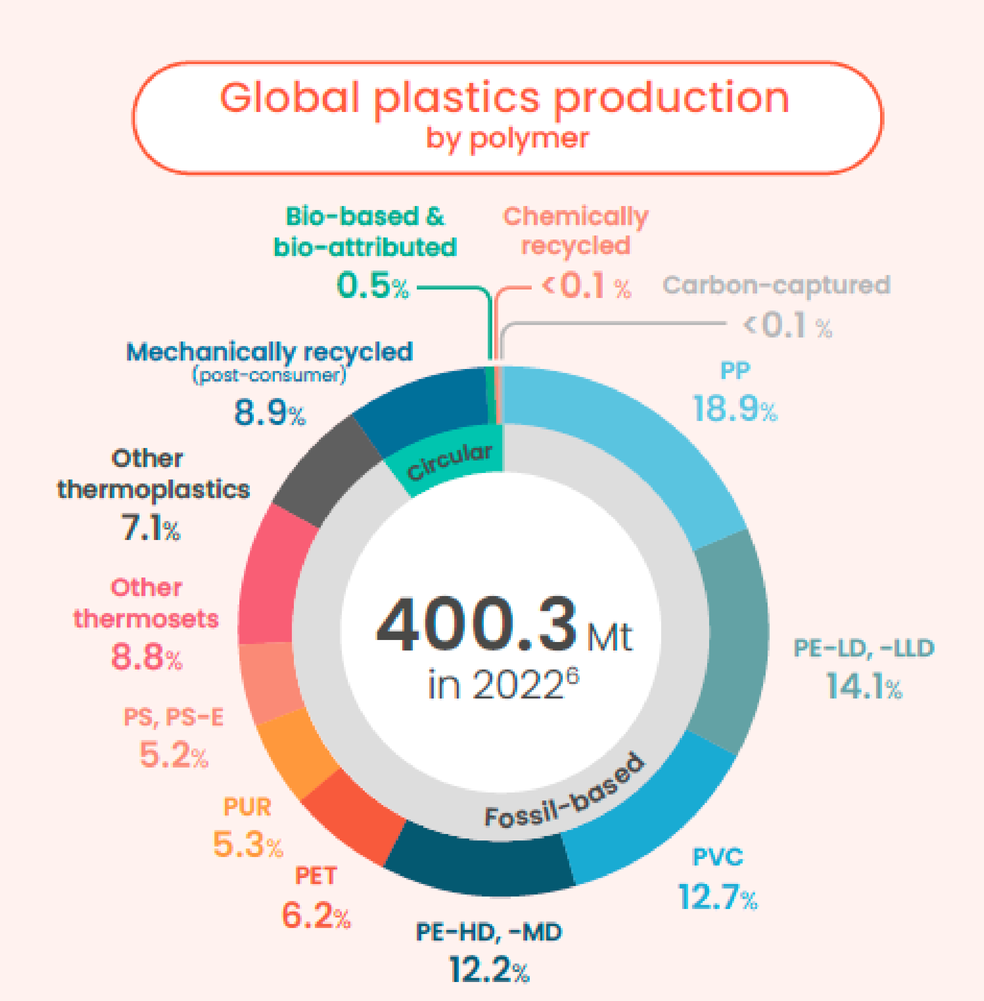
UNIVERSITÀ DEGLI STUDI DI TRIESTE
DSCF Dipartimento di Scienze Chimiche e Farmaceutiche

The success of fossil-based plastics

Plastics are expected to substitute wood, glass and other heavy materials while displaying good mechanical and thermal properties, stability and durability, when they are not designed for short-term applications such as packaging.

- Broad variety of monomers available from petrol-chemistry
- combined through various chemical routes
- structural design that meets specific technological demands



PLASTICS EUROPE
Enabling a sustainable future

Plastics – the *fast* Facts 2023

Plastics – the *fast* Facts shows preliminary global and European plastics production data. It also provides European plastics industry's key economic figures, trade balance, top trade partners, and preliminary estimations of European plastics conversion.

For a more complete and in-depth analysis of the plastics circular economy in Europe, please refer to Plastics Europe's biennial *"Circular Economy for Plastics – A European Overview"* reports.

2022 key economic figures[1]

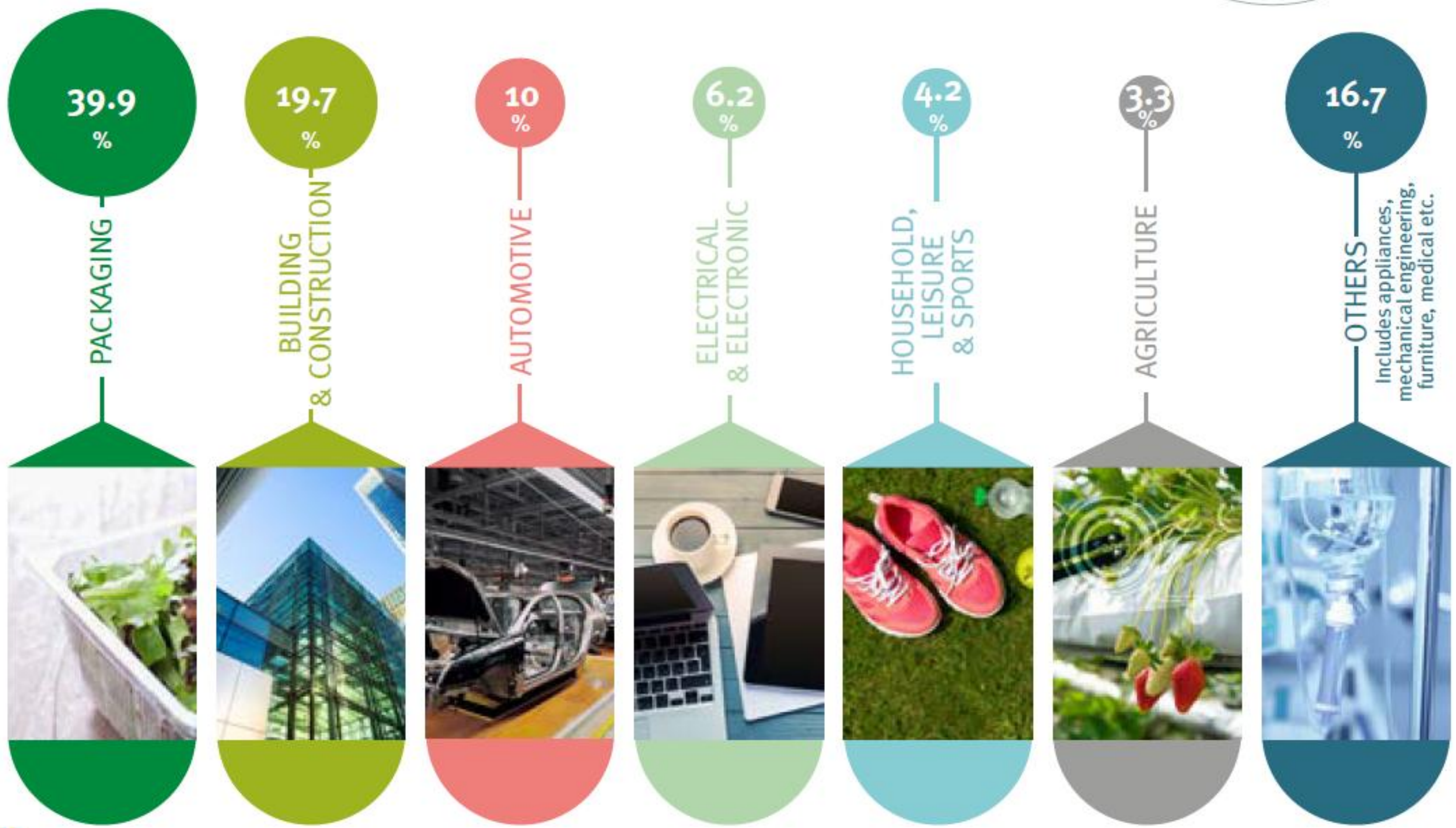
- **>1.5** million employees
- **53,150** companies
- **9.2** billion € trade balance
- **>400** billion € turnover

Plastics converter demand main market sectors

Distribution of European (EU28+NO/CH) plastics converter demand by segment in 2016.

Source: PlasticsEurope Market Research Group (PEMRG) and Conversio Market & Strategy GmbH

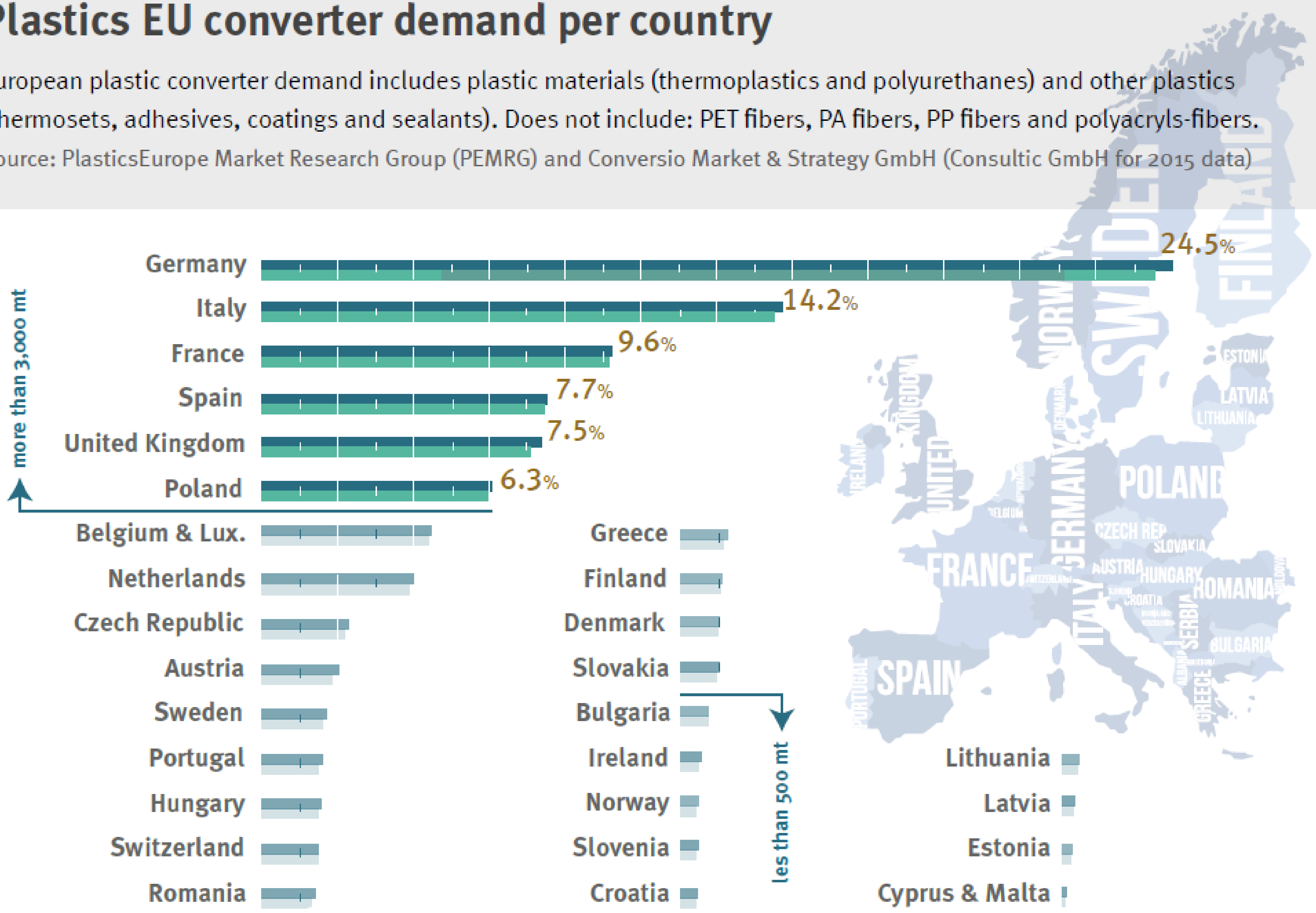
Total converter demand **49.9 m t**



Plastics EU converter demand per country

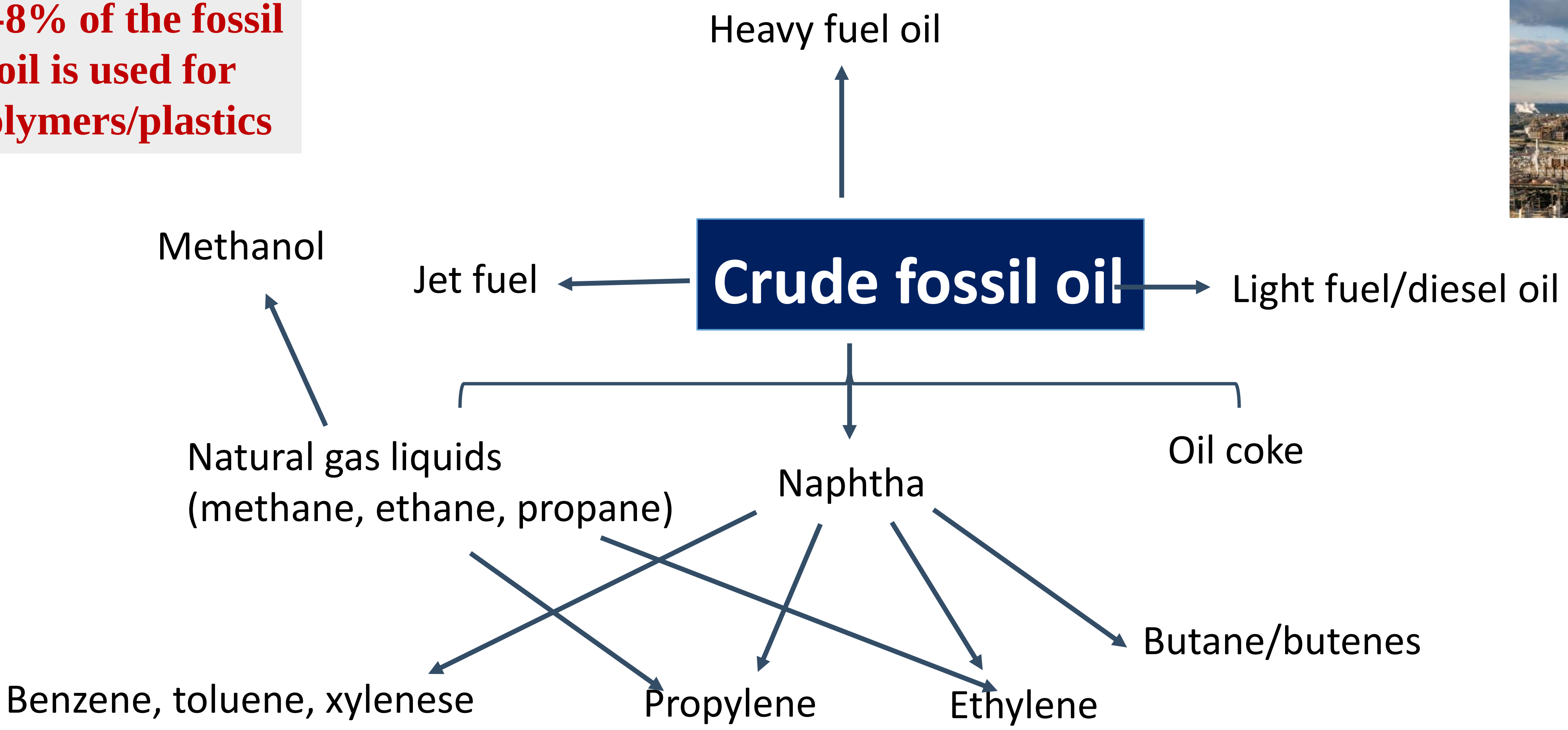
European plastic converter demand includes plastic materials (thermoplastics and polyurethanes) and other plastics (thermosets, adhesives, coatings and sealants). Does not include: PET fibers, PA fibers, PP fibers and polyacryls-fibers.

Source: PlasticsEurope Market Research Group (PEMRG) and Conversio Market & Strategy GmbH (Consultic GmbH for 2015 data)



The building blocks of fossil based chemistry

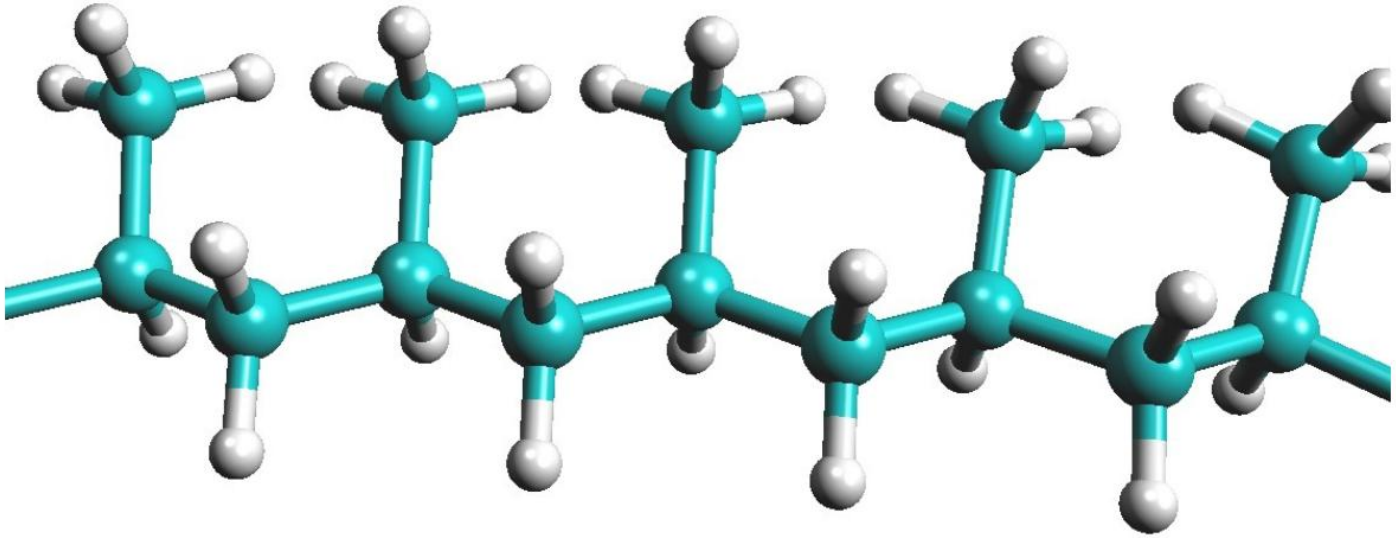
~6-8% of the fossil oil is used for polymers/plastics

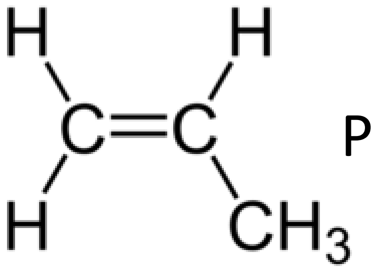


The chemical industry relies on six basic chemicals

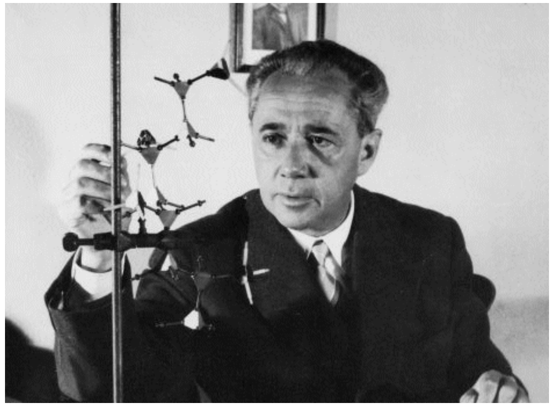
Koutinas AA, Vlysidis A, Pleissner D, Kopsahelis N, Garcia IL, Kookos IK, et al. Chem. Soc. Rev. 2014, 43, 2587–627.

Giulio Natta e il polipropilene





Propilene



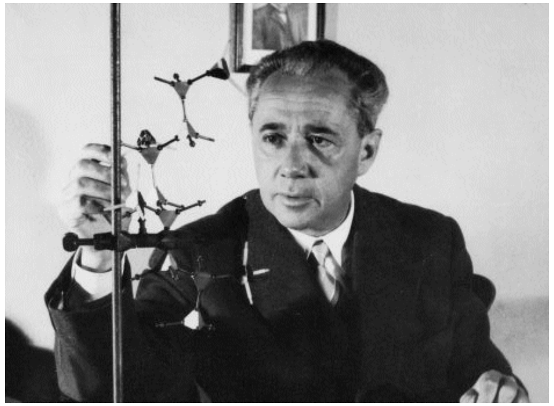
Giulio Natta

Questa è un'immagine semplificata del polipropilene isotattico che mette bene in evidenza la regolarità dai centri chirali.

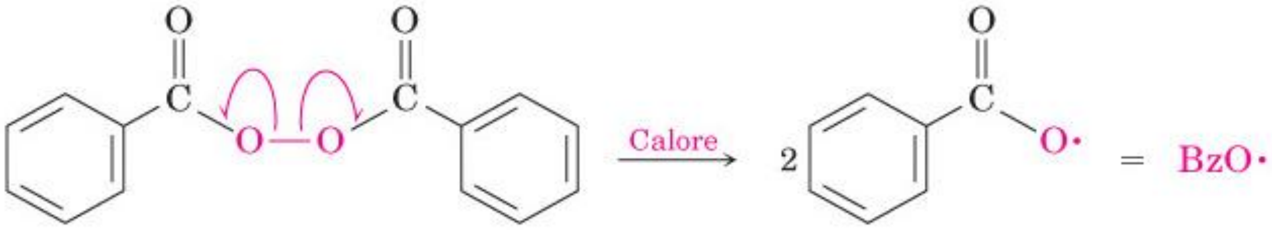
Il polipropilene isotattico ad alta cristallinità ha come caratteristiche principali: rigidità, lucentezza, buona resistenza al calore anche oltre i 100 °C (p.f. 165 °C), alta resistenza agli agenti chimici.

Il **10 dicembre del 1963 Natta venne insignito del Premio Nobel per la chimica**, insieme a Karl Ziegler, per i suoi studi sulla sintesi di polimeri stereospecifici lineari ottenuti utilizzando catalizzatori organometallici.

Le poliolefine sono ottenute per polimerizzazione radicalica: non biodegradabili



Giulio Natta



Benzoile perossido

Radicale benzoilossile

$$BzO\cdot + H_2C{=}CH_2 \longrightarrow BzO{-}CH_2CH_2\cdot$$

iniziazione

$$BzOCH_2CH_2\cdot + H_2C{=}CH_2 \longrightarrow BzOCH_2CH_2CH_2CH_2\cdot \xrightarrow[\text{molte volte}]{\text{Ripetuto}} BzO(CH_2CH_2)_nCH_2CH_2\cdot$$

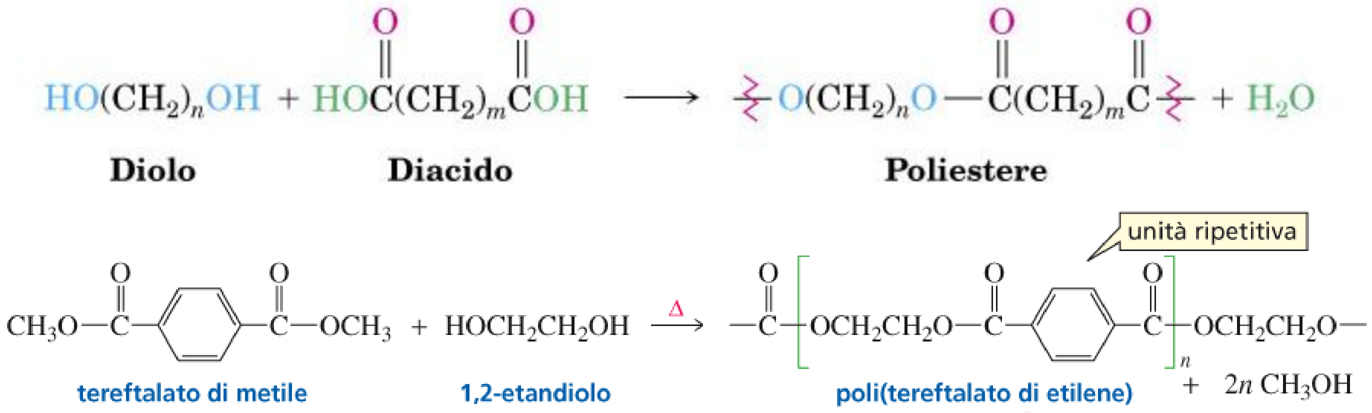
propagazione

$$2\,R{-}CH_2CH_2\cdot \longrightarrow R{-}CH_2CH_2CH_2CH_2{-}R$$

termine

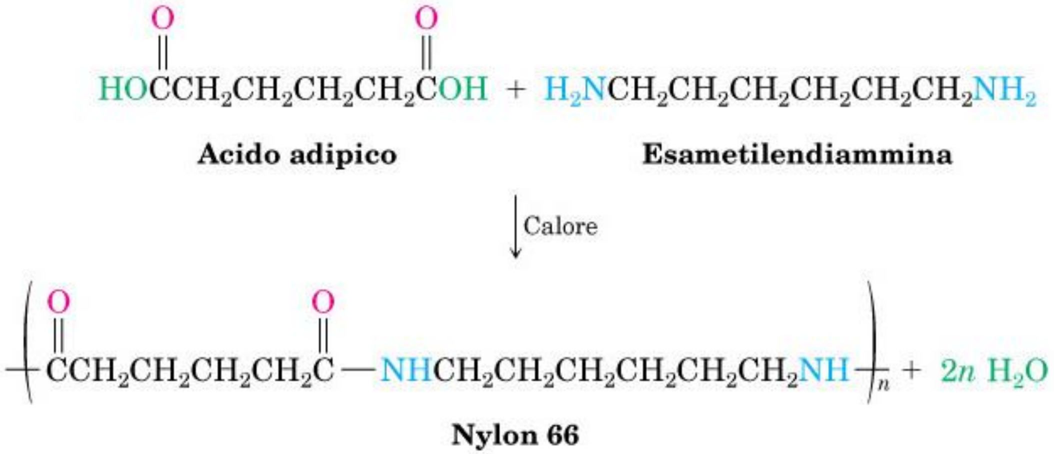
Poliesteri e poliammidi sono sintetizzati per policondensazione (a stadi)

Poliestere: (PET)



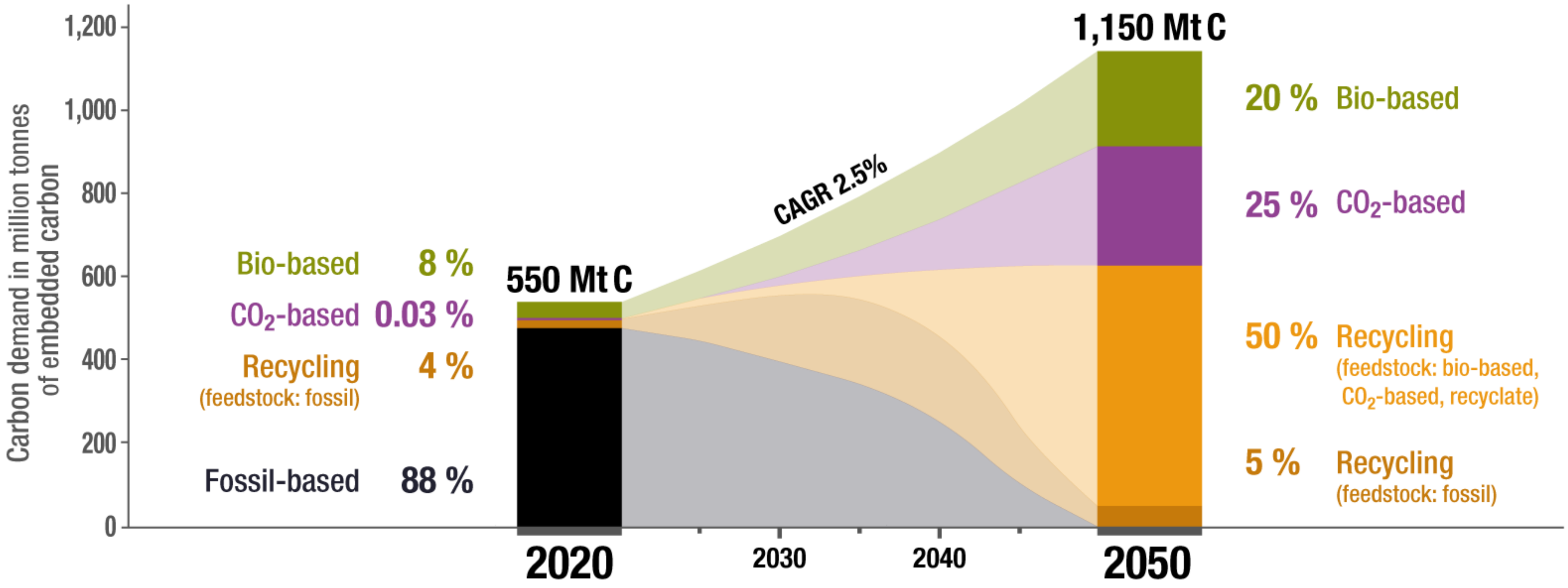
La sintesi del legame estereo è una reazione reversibile e può essere idrolizzato in presenza di catalizzatori acidi. Inoltre esistono numerosi enzimi in natura che catalizzano la sua idrolisi ma non tutte le strutture chimiche dei poliesteri sintetici vengono riconosciute e degradate dagli enzimi naturali.

Poliammide: (Nylon)



La formazione del legame ammidico è una reazione irreversibile. Per quanto in natura esistano le proteasi che idrolizzano il legame ammidico delle proteine, tali enzimi non riconoscono le strutture delle comuni poliammidi

Carbon Embedded in Chemicals and Derived Materials



available at www.renewable-carbon.eu/graphics

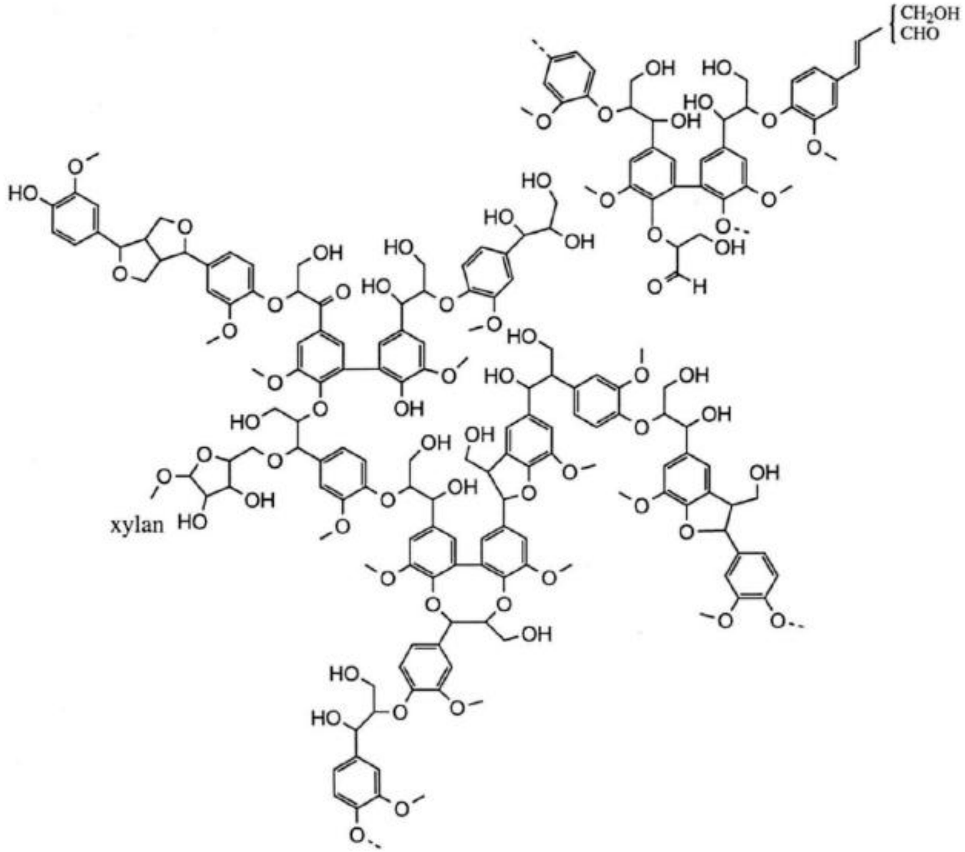
Ma cosa veniva usato prima dell’avvento della plastica?

Polimeri precedenti alle plastiche fossili: Biopolimeri

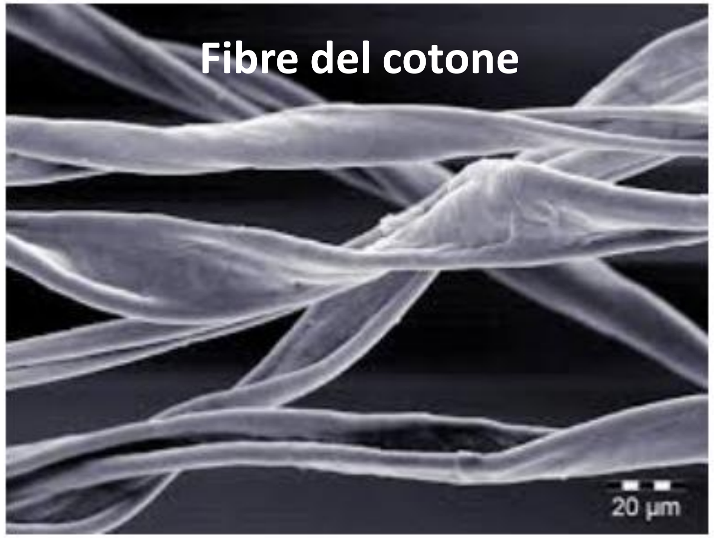
Macromolecole biologiche biosintetizzate

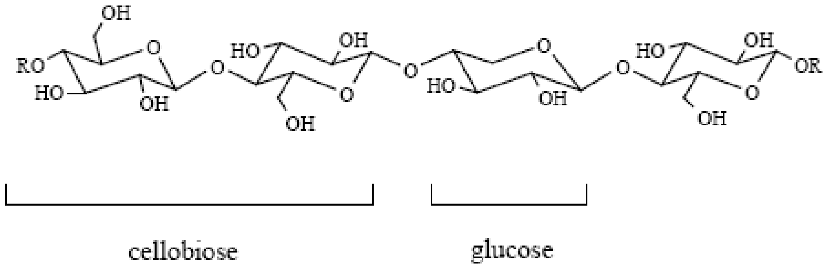
La lignina: biopolimero biodegradabile solo mediante enzimi ossidativi detti laccasi (reazione radicalica)

Difficile da sfruttare per produzione di fibre e polimeri

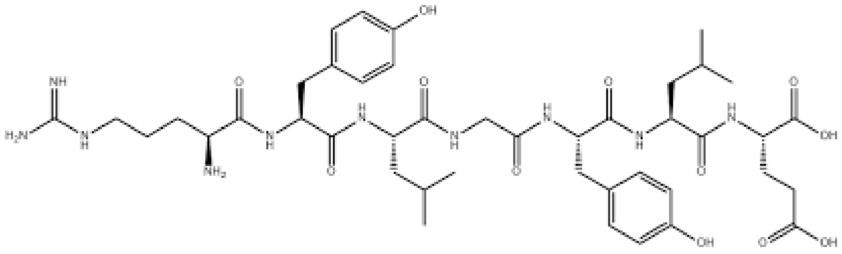


Cellulosa: polisaccaride biodegradabile grazie ad enzimi idrolitici (cellulolitici)





Proteine: biodegradabili attraverso l’azione di enzimi idrolitici (proteasi)



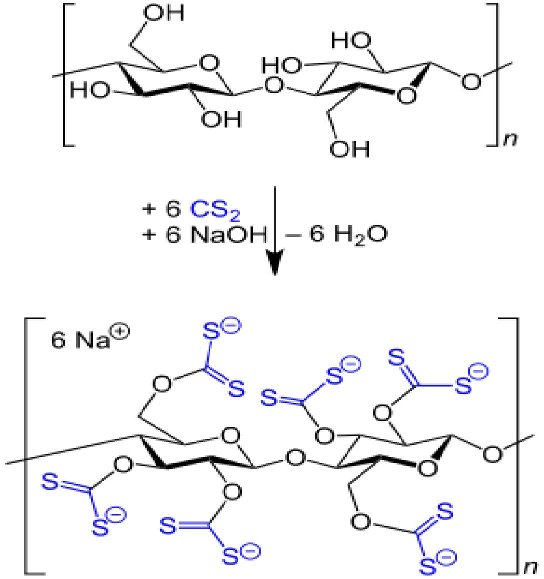
α-caseina

Conversione della cellulosa in viscosa

Torviscosa e la cellulosa della Arundo donax

Costruita tra il 1937 e il 1942, legata ad una grande azienda italiana, la SNIA Viscosa che all'epoca si dedicava soprattutto alla produzione di fibre artificiali ricavate dalla cellulosa

Pubblicato da Simona Politini in Il Patrimonio in Italia, Villaggi operai aprile 10, 2014



Michelangelo Antonioni

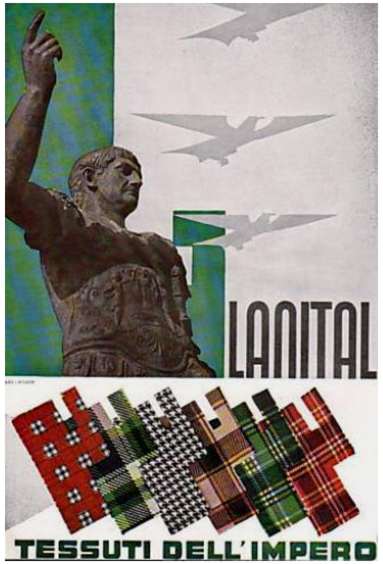
Polimeri derivati dalla caseina

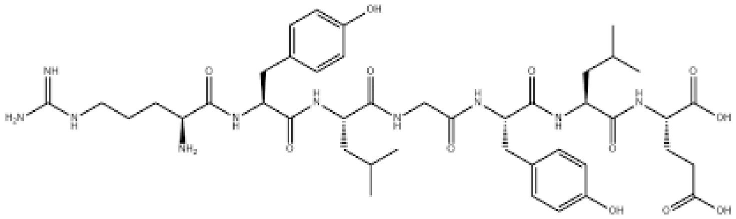
LANITAL

Galalith:
Caseina + formaldehyde

1935, fibra autarchica tratta dalla caseina

.





α-caseina

Le caseine non coagulano con il calore; per questo motivo non subiscono perdite significative durante la pastorizzazione o la sterilizzazione del latte. Le caseine coagulano invece per acidificazione o per l'azione di alcuni enzimi proteolitici.

Qmilk

Advanced Textiles Source (IFAI PUBLICATION)

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- My Take
- Of Interest
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- What's New?

Make it from milk

November 12th, 2013 / By: Anke Domaske, Janet Preus / Featured

A lot of milk in the world is simply thrown away as unsuitable—for food, that is. German-based company Qmilch IP GmbH has found a use for discarded milk: fabric. In fact, it makes a silky smooth, beautiful fabric desirable for high fashion, appealing to high-end consumers who are not only interested in the ecology, but in the economic and social responsibility supporting the fashionable collections.

In addition to apparel, the fibers are particularly suitable for use in home textiles, the automobile industry and medical technology, and they offer advantages as well for thermal insulated seat covers or hygienic diaphragms. With interest in, and the use of, these textile fibers growing, supply is challenged to meet the demand.

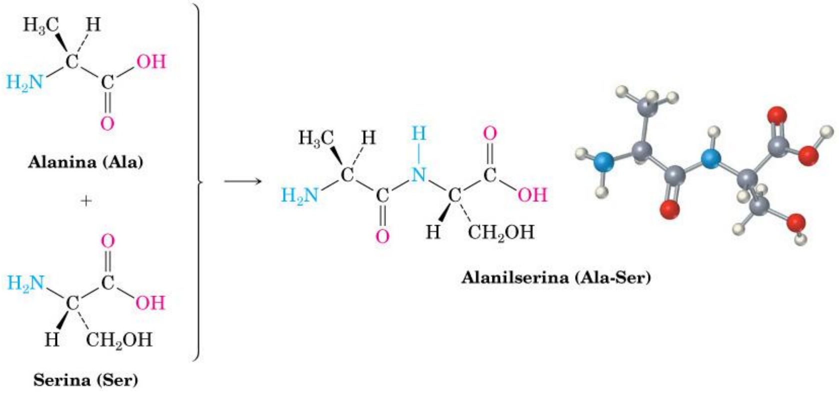
Silk: a protein

natural protein composed of a pattern of amino acids in a secondary protein structure. The secondary structure of silk is the beta pleated sheet.

The primary structure of silk contains the amino acids of **glycine, alanine, serine**, in specific repeating pattern. These three amino acids make up 90% of the protein in silk.

The last 10% is comprised of the amino acids glutamic acid, valine, and aspartic acid.

These amino acids are used as side chains and affect things such as elasticity and strength. they also vary between various species. The **beta pleated sheet** of silk is connected by hydrogen bonds.



Silk is a great example of a **beta pleated sheet**. The formation of the secondary protein structure in silk allows it to have very strong tensile strength.

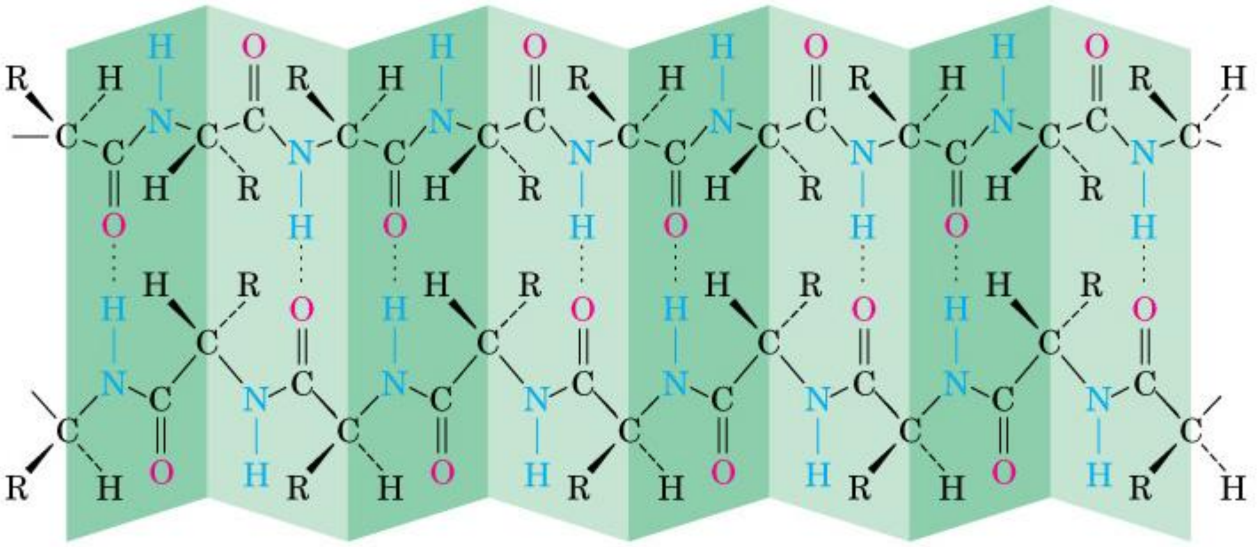
Struttura secondaria: foglietto-β

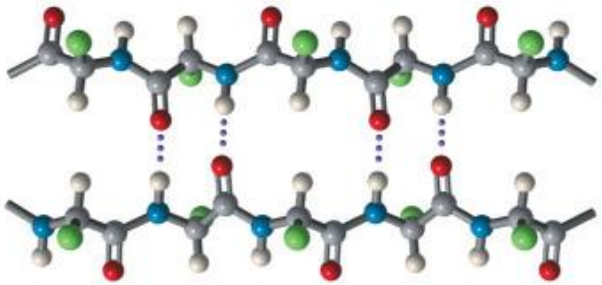
FIGURA 26.7 La struttura a foglietto β pieghettato nella fibroina della seta.

antiparallelo

Catena 1

Catena 2

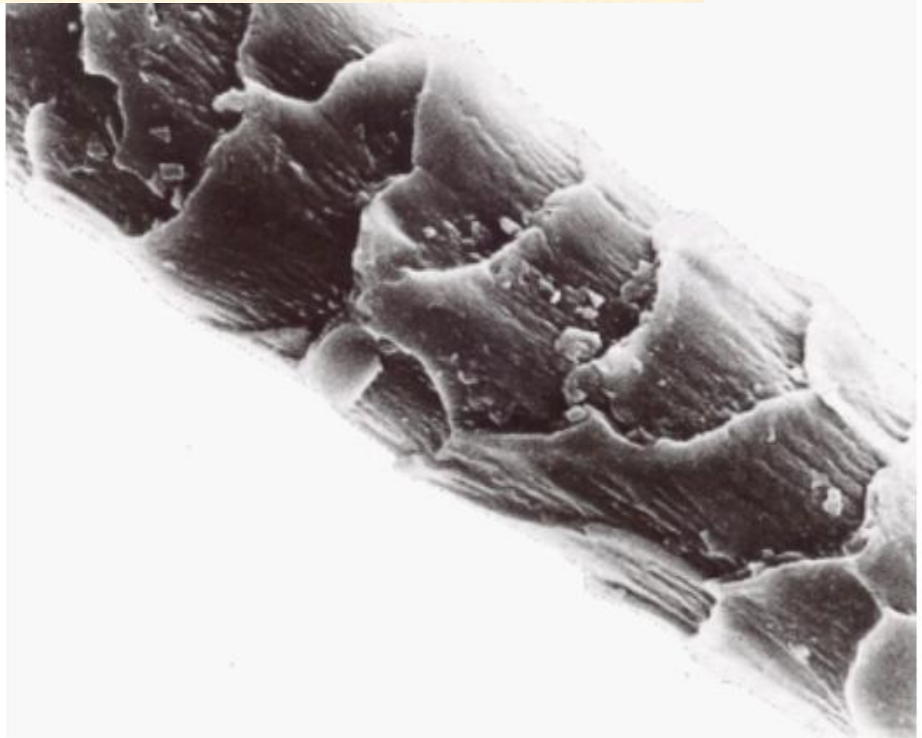




Più *filamenti β* disposti uno accanto all'altro e collegati tra loro da tre o più legami idrogeno che formano una struttura planare molto compatta. Si definisce **filamento β** una sequenza peptidica di amminoacidi (tipicamente composta da 5-10 amminoacidi) che si dispone linearmente ed è in grado di instaurare legami idrogeno.

COMPOSIZIONE CHIMICA DELLA LANA

E'COSTITUITA
- PER L'85% DA CHERATINA
- PER IL 12% DA PROTEINE NON CONTENENTI ZOLFO,
- PER L'1-2% DA SOSTANZE LIPIDICHE
- PER LA RESTANTE % DA SALI MINERALI.



La fibra di lana si può pensare costituita da 3 strati, partendo dall'esterno.

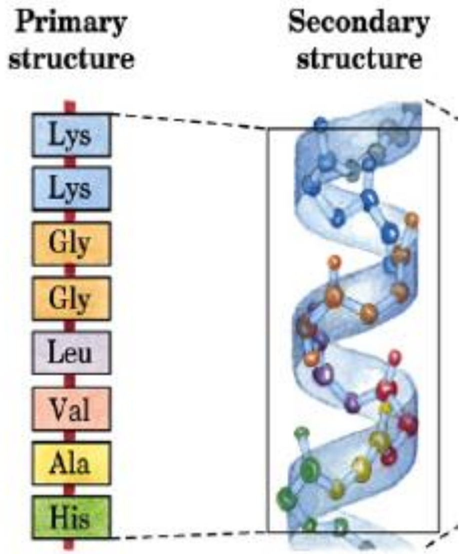
Il primo strato è una membrana idrofoba che protegge la fibra come una specie di vernice. Unica parte non proteica, l'**epicuticola**, è però fornita di fori sottilissimi che lasciano passare il vapore d'acqua.

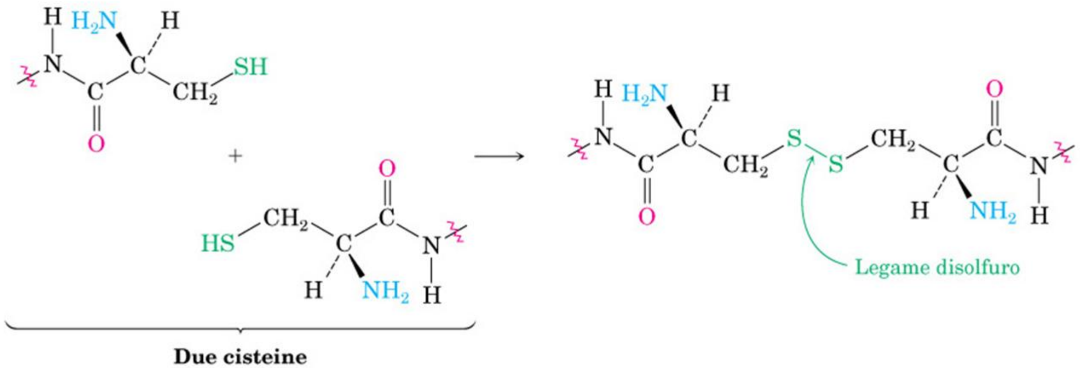
Sotto tale membrana si trova il secondo strato detto **cuticola**, formato da tante scaglie, fissate in modo univoco e tutte disposte nel senso della punta della fibra. Questa disposizione è di fondamentale importanza per alcune proprietà della lana, come il potere feltrante.

α-cheratina costituita da **α eliche** destrorse intrecciate che è debolmente basica

β-cheratina costituita da foglietti β che è debolmente acida.

Le cheratine contengono una elevata quantità di **cisteina**, amminoacido caratterizzato dalla presenza del gruppo –SH. I gruppi tiolici tendono ad accoppiarsi e formano un legame covalente –S-S- a seguito di una ossidazione.
I ponti disolfuro conferiscono alla cheratina robustezza e rigidità oltre che stabilità termica; se è bruciata la cheratina emana un odore pungente dovuto alla presenza di composti solforati che si formano.

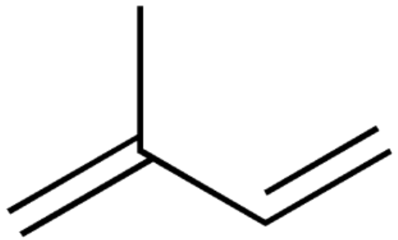


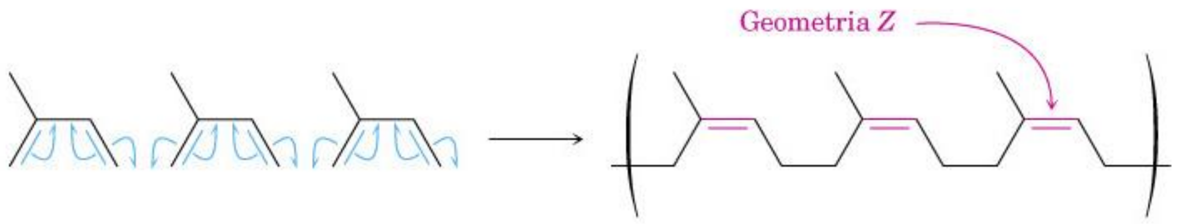


Gomma naturale: non biodegradabile

elastomero amorfo formato per addizione 1,4-cis dell'isoprene.

Isoprene (naturale)



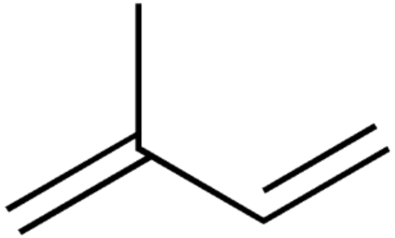


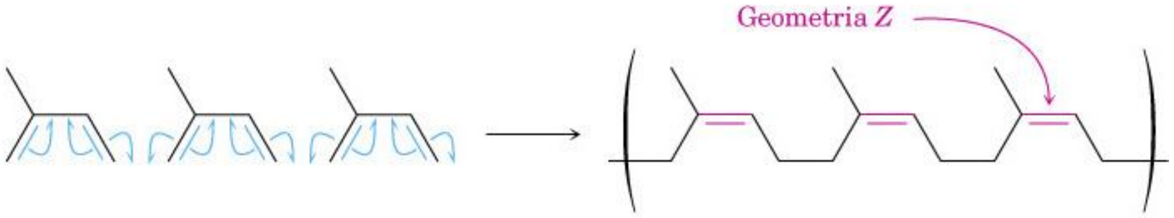
1.500 BCE – MesoAmerican cultures (Olmec, Maya, Aztecs) use natural latex and rubber to make balls, containers and make their clothes waterproof.

Gomma naturale: non biodegradabile

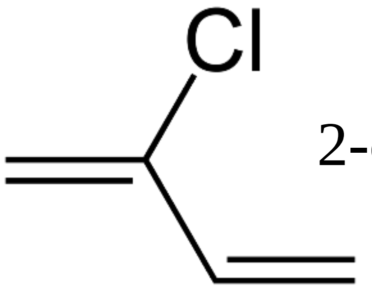
elastomero amorfo formato per addizione 1,4-cis dell'isoprene.

Isoprene (naturale)





Il neoprene mima la gomma naturale: non biodegradabile



2-cloro-1,3-butadiene

Neoprene
(derivato dal petrolio)

Presidenza del Consiglio dei Ministri

CNBBSV

COMITATO NAZIONALE PER LA BIOSICUREZZA LE BIOTECNOLOGIE E LE SCIENZE DELLA VITA

G20 ITALIA 2021

OECD* BETTER POLICIES FOR BETTER LIVES

G20 OECD-BNCT WORKSHOP
Bioeconomy in the OECD countries
Presidency of council of Ministers
July 16, 2021

*Organizzazione per la cooperazione e lo sviluppo economico

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Bioeconomy national strategies in the G20 and OECD countries: Sharing experiences and comparing existing policies

Lucia Gardossi[a], Jim Philp[b,*], Fabio Fava[c,*], David Winickoff[b], Laura D'Aprile[d], Benedetta Dell'Anno[d], Ole Jørgen Marvik[e], Andrea Lenzi[f]

[a] University of Trieste, Trieste, Italy & National Bioeconomy Coordination Board, National Committee of Biosafety, Biotechnology and Life Sciences of the Presidency of Council of Ministers, Rome Italy
[b] OECD, Directorate for Science, Technology and Innovation, Paris, France
[c] University of Bologna, Bologna, Italy & National Bioeconomy Coordination Board, National Committee of Biosafety, Biotechnology and Life Sciences of the Presidency of Council of Ministers, Rome Italy
[d] Ministry of Ecological transition, Rome Italy
[e] Innovasjon Norge, Oslo, Norway
[f] University of Rome La Sapienza, Roma & National Committee of Biosafety, Biotechnology and Life Sciences of the Presidency of Council of Ministers, Rome Italy

The transition towards carbon neutrality

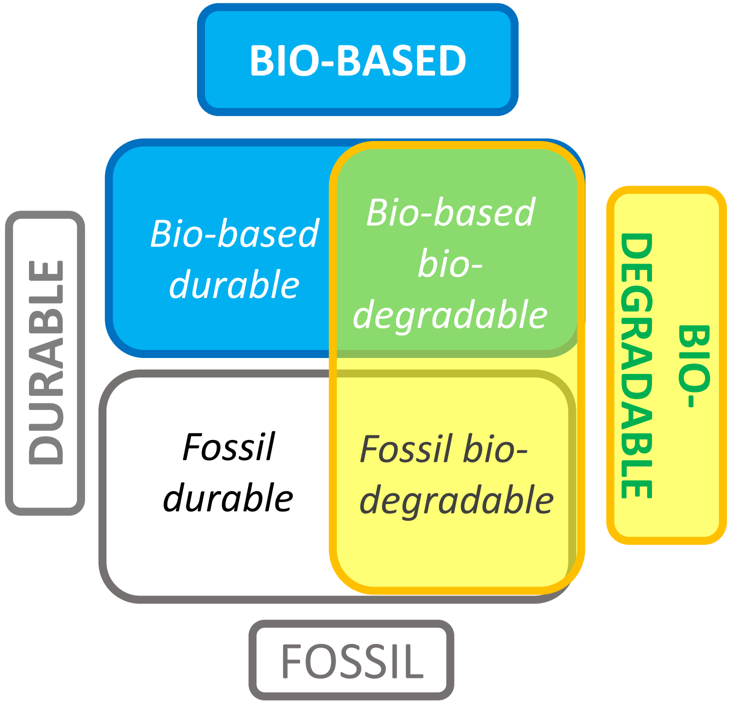
How industry can be supplied with carbon feedstocks when the use of fossil carbon is discontinued?

It is entirely foreseeable that the increasing use of biomass for food, materials, and chemicals, could lead to overexploitation of natural resources.

That would lead to competition for land between bioenergy (climate action) and food crops (food security) or between the bio-based production and the preservation of biodiversity and natural ecosystems.

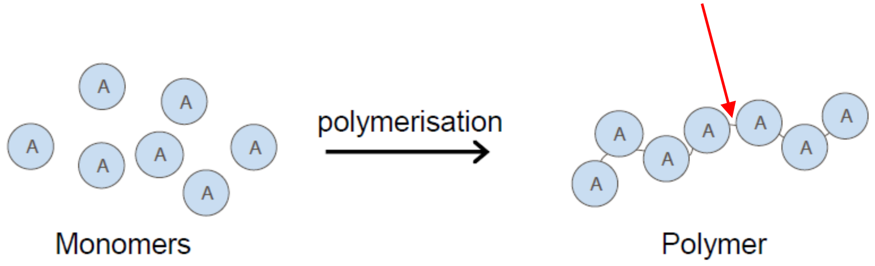
How much land should be made available for human activities?

Plastics, bio-based plastics, biodegradable plastics



Bio-based: from biogenic feedstock

Bio-degradable: consequence of a)chemical structure of polymers; b) chemical nature of bonds connecting monomers

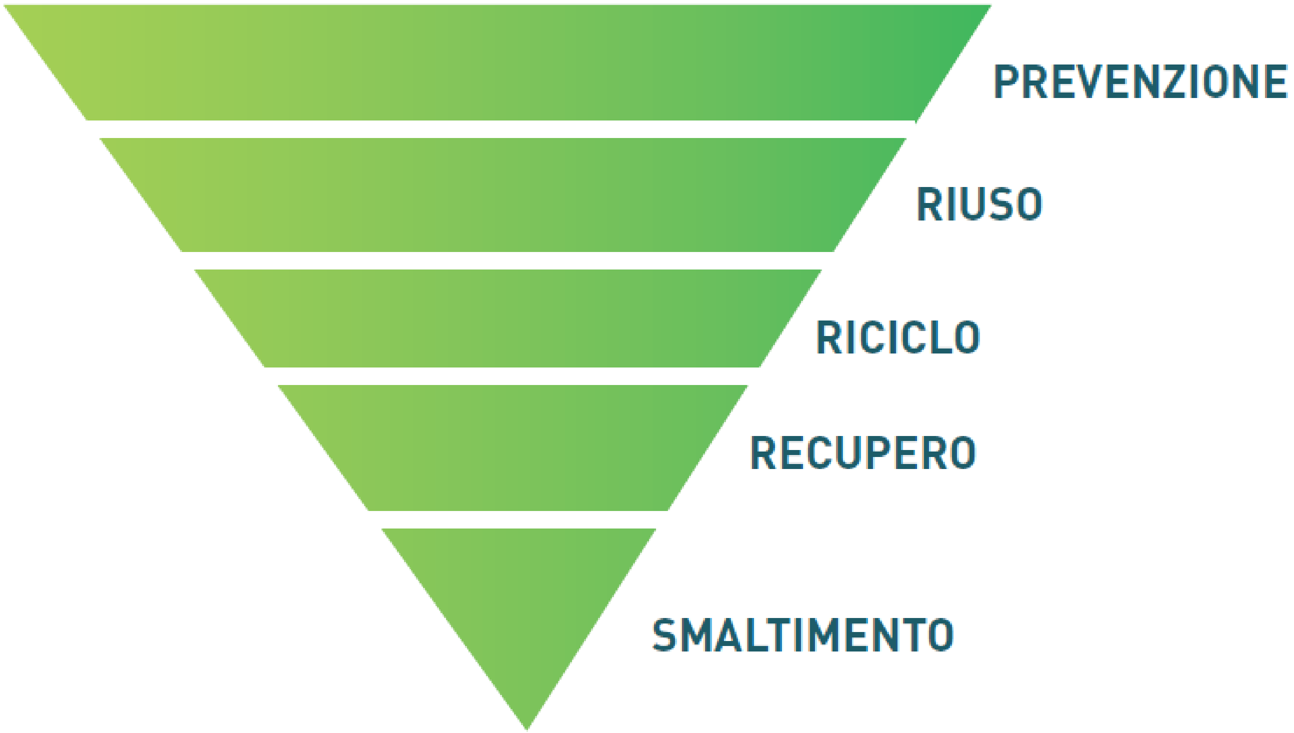


At their end of life each type of plastic requires a different management of waste to enable effective circularity

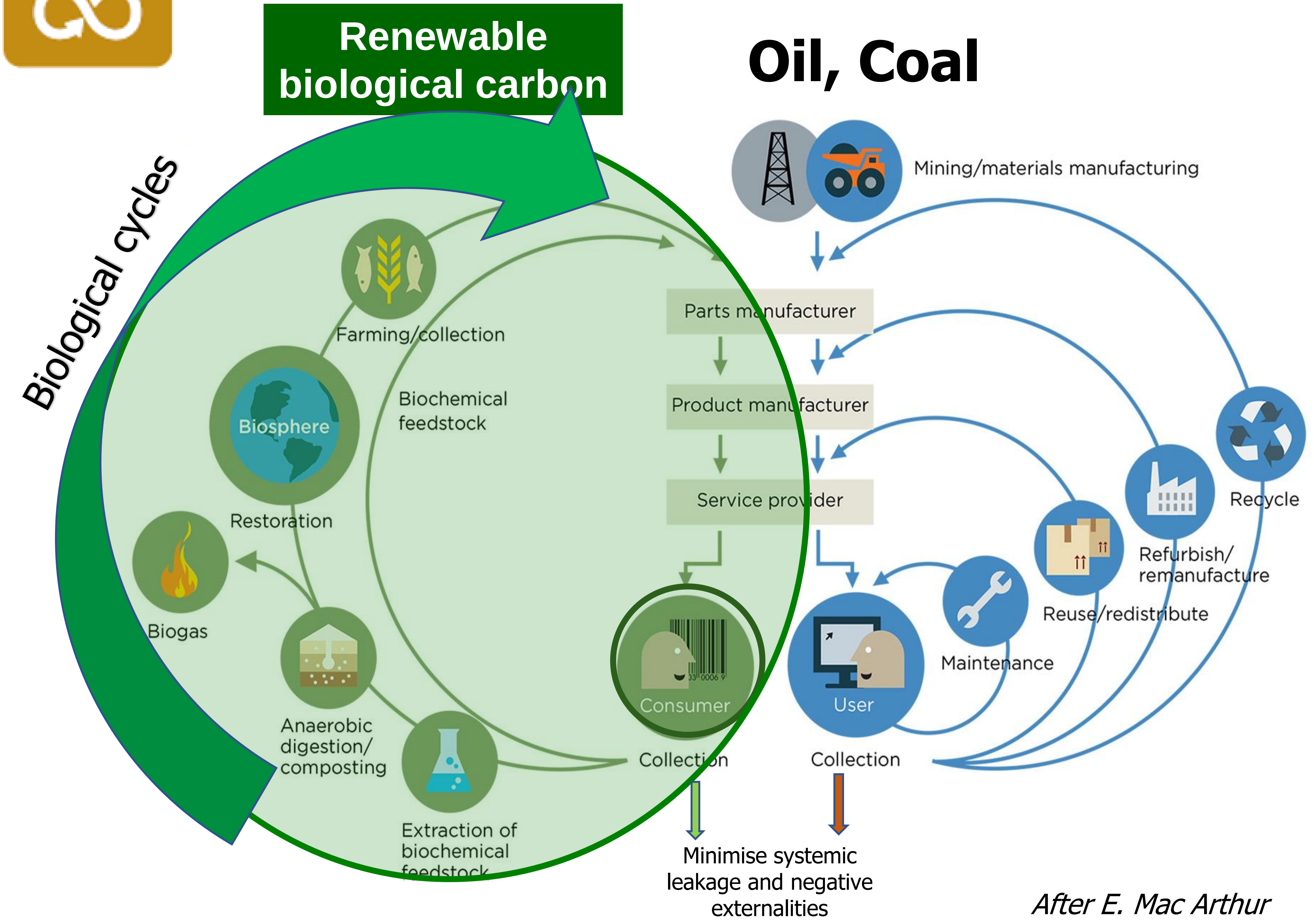
Eco-design must take into account their entire cicle of life

GERARCHIA DEI RIFIUTI

Direttiva 98/2008 – Normativa comunitaria sulla gestione dei rifiuti



The different circularities of economy



After E. Mac Arthur

What is Circular Economy in EU?

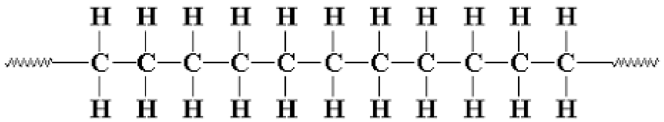
It aims to maintain the value of products, materials and resources for as long as possible by returning them into the product cycle at the end of their use, while minimising the generation of waste.

What is Circular Bioeconomy?

"The production of renewable biological resources and the conversion of these resources and waste streams into value added products, such as food, feed, bio-based products and bioenergy."

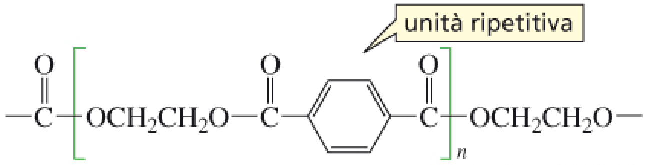
Example of Circular Economy: Recycling plastics

Lid — High Density Polyethylene (HDPE)

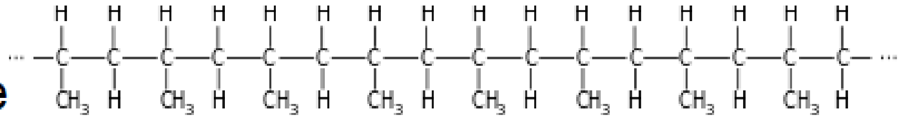


„Body" — Poly(ethylene terephthalate) (PET)

Polyester



„Label" — Polypropylene



Polyolefin

1 Bottle = 2 (or more) different materials!

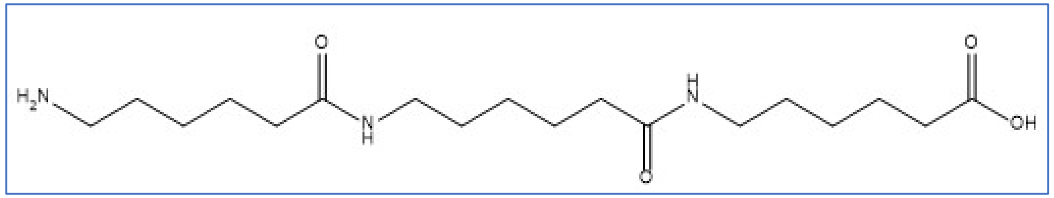
15/04/202

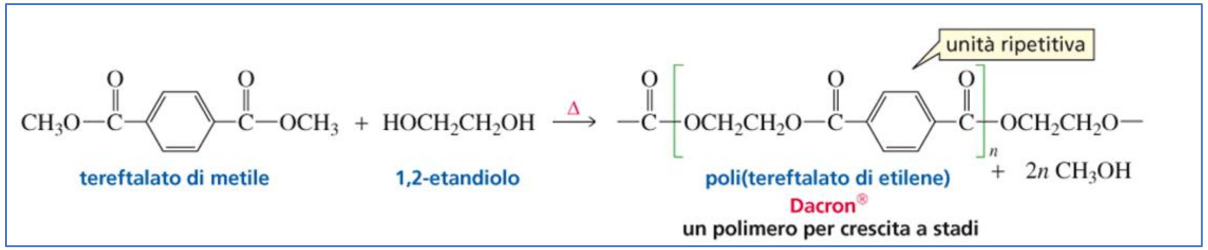
How to recycle durable plastics?

Polymers such as polyamides (Nylon), some polyesters (PET), polyurethanes (PUR) and polyepoxides are used in technical applications like textile fibers or automotive applications, etc.

Their operating life lasts several years (**durable plastics**) and, therefore, biodegradability is not desired.

Polyamide: Nylon 6



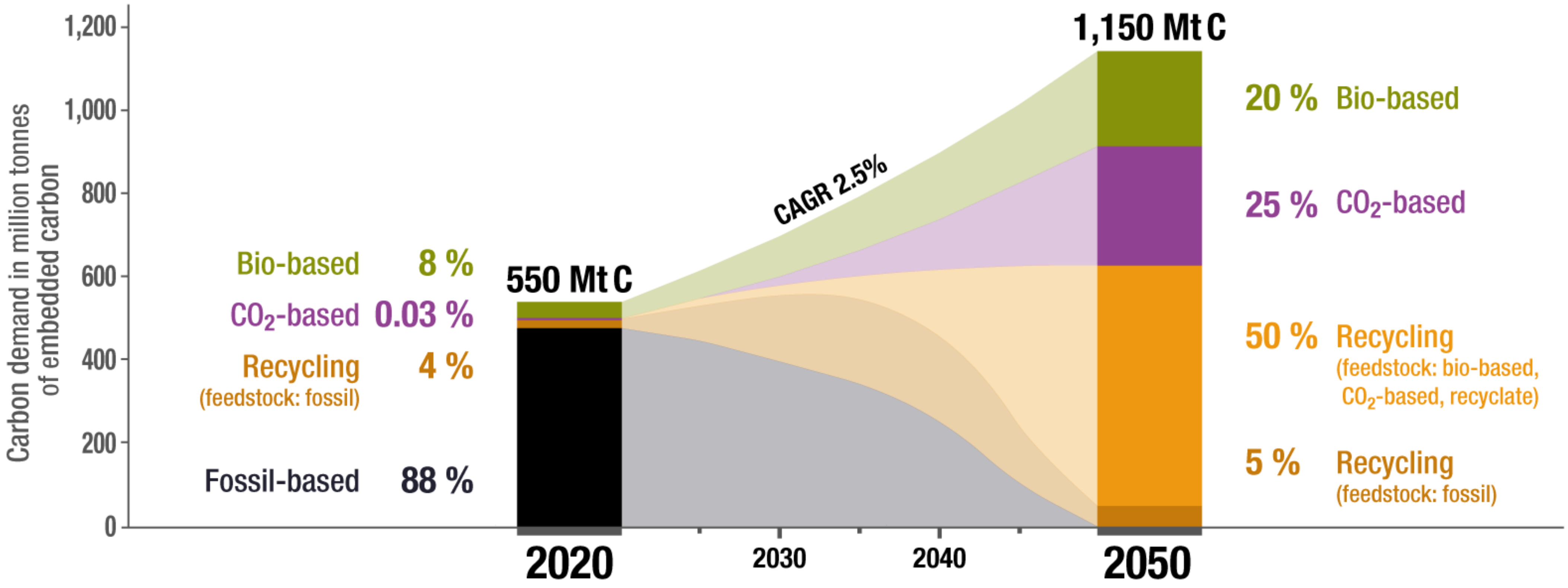


Recovery and mechanic recycling of plastics is feasible but many cycles cause a downgrading of plastics.

Ideally, polymers should be degraded into the original monomers to be re-used in new polymerization cycles

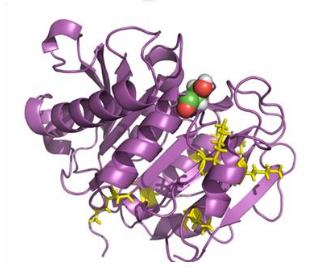
A. Pellis, M. Malinconico, A. Guarneri, L. Gardossi *New Biotechnol.* **2021**, *60*, 146-158.

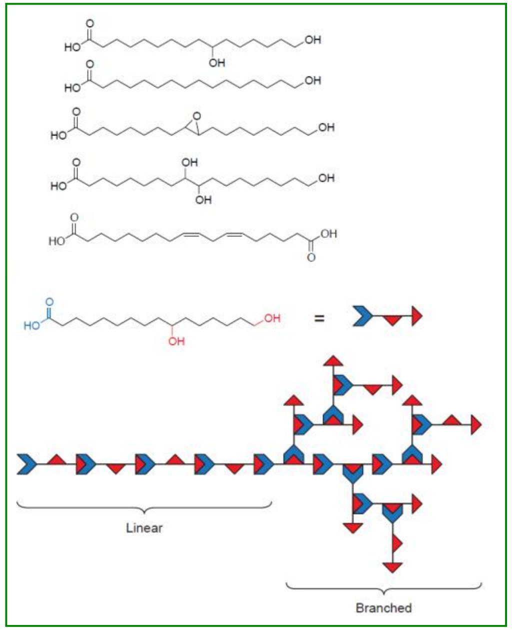
Carbon Embedded in Chemicals and Derived Materials

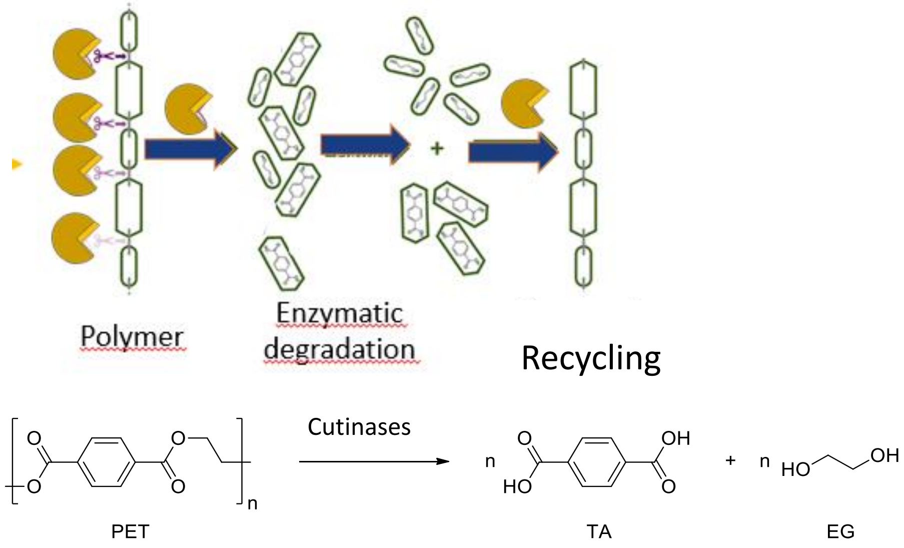


Enzymes for the degradation and recycling of polyesters

Cutinases https://www.carbios.com/en/enzymatic-recycling/

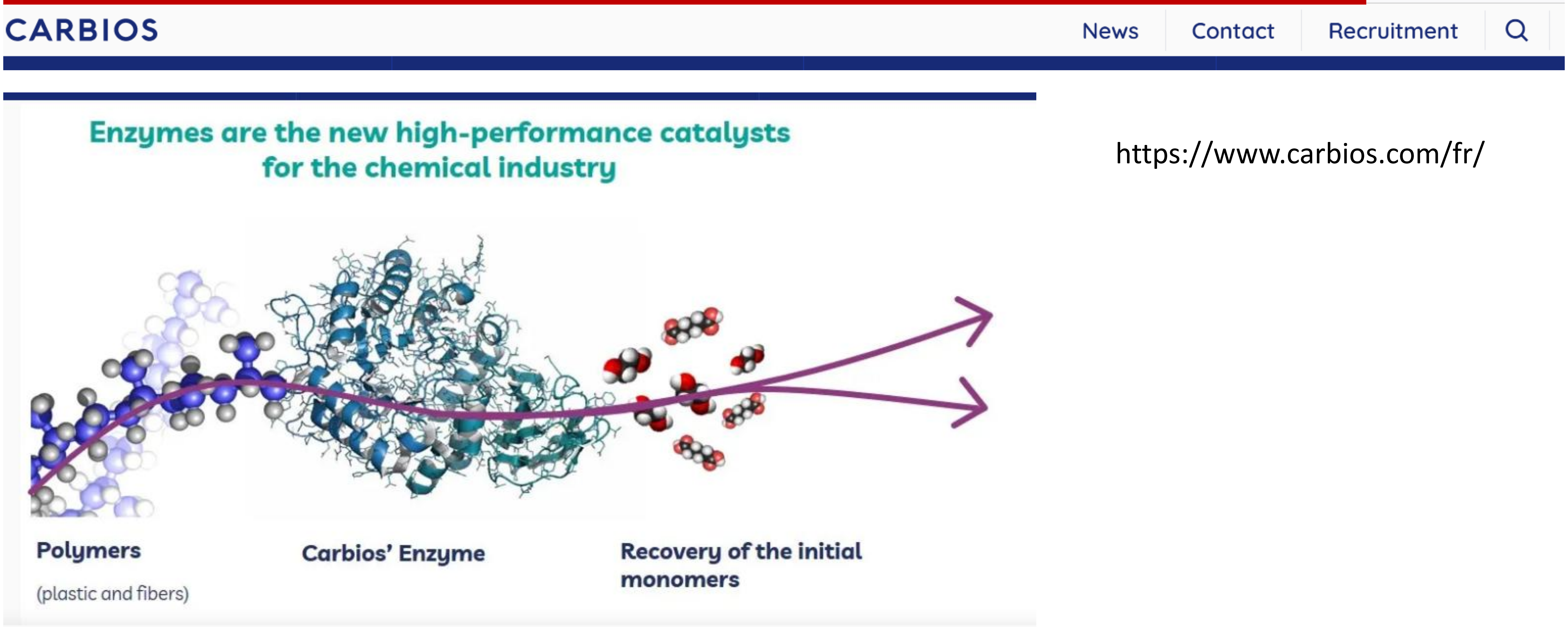




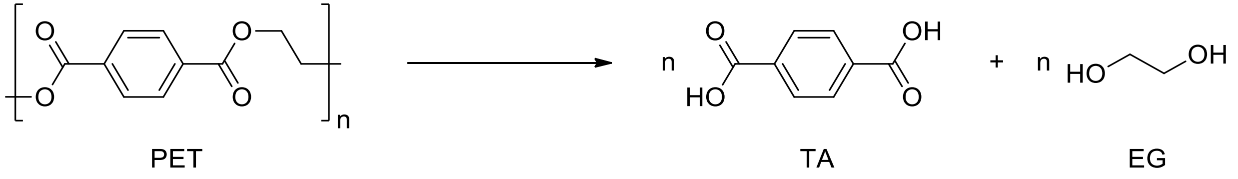


Green Chem., 2017, **19**, 490-502. DOI: 10.1039/C6GC02142E

Enzymatic hydrolysis to monomers and recycling

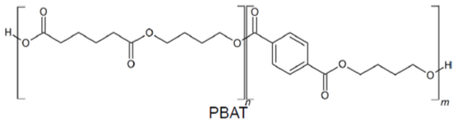


https://www.carbios.com/fr/



Biobased or Biodegradable Polymers, what's the difference?

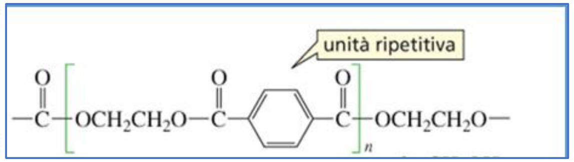
PBAT Fossil or partially biobased Compostable and biodegradable



plantbottle
up to 30% plant-based
100% recyclable bottle
redesigned plastic, recyclable as ever.

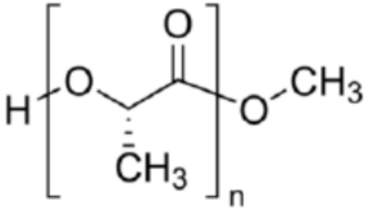
PET — past → Fossil-based — Non biodegradable

PET — present → 20% plant based — Non biodegradable



PLA Fully biobased

Biodegradable in industrial composting plants



BIO PLASTICS EUROPE

Definitions regarding the concepts of bio-based polymers and biodegradability.

Bio-based (material or product)	**Fully or partly derived from biomass (plants).** Bio-based carbon content is the variable describing the amount of bio-based carbon (in relation to fossil-based carbon) contained in a material or product and it is measured via the 14C method.
Biodegradation	Chemical process during which microorganisms available in the environment convert materials into natural substances such as **water, carbon dioxide**, and **compost** (artificial additives are not needed to accelerate degradation). This process depends on the surrounding environmental conditions (e.g. location or temperature), on the material and on the application.
Biodegradable plastic	**Bio-based or oil-based plastics that meet standards for biodegradability and compostability**. If a material or product is advertised to be biodegradable, further information about the timeframe, the level of biodegradation, and the required surrounding conditions should be provided and a timeframe for biodegradation must be set in order to make claims measurable and comparable. This is regulated in the applicable standards.
Compostable plastic	**Bioplastic that has proven its compostability according to international standards and can be treated in industrial composting plants**. Plastic products can provide proof of their compostability by successfully meeting the harmonised European standards (ISO 17088, EN 13432 / 14995 or ASTM 6400 or 6868), a certification, and an according label (seedling label via Vinçotte or DIN CERTCO, OK compost label via Vinçotte).
Degradable or oxo-degradable plastics	Plastics to which additives have been added to enhance the degradation, but **do not meet biodegradability and compostability standards.** Oxo-biodegradable plastic do not fulfil the requirements of EN 13432 on industrial compostability, and are therefore not allowed to carry the seedling label
Bio-based, non-biodegradable technical/performance polymers	Polymers such as bio-based polyamides (PA), polyesters (e.g. PTT, PBT), polyurethanes (PUR) and polyepoxides **used in technical applications** like textile fibers (seat covers, carpets) or automotive applications (foams for seating, casings, cables, hoses), etc. Their **operating life lasts several years (durable plastics) and, therefore, biodegradability is not desired**.
Bio-based, biodegradable plastics	Include starch blends made of **thermo-plastically modified starch and other biodegradable polymers** as well as polyesters such as polylactic acid (PLA) or polyhydroxyalkanoates (PHAs). Unlike cellulose, materials such as regenerate-cellulose or cellulose-acetate have been available on an industrial scale only for the past few years and **primarily used for short-lived products**.
Fossil-based, biodegradable plastics	Biodegradable plastics currently still made in petrochemical production processes. **Mainly used in combination with starch or other bioplastics** because the latter improve the biodegradability and mechanical properties. Partially bio-based versions of these materials are already being developed.

Standards produced by CEN: European Committee for Standardization: BioBased

- Bio-based **carbon content** in bio-based **products** and its determination (EN 16640:2017; EN 16785-1:2015; EN 16785-2: 2015)
- **Determination of biobased carbon content** in **plastics** (ISO 16620-2:2015)

Fully or partly derived from biomass. Bio-based carbon content is the variable describing the amount of bio-based carbon (in relation to fossil-based carbon) and it is measured via the 14C method.

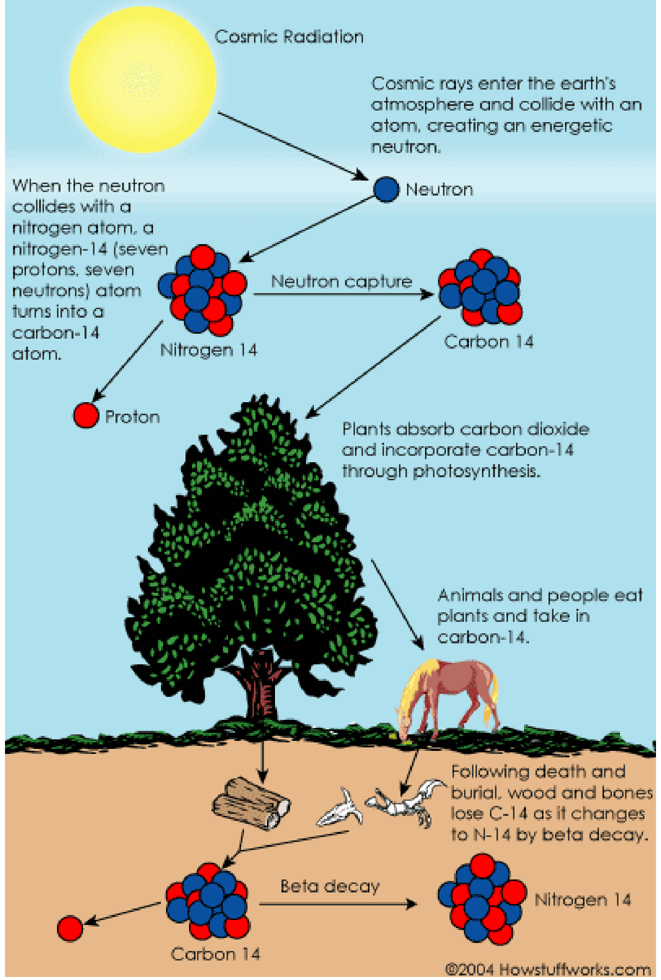
New Biotechnology, 2021, 60, 146-158. DOI: 10.1016/j.nbt.2020.10.003

Determination of biobased carbon content

• **EN 16785-1:2015- Prodotti a base biologica – Contenuto di rinnovabili – parte 1: Determinazione del contenuto di rinnovabili mediante il metodo del Carbonio-14 e della composizione elementare.**
Lo standard dettaglia un metodo per la determinazione di sostanze rinnovabili attraverso l'analisi del Carbonio-14 e della composizione elementare del prodotto oggetto di studio.

- Measurement of C^{12} / C^{14} ratio of isotopes

  C14 is formed in atmosphere and is characteristic of biobased carbon while it diminished in fossil sources
- C^{14} $t_{1/2}$ = 5730 years
- After 50.000 years very low conc.



between 20 and 40 % Biobased | between 40 and 60 % Biobased | between 60 and 80 % Biobased | more than 80 % Biobased

Bio-Based alternatives?

PET Substitution

Monomer	Biotechnological route	Company	Status
Sorbitol	Fermentation + hydrogenation	Roquette, ADM	Market
Isosorbide	Sorbitol dehydration	Roquette	Market
Ethylene glycol	Ethanol dehydration	India Glycols Ltd, Greencol Taiwan	Market
1,3-propanediol	Fermentation	Du Pont, Tate & Lyle, Metabolic Explorer	Market
1,4-butanediol	Fermentation, succinic acid hydrogenation	BioAmber, Genomatica, Mitsubishi	Market
Adipic acid	Fermentation + hydrogenation	Celexion LLC, BioAmber, Rennovia, Verdezyme	Market
Itaconic acid	Fermentation	Qingdao Kehai Biochemistry, Itaconix	Market
Lactic acid	Fermentation	Nature Works, BASF, Purac, Cargill, BBCA, Galactic	Market
Succinic acid	Fermentation	BioAmber, Myriant, Reverdia, BASF, Purac, Succinity	Market
Terephthalic acid	Isobutylene oxidation, fermentation	Virient, Annellotech, Genomatica	Pilot plant
Levulinic acid	Fermentation, acid treatment of C6 sugars	GFBiochemicals, Bio-on, Biofine Renewables	Market
Malic acid	Fermentation	Novozymes	Pilot plant
2,5-furandicarboxylic acid	Fermentation + dehydration + oxidation	Avantium	Pilot plant

Pellis et al. **2016**, *Trends Biotechnol.*, 34, 316-328

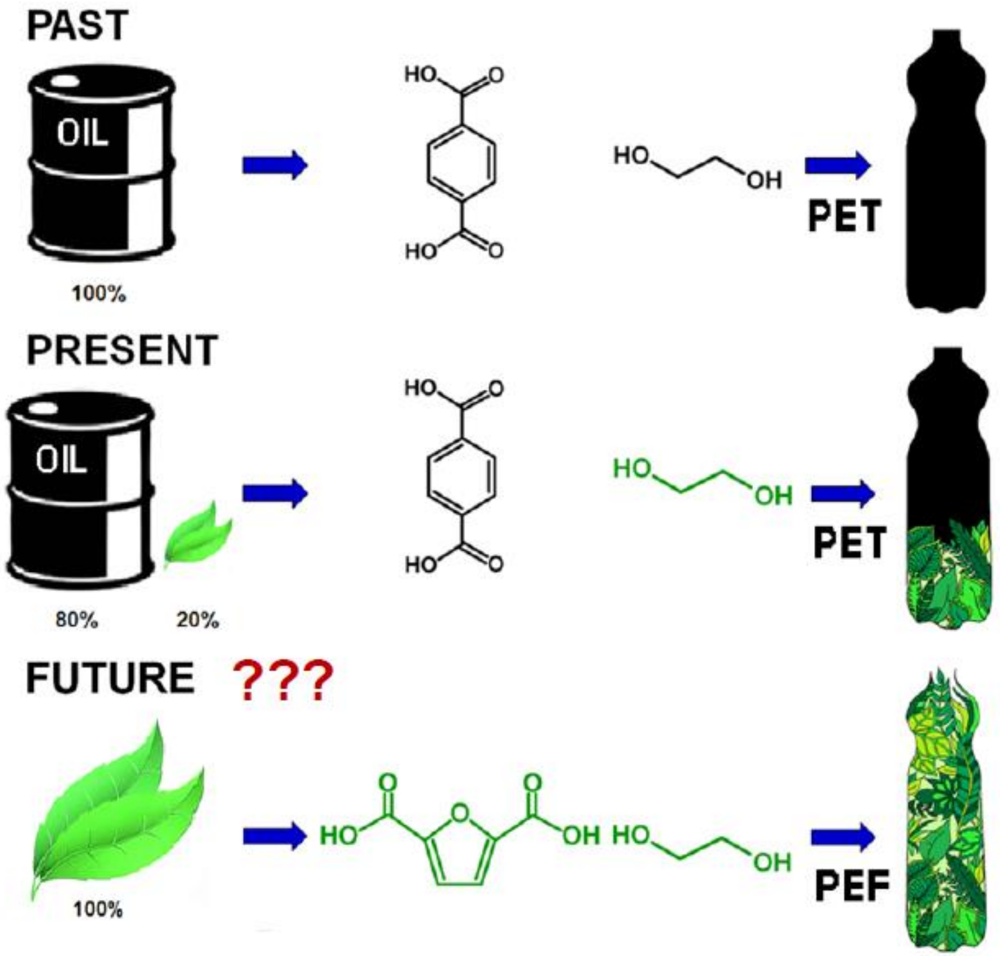


Figure inspired from: https://www.avantium.com

Bio-Polietilene ottenuto da bioetanolo: non biodegradabile

Zucchero da canna
↓ fermentazione
Etanolo
↓ disidratazione chimica
Etilene
↓ polimerizzazione
Polietilene

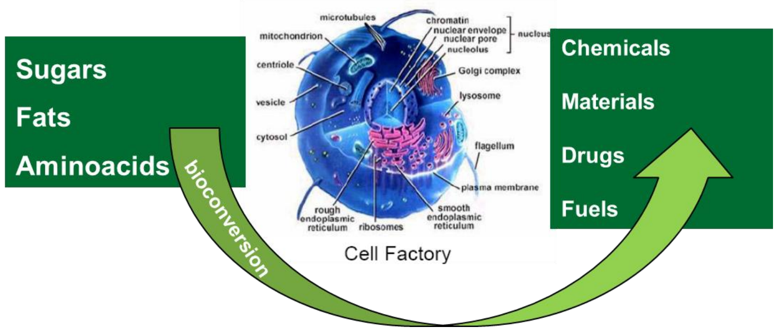
$$R-CH_2CH_2CH_2CH_2-R$$

- Identico al polietilene a base fossile

- Braskem 2009, 200.000 t/a
- Dow 2011, 350,000 t/a

Bio-refineries based on fermentation

The cell:
The most complex and efficient chemical laboratory at low environmental impact



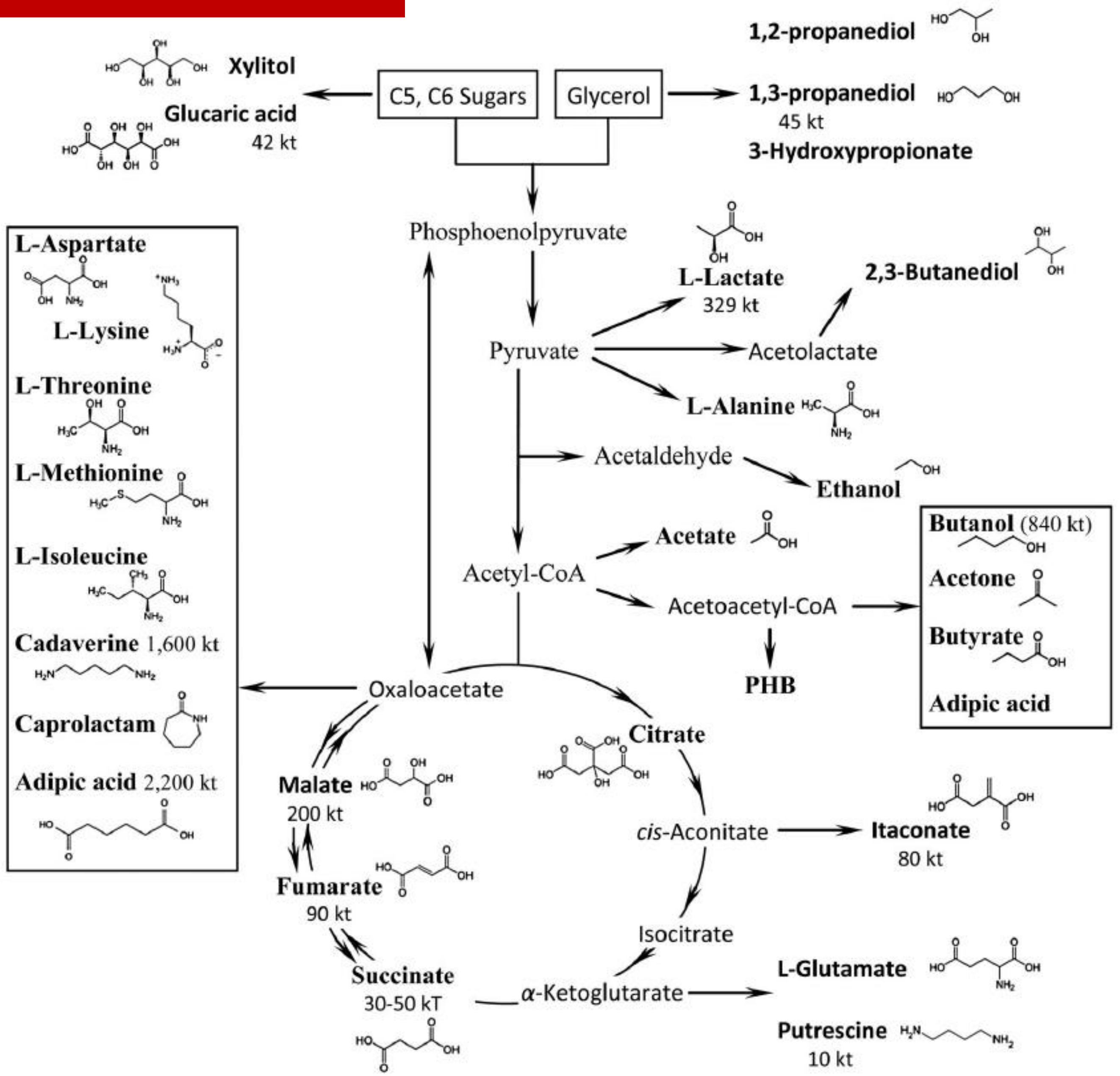


Fig. 2 Building blocks that could be produced *via* fermentation. Numbers next to biochemicals designate the total annual production in thousands of t.

Biobased monomers for polyester synthesis

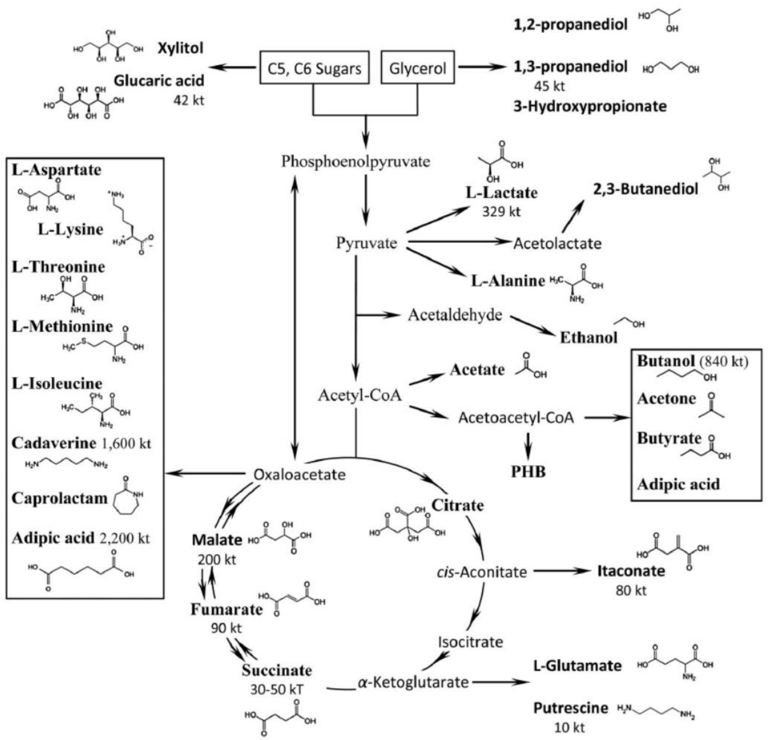
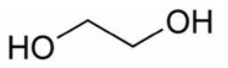


Fig. 2 Building blocks that could be produced *via* fermentation. Numbers next to biochemicals designate the total annual production in thousands of t.

Enzymatic Synthesis and Structural Modeling of Bio-Based Oligoesters as an Approach for the Fast Screening of Marine Biodegradation and Ecotoxicity. Int. J. Mol. Sci. 2024, 25, 5433. https://doi.org/10.3390/ijms25105433

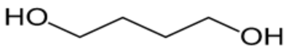
Polyols

Monoethylene glycol (MEG)

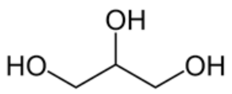


1,3-Propanediol (1,3-PDO)

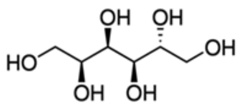
1,4-Butanediol (1,4-BDO)



Glycerol (Gly)

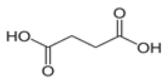


Sorbitol

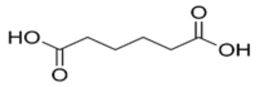


Diacids/Diesters

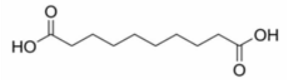
Succininc acid (SA)



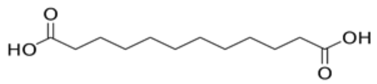
Adipic acid (AA)



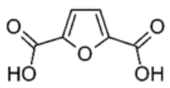
Sebacic acid (SBA)



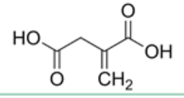
Dodecandioic acid (DDA)



2,5-Furandicarboxylic acid (FDCA)

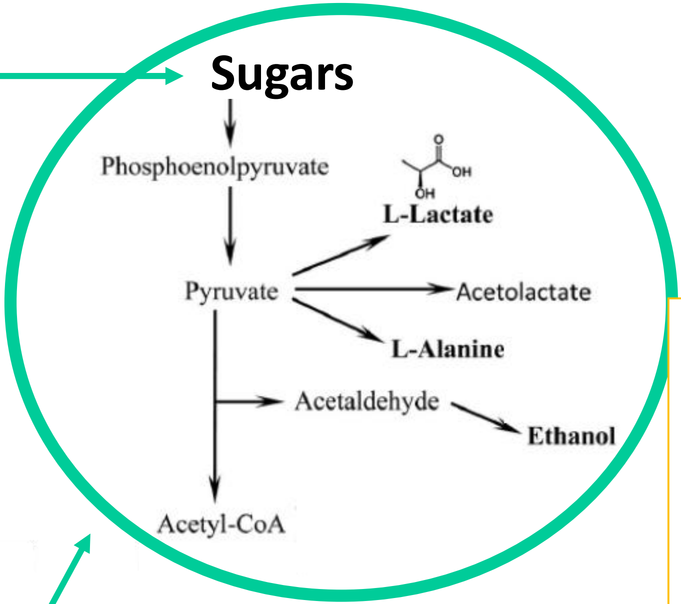


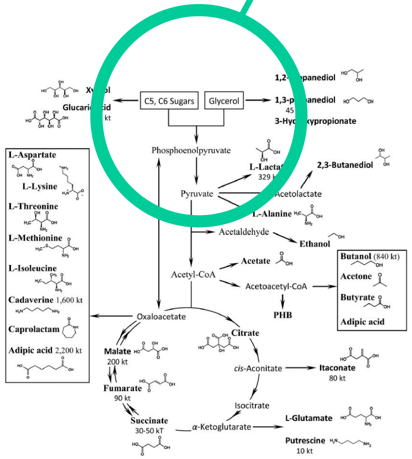
Itaconic acid (IA)



Production of PLA: integration of chemistry with biotechnologies

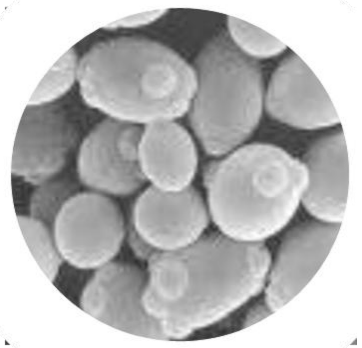
Biomass:

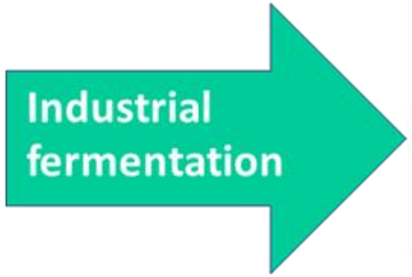


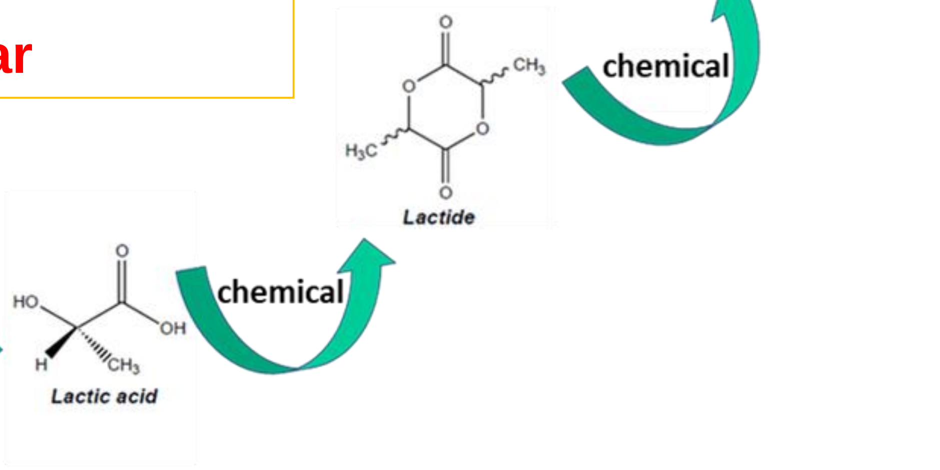


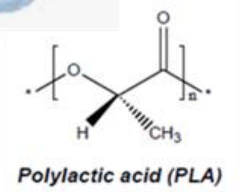
Polylactate - PLA

The most important bio-based polyester in terms of volume, with a **capacity of approximately 800 000 tons / year**









Pellis A, Cantone S., Ebert C., Gardossi L., *New Biotechnol.*, **2018**, *40*, 154-169.

Poly(lactic acid) (PLA) - Applications

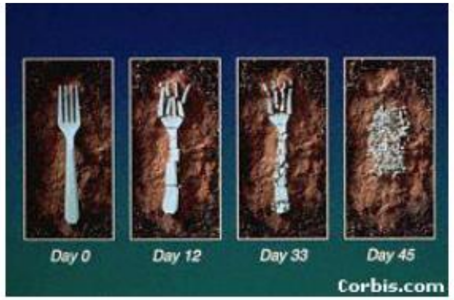
The PLA materials have mechanical properties that lie somewhere in between that of polystyrene and PET.

Packaging:
- Films
- Packaging foam
- Containers (biodegradable)
- Coatings for papers and boards

Fibres:
- Clothing
- Carpet tiles (Interface Inc.)
- Nappies

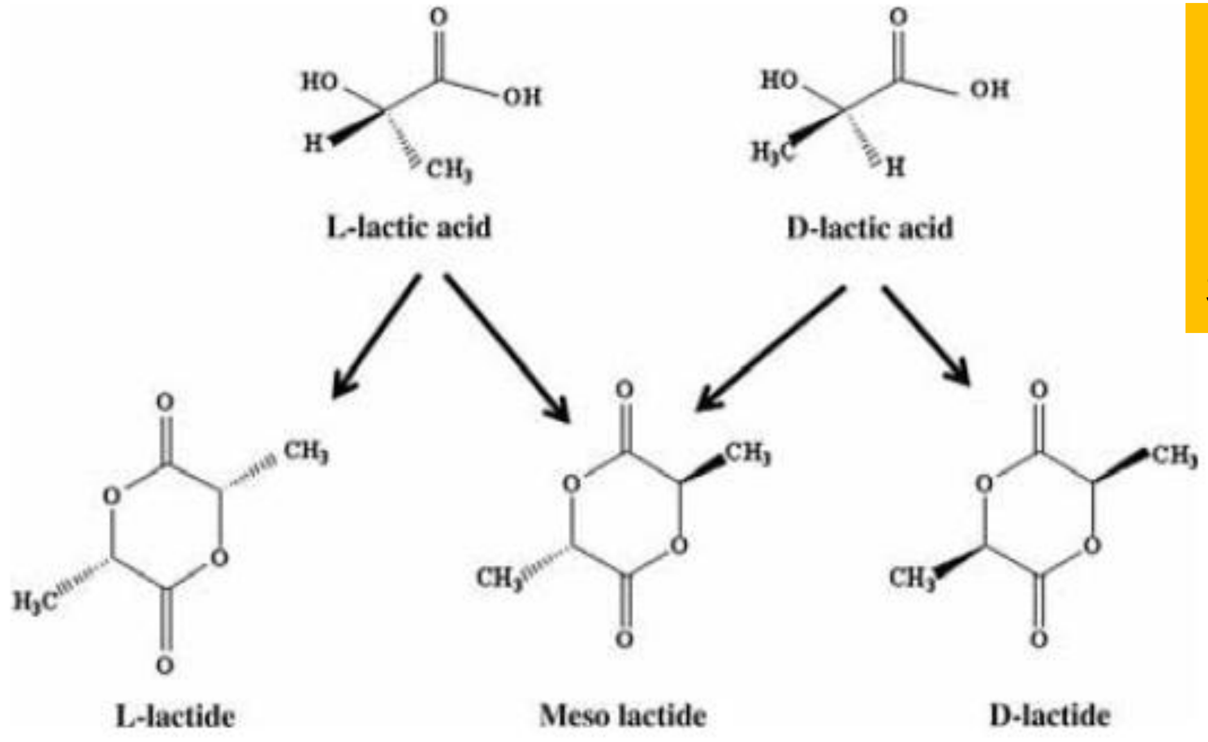
The most important bio-based polyester in terms of volume, with a **capacity of approximately 800 000 tons / year**

Compostable in industrial composting plants (controlled conditions)



www.cargilldow.com

Lactic acid and lactide have stereoisomers



LL-Lactide (mp 97 C)

LD-Lactide (mp 52 C)

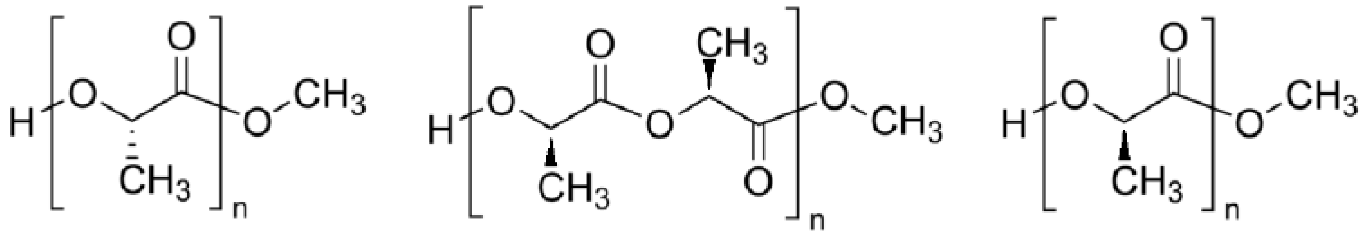
DD-Lactide (mp 97C)

Depending on methods used for synthesis, PLA can have different stereoisomers:

- Poly(L-lactide) (PLLA) and Poly(D-lactide) (PDLA) are **isotactic** forms, in which the configurational repeating unit is essentially an isomer of lactic acid (L-lactic and D-lactic respectively). These are optically pure forms of PLA and have crystalline form.
- Poly(DL-lactide) (PDLLA) is the **syndiotactic** polymer, in which configurational repeating unit consists of two monomers that are enantiomeric.

- If enantiomeric forms of lactic acid are bonded in a random sequence distribution, the polylactide is **atactic**.

Stereoisomers of PLA:



Poly-L-Lactic Acid (PLLA) — Poly-D-L-Lactic Acid (PDLLA) — Poly-D-Lactic Acid (PDLA)

Figure 5. Structure of polylactide stereoisomers.

isotactic — syndiotactic — isotactic

A very important property is the rate of **crystallinity,** which is the degree of structural order respect to **amorphous** content.
PLA with a high rate of crystallinity can be obtained with an optically pure PLA, while the lower optically pure is amorphous.
The crystallinity influences many properties, such as the melting temperature (Tm), and the glass transition temperature (Tg) of PLA.

1,4-Butanediol (1,4-BDO)

1,4-BDO is an important chemical that is used for the manufacture of over 2.5 million tons of polymers annually. Nowadays its production is almost entirely based on fossil carbon resources (production via the Reppe process in which acetylene is reacted with formaldehyde) with the exception of BASF and Bioamber that started production via hydrogenation of SA which is accessible from biogenic sources as described below.

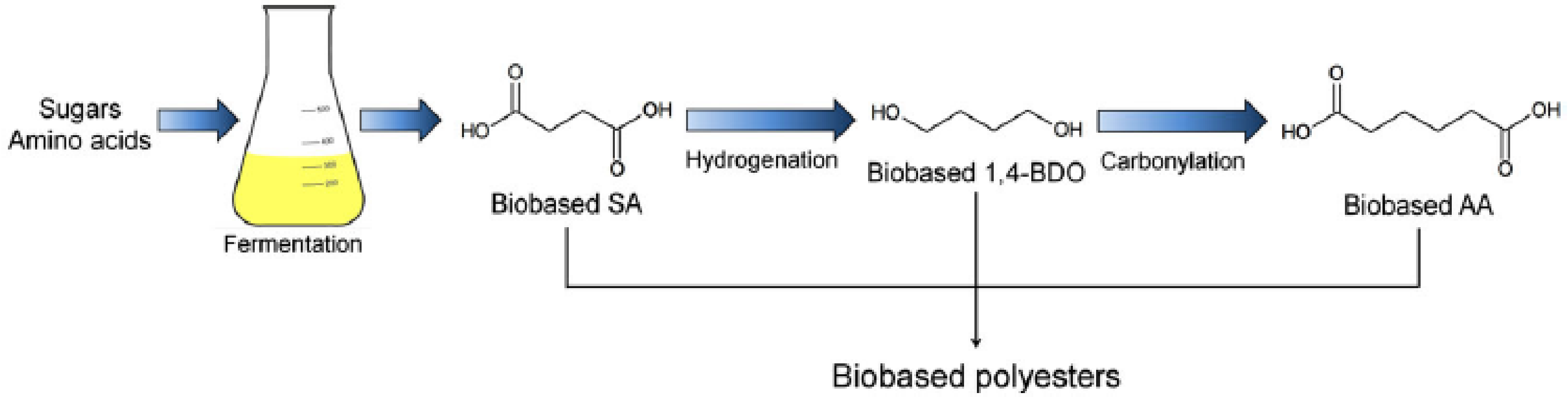


Figure 3. Biotechnological process for the production of bio-based succinic acid (SA) and its derivatives 1,4-butanediol (1,4-BDO) and adipic acid (AA).

In September 2016 Novamont opened the first plant at commercial scale in the world for the direct fermentation of sugar to produce 1,4-butandiol.

nature chemical biology

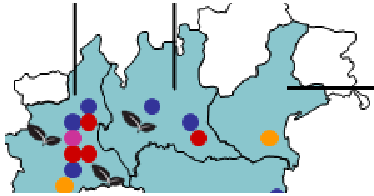
ARTICLE

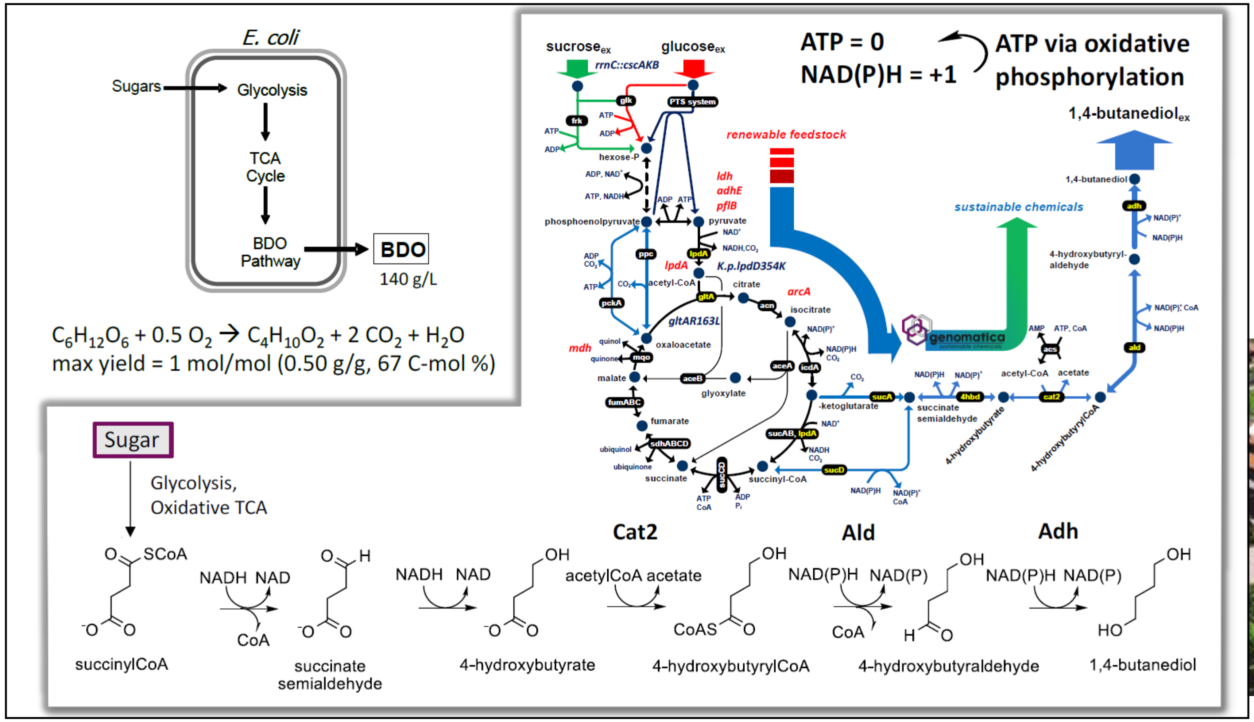
PUBLISHED ONLINE: 22 MAY 2011 | DOI: 10.1038/NCHEMBIO.580

Metabolic engineering of *Escherichia coli* for direct production of 1,4-butanediol

Harry Yim[1,3], Robert Haselbeck[1,3], Wei Niu[1,3], Catherine Pujol-Baxley[1,3], Anthony Burgard[1,3], Jeff Boldt[1], Julia Khandurina[1], John D Trawick[1], Robin E Osterhout[1], Rosary Stephen[1], Jazell Estadilla[1], Sy Teisan[1],

[1]Genomatica, Inc., San Diego, California, USA. [2]Department of Chemical and Biomolecular Engineering (BK21 program), Center for Systems and Synthetic Biotechnology, Institute for the BioCentury, Korea Advanced Institute of Science and Technology, Daejeon, South Korea. [3]These authors contributed equally to this work. *e-mail: svandien@genomatica.com

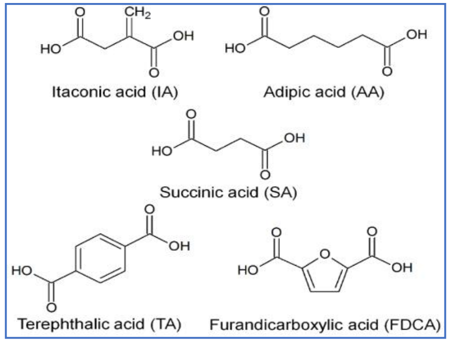


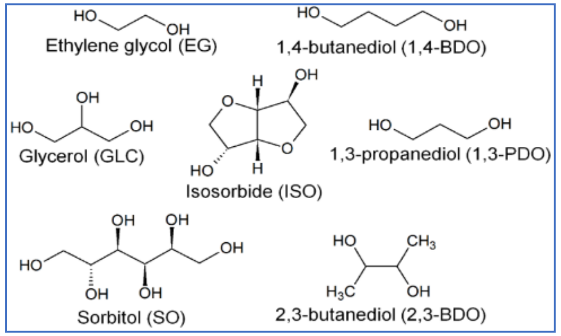


In September 2016 Novamont opened the first plant at commercial scale in the world for the direct fermentation of sugar to produce 1,4-butandiol.

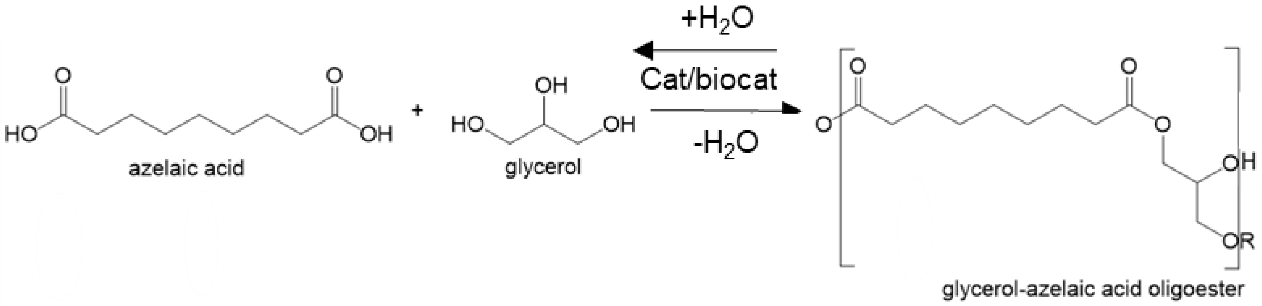
Polymers chemically synthetized from biobased monomers or in combinations with fossil monomers

Poly(trimethylene terephthalate) -PTT
Poly(ethylene terephthalate)-PET
Poly(1,4-butylene succinate) - PBS
Poly(ethylene succinate) - PES
Poly(ethylene furanoate) - PEF
Poly(trimethylene furanoate) - PTF
Poly(butylene furanoate) - PBF
Poly(1,4-butylene adipate-*co*-1,4-butylene terephthalate) - PBAT
Unsaturated polyester resins - UPR
Poly(L-lactide) -PLLA





Polyamides containing four carbons - 4C PAs: 4; 4.6 and 4.10
Polyamides with longer chains. PAs: 6.10; 10.10; 11 and 12
Polyvinyl chloride – PVC
Polyethylene – PE (from bio-ethanol)
Polypropylene - PP
Poly(methyl methacrylate)–PMMA
Ethylene propylene diene monomer – EPDM (synthetic rubber)



Polyurethanes -PURs
Poly(furfuryl alcohol) - PFA
Acrylonitrile butadiene styrene - ABS
Polyacrylic superabsorbent polymers - PA-SA
Poly(itaconic acid) - PIA
Polyvinyl chloride – PVC

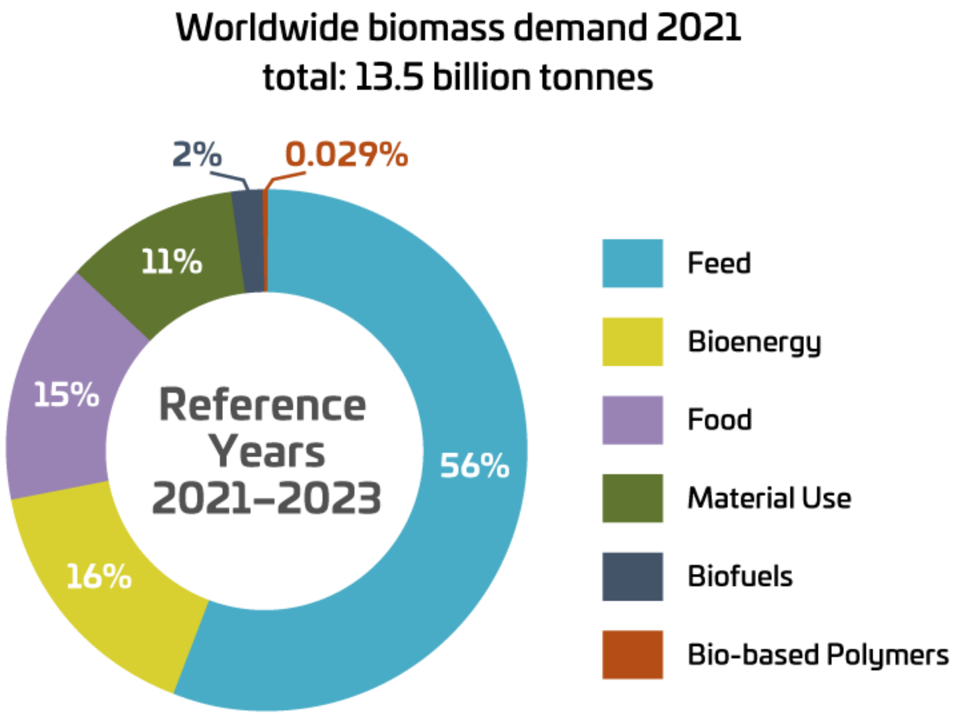
Biodegradable/compostable

Biocompostable under industrially controlled conditions

Durable

A. Pellis, M. Malinconico, A. Guarneri, L. Gardossi *New Biotechnol.* **2021**, *60*, 146-158.

Biomass Utilisation Worldwide



available at www.renewable-carbon.eu/graphics

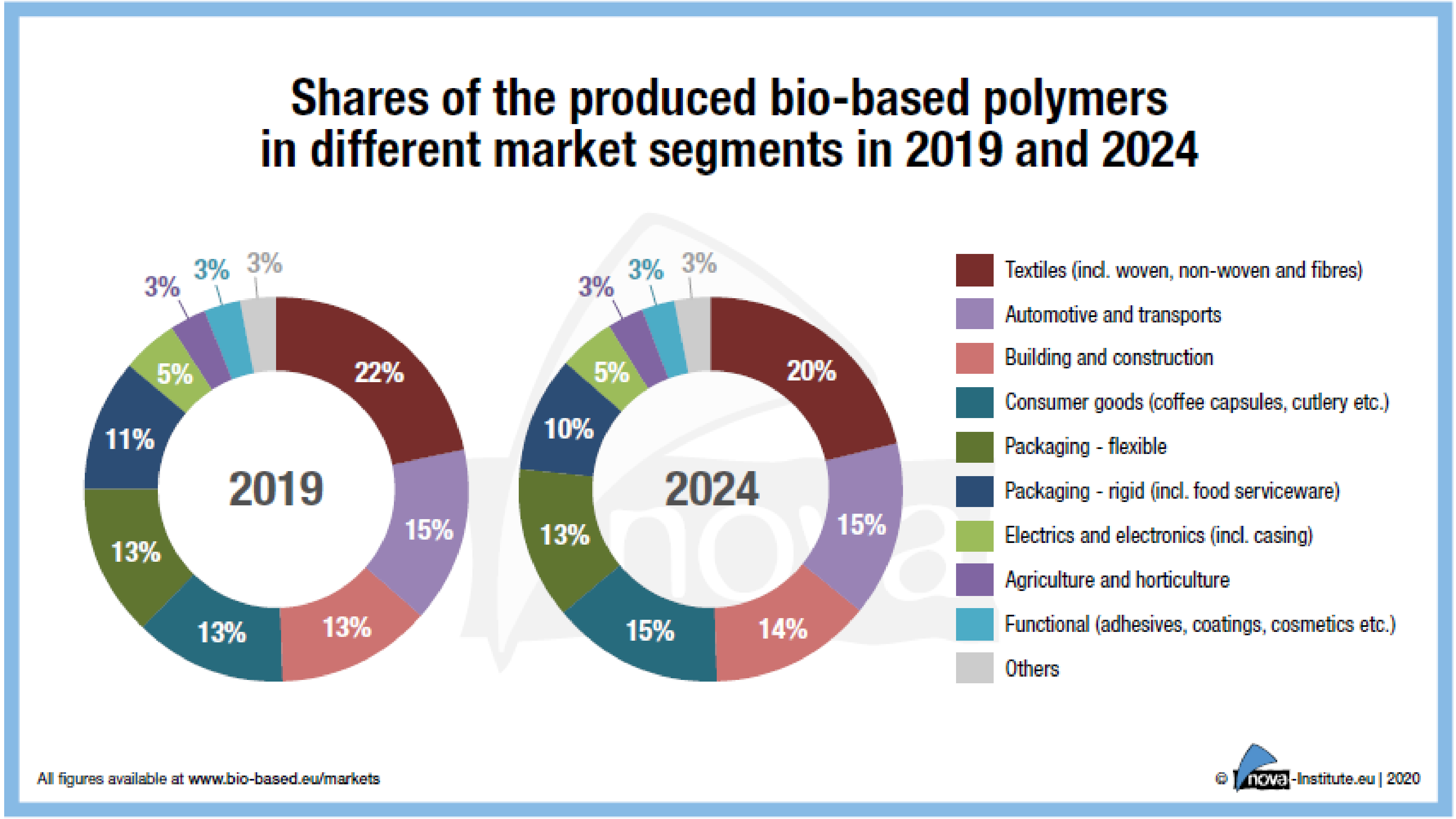


Figure 9: Shares of the produced bio-based polymers in different market segments in 2019 and 2024

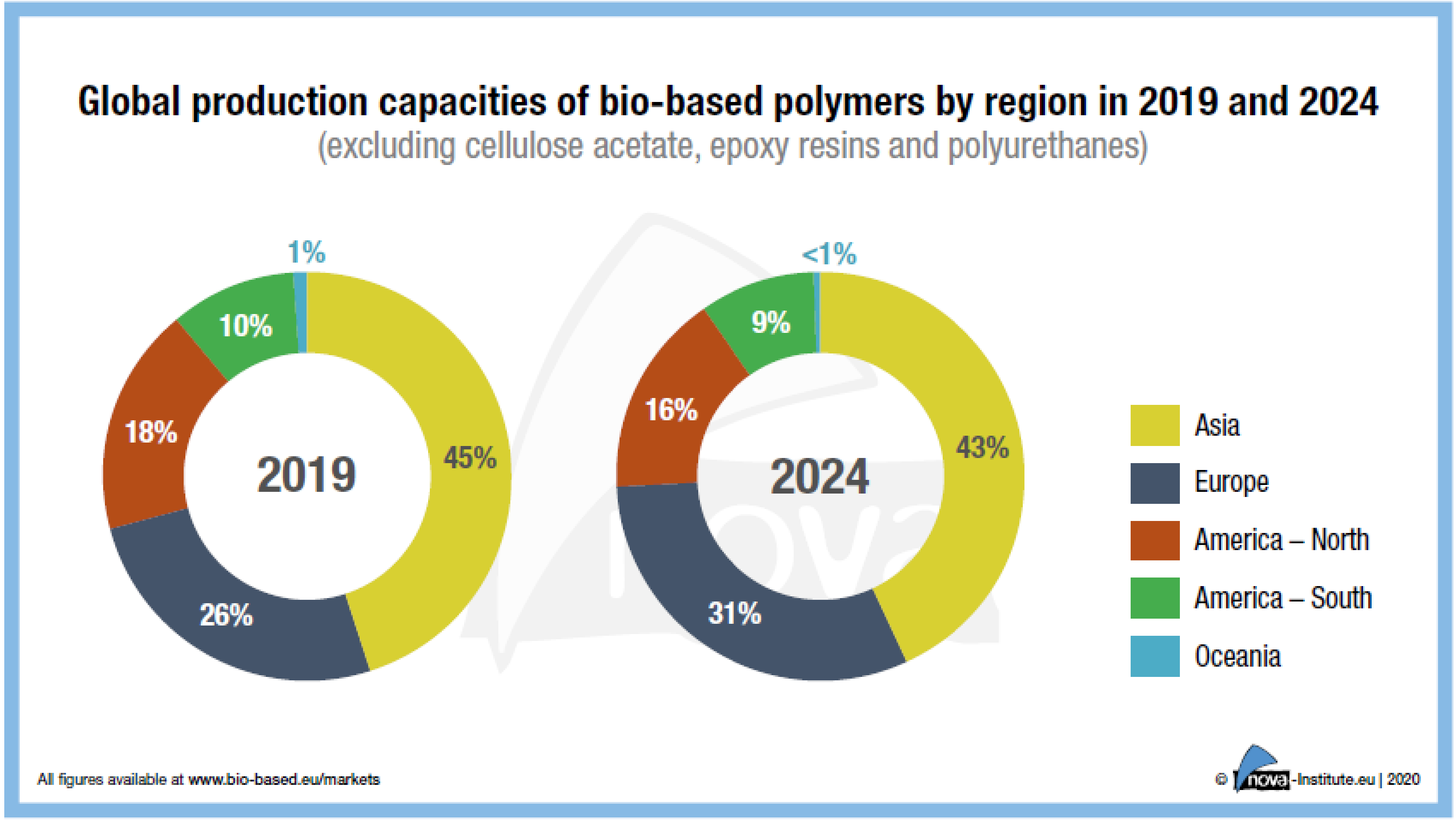
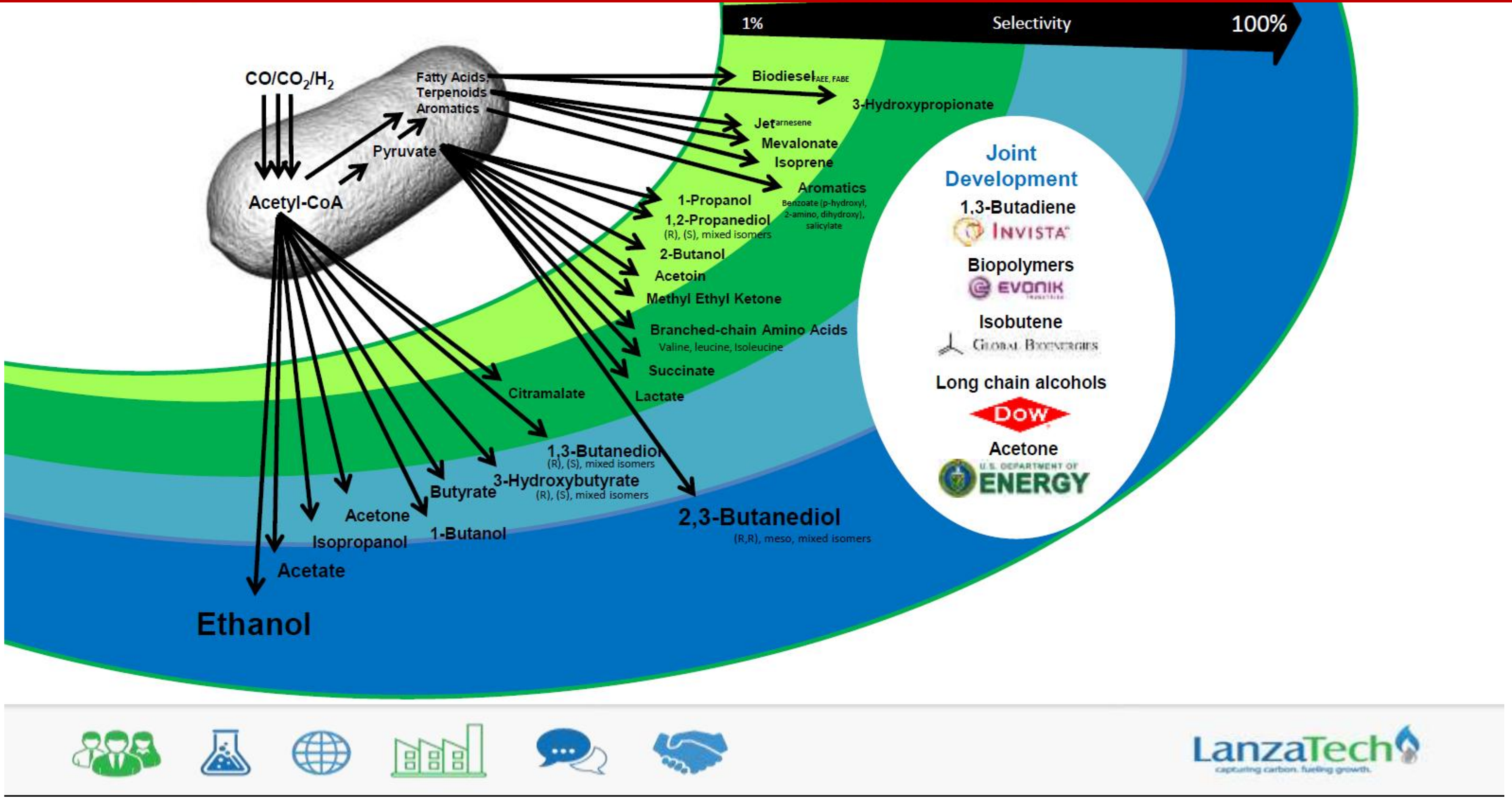
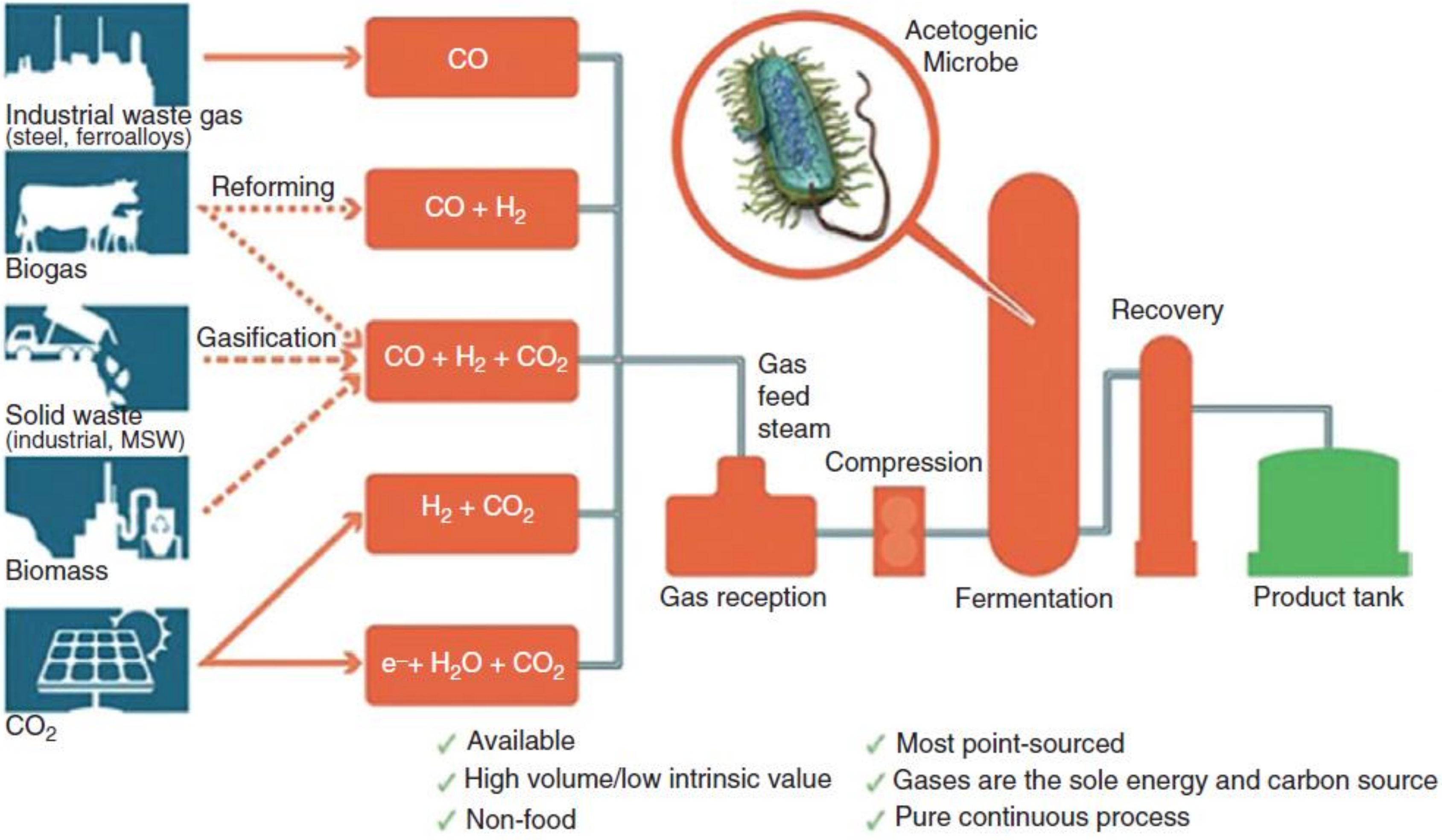


Figure 8: Global production capacities of bio-based polymers by region in 2019 and 2024 (excluding cellulose acetate, epoxy resins and polyurethanes)

Biotechnologies for CO and CO2 transformation into chemicals and fuels: metabolic engineering of acetogenic bacteria





I&EC research
Industrial & Engineering Chemistry Research

Article
pubs.acs.org/IECR

Life Cycle Assessments of Ethanol Production via Gas Fermentation: Anticipated Greenhouse Gas Emissions for Cellulosic and Waste Gas Feedstocks

Robert M. Handler,[*,†] David R. Shonnard,[†] Evan M. Griffing,[‡] Andrea Lai,[§] and Ignasi Palou-Rivera[§]

[†]Sustainable Futures Institute, Department of Chemical Engineering, Michigan Technological University, Houghton, Michigan 49931, United States

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[§]LanzaTech, 8045 Lamon Avenue Suite 400, Skokie, Illinois 60077, United States

ABSTRACT: LanzaTech has developed novel microbial bioreactor systems capable of direct gas fermentation to produce ethanol from carbon-containing gases. In this study, a life-cycle assessment method is used to quantify the global warming potential of several scenarios for producing renewable ethanol with the LanzaTech process. Scenarios considering ethanol produced from steel mill waste gases or biomass (corn stover, forest residue, or switchgrass, via gasification) have been considered, using input data from peer-reviewed literature, government reports, life cycle inventory databases, and LanzaTech process engineering estimates. Using standardized life-cycle assessment methods, ethanol produced via LanzaTech fermentation appears to result in greenhouse gas emissions that are at least 60% lower than that of conventional fossil gasoline, with biomass-based ethanol achieving close to 90% emission reductions. Results indicate that the LanzaTech gas fermentation technology can be a viable alternative for producing next-generation biofuels that satisfy United States Renewable Fuels Standard policies concerning fuels with a reduced greenhouse gas emissions footprint.

Article *in* Industrial & Engineering Chemistry Research · December 2015
DOI: 10.1021/acs.iecr.5b03215

https://www.youtube.com/watch?v=oZXAb4fUlq8

https://www.youtube.com/watch?v=k3WLwKrEu7c
https://www.youtube.com/watch?v=7aw2eoJLyug

https://www.youtube.com/watch?v=A3Uq6otg7fQ

https://www.youtube.com/watch?v=RIT3UyoDE9Q

Fermentation of waste gases

LanzaTech, 2012

ArcelorMittal, 2017

"ArcelorMittal, LanzaTech and Primetals Technologies announce partnership to construct breakthrough €87m biofuel production facility"

PRIMETALS TECHNOLOGIES

ArcelorMittal

LanzaTech

Business & Financial News | May 11, 2021

Joint News Release

LanzaTech and BASF achieve first milestone in utilizing industrial off-gases for chemical production

With appropriate enzymes or bacteria, CO and CO2 can be converted into chemicals through bioreactions. One advantage of bioconversion is that it normally takes place at low temperature and pressure, so energy consumption is low. The process is, in general, simple, with mainly bioreactor(s) and a product-separation/purification process leading to low costs. The processes can take the exhaust from emission sources without the need to treat and purify the flue gas.

PRESS RELEASE

H&M MOVE PARTNERS WITH LANZATECH TO LAUNCH CAPSULE COLLECTION USING CAPTURED CARBON EMISSIONS

This is the stuff of science fiction: LanzaTech diverts carbon emissions heading for the atmosphere, traps them, and turns them into thread. In a leap towards innovating sportswear, H&M Move partners with the

H&M Move is on a mission to democratise movewear and get the whole world and everybody moving. While inspiring people to move and breaking down barriers to sport is one part of the brand formula, moving the needle with innovation is another.

In partnership with carbon capture company LanzaTech, H&M Move is taking a step on its innovation journey: creating garments partly from captured emissions and infusing them with the brand's own DryMove™ technology – a trademarked material that pulls away moisture from the skin and keeps Movers comfortable and dry while moving.

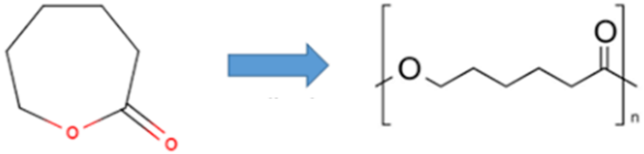
"In collaboration with LanzaTech, we are thrilled to offer our customers a capsule collection made with CarbonSmart™ polyester, a ground-breaking material using repurposed carbon emissions. This partnership enables H&M Move to explore innovative materials and playing our part in helping to create more sustainable sportswear in the future,"

says Simon Brown, General Manager at H&M Move.

Standards produced by CEN: European Committee for Standardization: biodegradation

1. CEN document EN 17228:2019 the property of **biodegradation does not depend on the resource basis of a material, but it is rather linked to its chemical structure.**

Fossil based polycaprolactone: biodegradable polyester



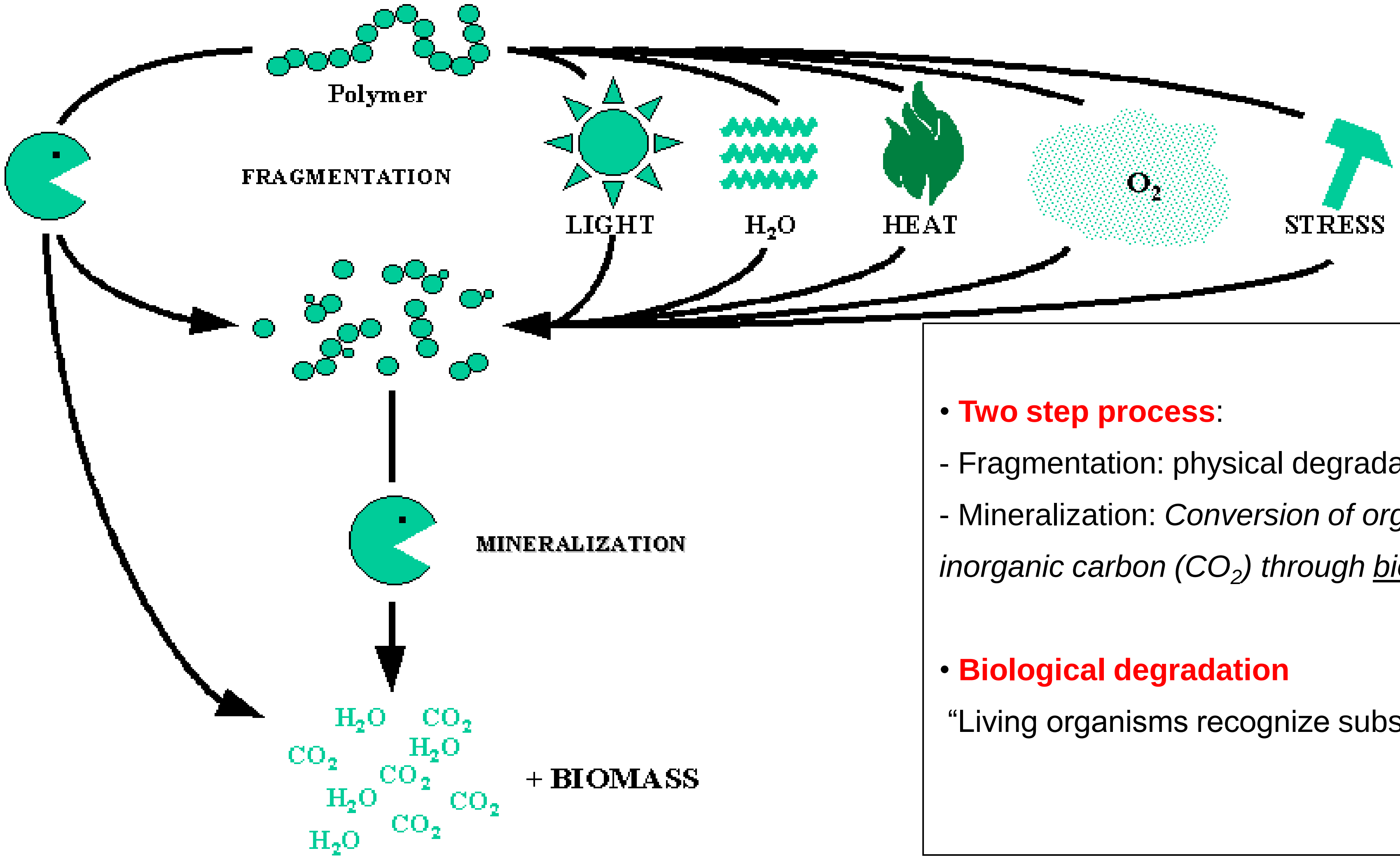
The process of biodegradation depends on material, on its form (e.g. thickness, shape), and on environmental conditions (e.g. temperature, inoculum, humidity).

2. The European standard **EN 13432: "Requirements for packaging recoverable through composting and biodegradation" entails "at least 90% disintegration after twelve weeks, 90% biodegradation (CO_2 evolvement) in six months, and includes tests on eco-toxicity and heavy metal content".**

3. Standard **ASTM D 6691 offers a test method to assess biodegradation in water.**

Biodegradation

The process of biodegradation depends on material, on its form (e.g. thickness, shape), and on environmental conditions (e.g. temperature, inoculum, humidity).



- **Two step process**:

- Fragmentation: physical degradation (biotic or abiotic)

- Mineralization: *Conversion of organic carbon to inorganic carbon (CO_2) through biotic digestion*

- **Biological degradation**

"Living organisms recognize substrate as food"

Biodegradation: certification and labelling

There is a number of certifications and labels that highlight the special end-of-life options of biobased products, such as compostability, biodegradability in soil, biodegradability in seawater, etc. Biodegradability is a relevant aspect in the life cycle of specific products, particularly those made of biobased materials.

VINÇOTTE	VINCOTTE			SOIL OK bio-degradable VINÇOTTE
	OK biodegradable SOIL : Initial acceptance tests			
	Doc Ref : OK10-e		Edition : C	
	Application Date : 2012-03-01		Page : 1 / 5	
	Replace : Edition B			
Program OK 10				
Bio products – degradation in soil				

VINÇOTTE	VINCOTTE			MARINE OK bio-degradable VINÇOTTE
	OK biodegradable MARINE : Initial acceptance tests			
	Doc Ref : OK12-e		Edition : A [1]	
	Application Date : 2015-03-02		Page : 1 / 5	
	Replace : -			
Program OK 12				
Bio products – degradation in seawater				

Bio-based and compostable plastics

They meet standard and can be recognised from labels

Biopolymers

Polisaccharides	Starch and derivatives
	Chitosan

Polymers from engineered microbes

Polyesters	Polyhydroxyalkanoates

Bio-based (material or product)

Fully or partly derived from biomass. Bio-based carbon content is the variable describing the amount of bio-based carbon (in relation to fossil-based carbon) and it is measured via the 14C method.

A. Pellis, M. Malinconico, A. Guarneri, L. Gardossi *New Biotechnol.* **2021**, *60*, 146-158.

COS'E' IL MATER-BI®

Polimero Biodegradabile e Compostabile
Mater-Bi®: la prima famiglia di biopolimeri che utilizza componenti vegetali come l'amido di mais, preservandone la struttura chimica

Attraverso un processo di "complessazione" dell'amido con quantità variabili di agenti complessanti biodegradabili (naturali, da fonte rinnovabile, da fonte sintetica o mista), vengono create diverse sovrastrutture molecolari caratterizzate da un'ampia gamma di proprietà.

Mater-Bi® è prodotto nello stabilimento di Terni, in forma di granulo e può essere lavorato secondo le più comuni tecnologie di trasformazione, per realizzare prodotti dalle caratteristiche analoghe o migliori rispetto alle plastiche tradizionali, ma perfettamente biodegradabili e compostabili, minimizzando l'impatto ambientale. I prodotti in Mater-Bi® dopo l'uso si biodegradano nel tempo di un ciclo di compostaggio.

MATER-BI

Bio-based and compostable plastics

Thermoplastic starch

based plastics

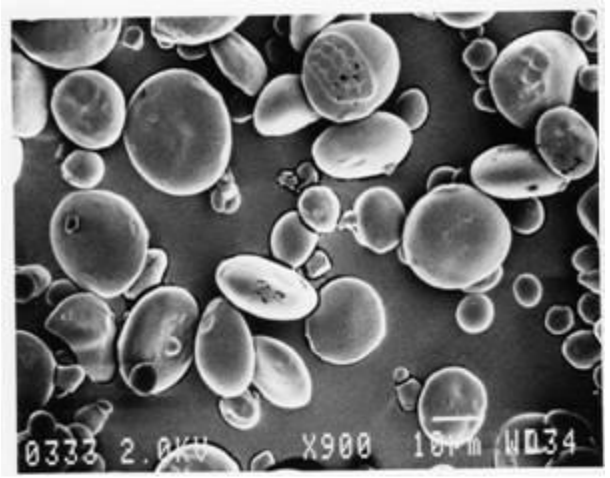
Starch polymer structure retained while granular structure is destroyed under influence of heat, mixing and plasticizers (e.g. water, glycols)

Used in composites, blends, multilayers

Biodegradable

Organic waste collection, vapour permeable packaging

Mater-bi (Novamont) 60.000 t/a cap.
Foamed starch for packaging



L. Averous, University Strasbourg:
www.biodeg.net/biomaterial.html

The Italian model: an example of circular bioeconomy

1) **Research and innovation**: compostable plastics
2) **Legislation**: banning of non-compostable plastic bags
3) **Pubblic-Private investments**: revamping of waste-treatment plants, R&I

2019:

4.6 M tons of organic waste

Anaerobic fermentation

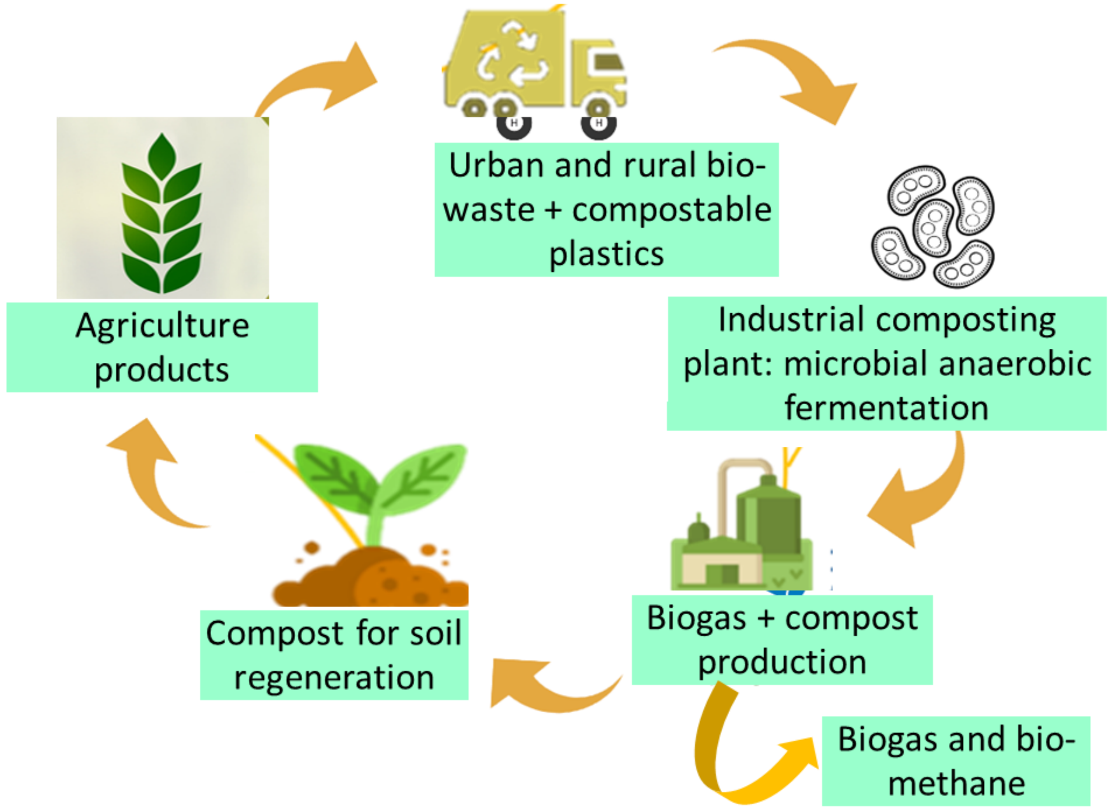
COMPOST
BIOGAS

2 M tons of compost:
375.000 tons of organic carbon back to the soil

BIOMETHANE

PRODUCED: 100 M m^3
SAVED: 4.3 M tons of CO_2 emissions

Compostable plastics can be recycled within biogenic carbon cycles

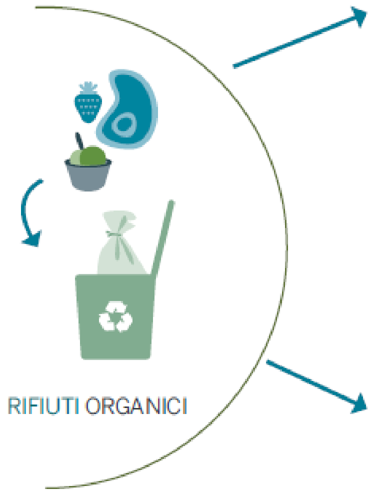


- Meaning a material's capacity to be converted into carbon dioxide (CO_2) through the action of microorganisms, under the same process occurring in natural waste.
- Being disintegrable, namely being fragmented and invisible in the final compost (absence of visual contamination).
- Absence of negative effects on the composting process.
- Almost complete absence of heavy metals and the absence of negative effects on compost quality.

A. Pellis, M. Malinconico, A. Guarneri, L. Gardossi *New Biotechnol.* **2021**, *60*, 146-158.

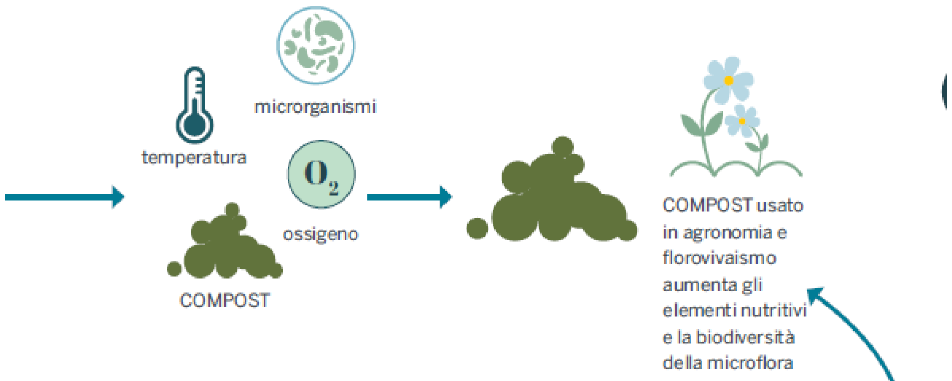
Lucia Gardossi

compostabilità



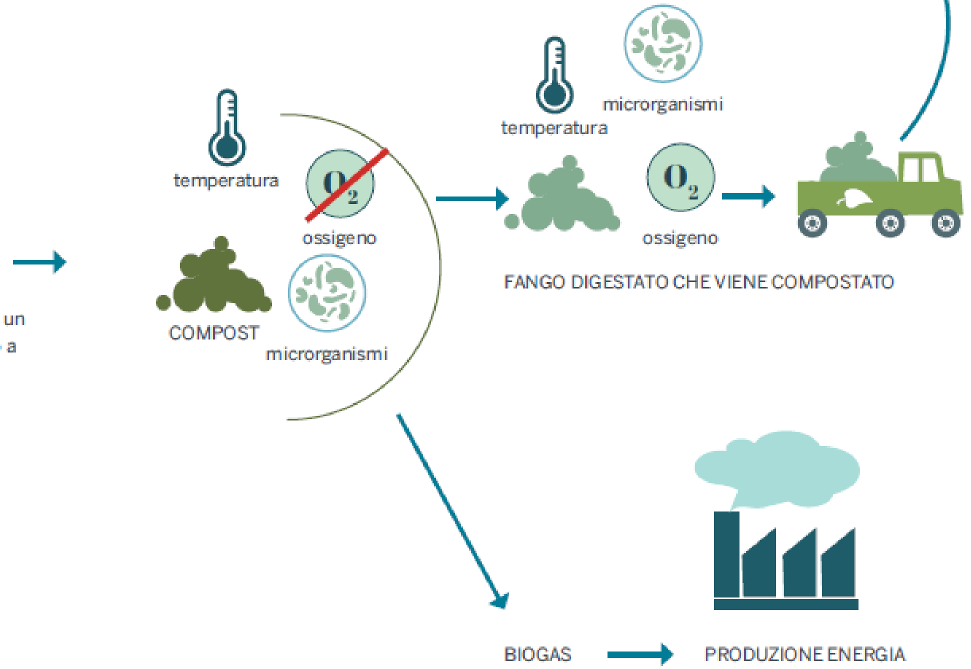
IL COMPOSTAGGIO

Questo processo ha luogo in ambiente a umidità e temperatura controllate, in presenza di ossigeno. Le maggiori quantità di rifiuti organici sono trattate in impianti industriali in cui i processi di compostaggio raggiungono temperature di 70°C. Quando il compostaggio è operato individualmente, come attività di giardinaggio su piccola scala, viene chiamato “compostaggio domestico” nel quale si raggiungono temperature meno elevate.



LA DIGESTIONE ANAEROBICA

È un altro processo di trattamento dei rifiuti organici. La sostanza organica è degradata da parte di microrganismi, in assenza di ossigeno, e si trasforma in biogas, utilizzabile per produrre energia e un fango chiamato digestato che, sottoposto a compostaggio dà origine a compost.



La compostabilità

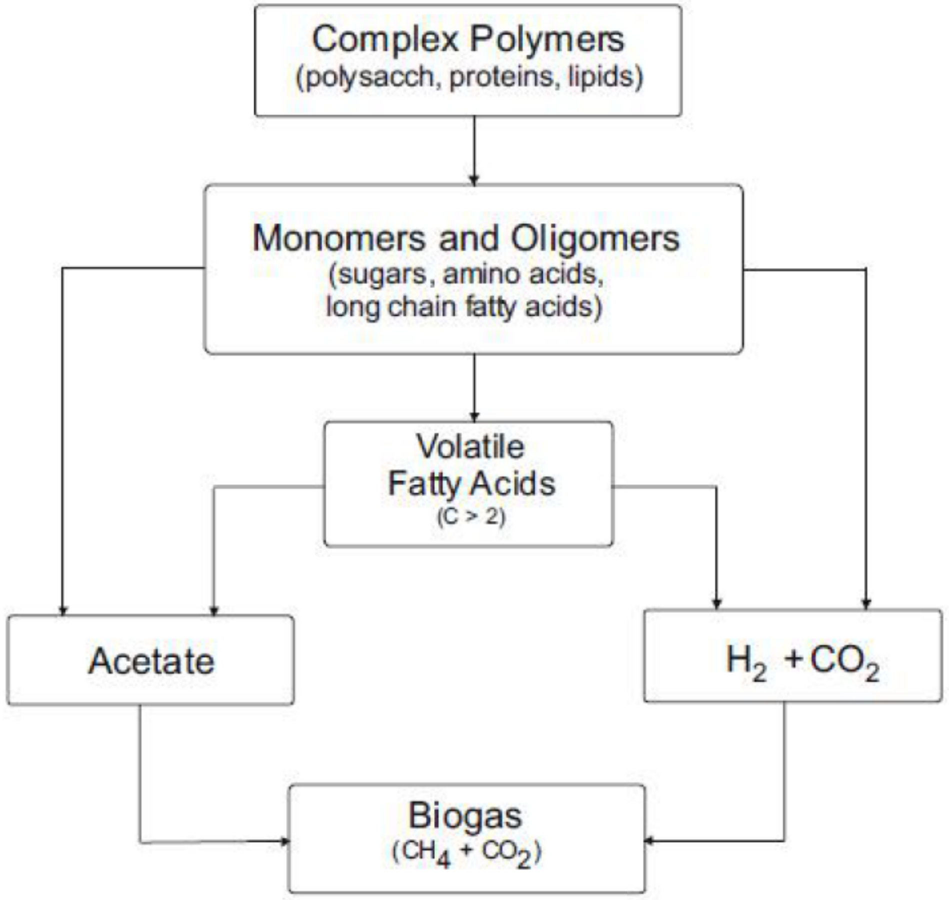
È la capacità di un materiale organico, animale o vegetale, di decomporsi trasformandosi in una miscela di sostanze detta compost, utilizzata in agronomia come fertilizzante e ristrutturante del terreno. Il processo che porta alla formazione di questo ammendante agricolo è detto compostaggio.

Anaerobic digestion

Performed by a microbial consortium, which has the ability to self acclimate to the inherent variability of the feedstock composition.

Volatile fatty acids are converted into acetate and hydrogen by hydrogen-producing **acetogenic bacteria.**

At the end of the degradation chain, different groups of metanogenic bacteria are involved in the **methane production from acetate and from hydrogen and carbon dioxide.**



Bio-based polymers and plastics: families of products, their biodegradability depends on the specific formulation

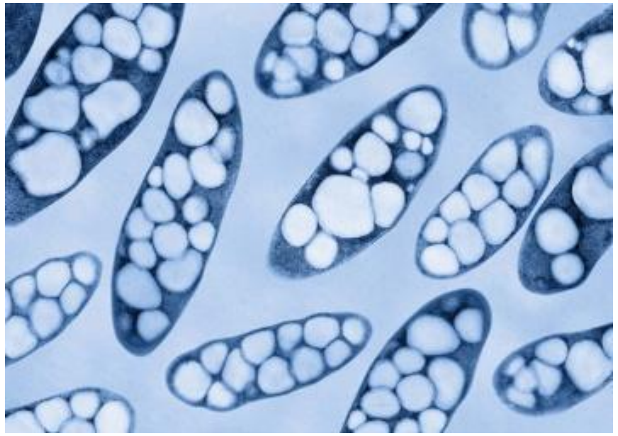
WATER OK bio-degradable TÜV AUSTRIA WATER

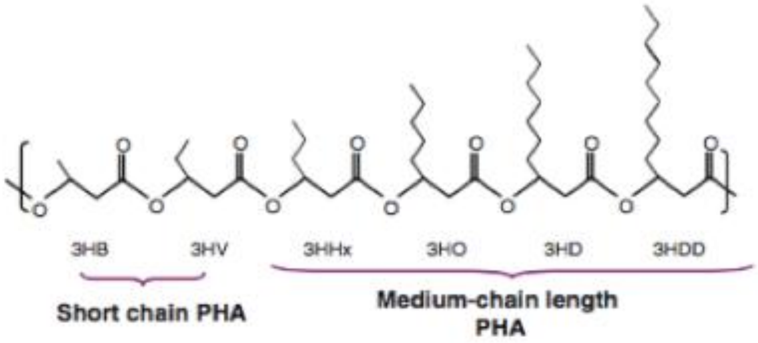
OK compost TÜV AUSTRIA INDUSTRIAL

SOIL OK bio-degradable TÜV AUSTRIA SOIL

Polymers from engineered microbes

Polyesters	Polyhydroxyalkanoates



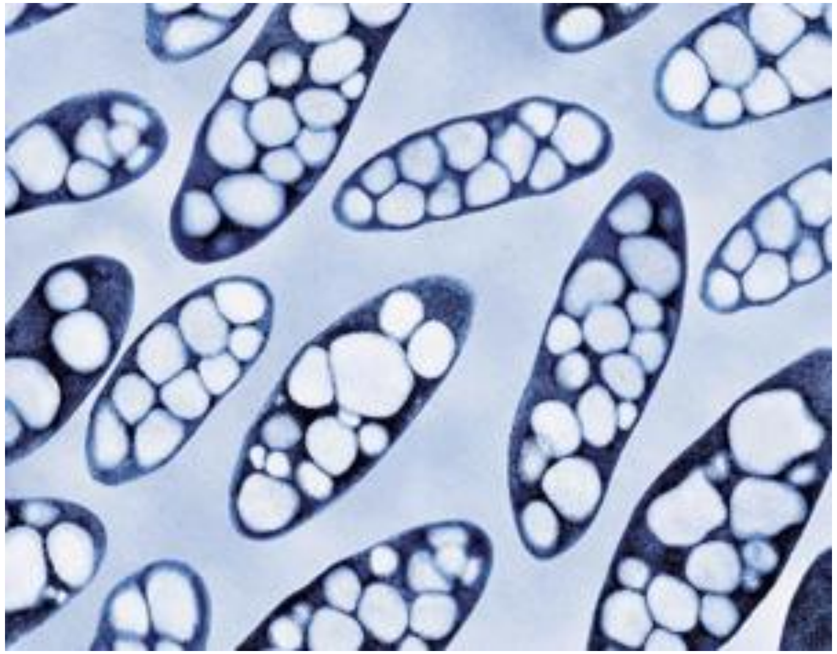


Common PHA monomers

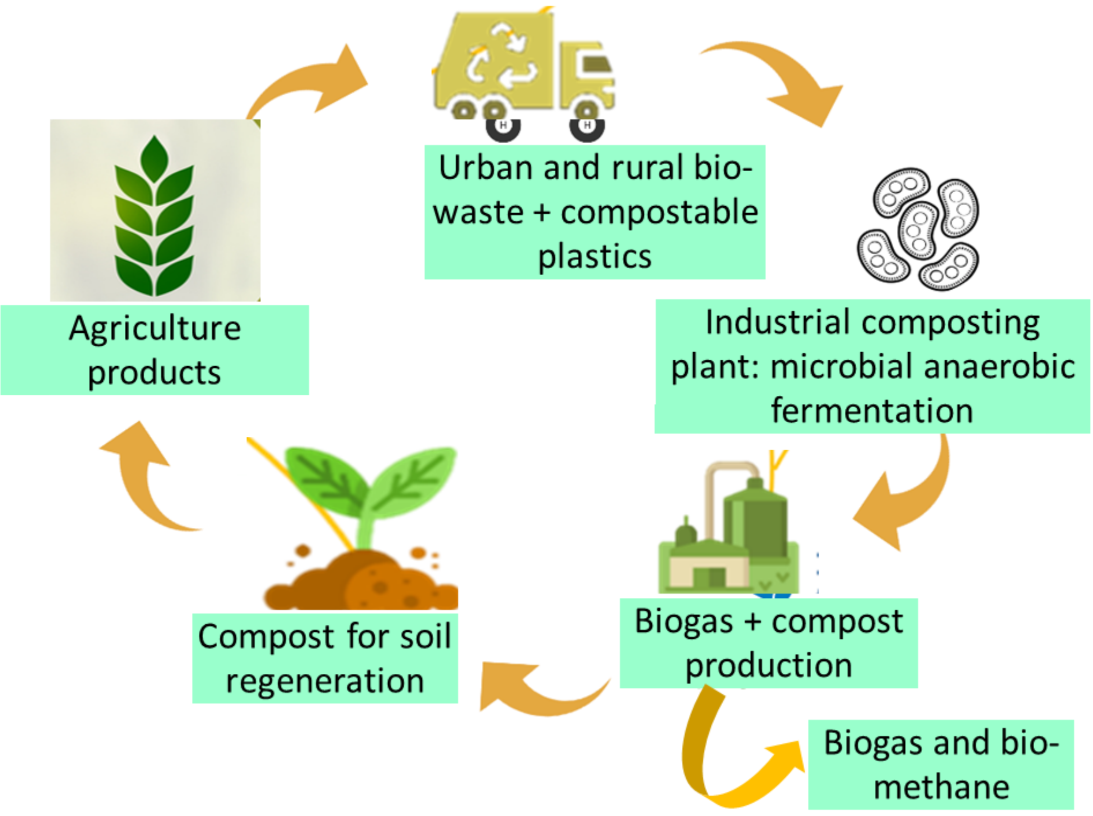
Polyhydroxyalcanoates (PHA)

- Polyester (thermoplastic) produced by microorganisms in response to conditions of physiological stress
- Represent a form of energy storage molecule to be metabolized when other common energy sources are not available

Current production based on sucrose, glucose
Established methodology using waste sources
- whey (lactose, salt conditions)
- glycerol
- bone and meat meal (N source)
- animal fats



Biological recycling of bio-waste and industrially biocompostable plastics



A. Pellis, M. Malinconico, A. Guarneri, L. Gardossi *New Biotechnol.* **2021**, *60*, 146-158.

Compostable plastic materials must have the following characteristics:

- **Biodegradability, meaning a material's capacity to be converted into carbon dioxide (CO_2) through the action of microorganisms, under the same process occurring in natural waste.**
- Being fragmented and gragments must be invisible in the final compost
- Absence of negative effects on the composting process.
- Almost complete absence of heavy metals and the absence of negative effects on compost quality.

European standard **EN 13432**

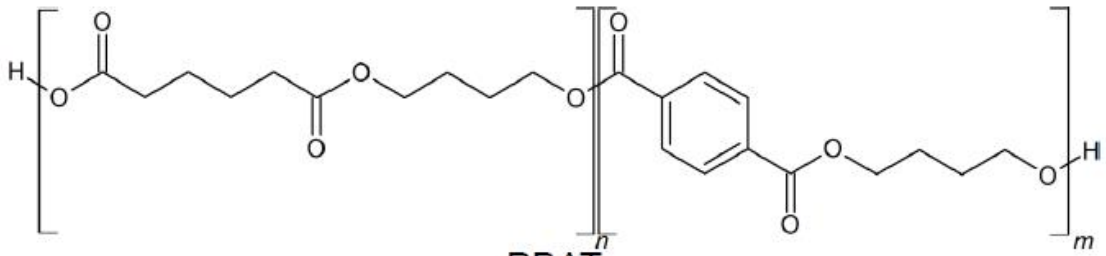
New biodegradable polymers?

Poly(butylene adipate-*co*-butylene terephthalate) (PBAT)

Monomer	Biotechnological route	Company	Status
Sorbitol	Fermentation + hydrogenation	Roquette, ADM	Market
Isosorbide	Sorbitol dehydration	Roquette	Market
Ethylene glycol	Ethanol dehydration	India Glycols Ltd, Greencol Taiwan	Market
1,3-propanediol	Fermentation	Du Pont, Tate & Lyle, Metabolic Explorer	Market
1,4-butanediol	Fermentation, succinic acid hydrogenation	BioAmber, Genomatica, Mitsubishi	Market
Adipic acid	Fermentation + hydrogenation	Celexion LLC, BioAmber, Rennovia, Verdezyme	Market
Itaconic acid	Fermentation	Qingdao Kehai Biochemistry, Itaconix	Market
Lactic acid	Fermentation	Nature Works, BASF, Purac, Cargill, BBCA, Galactic	Market
Succinic acid	Fermentation	BioAmber, Myriant, Reverdia, BASF, Purac, Succinity	Market
Terephthalic acid	Isobutylene oxidation, fermentation	Virient, Annellotech, Genomatica	Pilot plant
Levulinic acid	Fermentation, acid treatment of C6 sugars	GFBiochemicals, Bio-on, Biofine Renewables	Market
Malic acid	Fermentation	Novozymes	Pilot plant
2,5-furandicarboxylic acid	Fermentation + dehydration + oxidation	Avantium	Pilot plant

Novamont, IT

Pellis et al. **2016**, *Trends Biotechnol.*, 34, 316-328



PBAT

Poly(butylene adipate-*co*-butylene terephthalate) (PBAT)

Ecoflex®

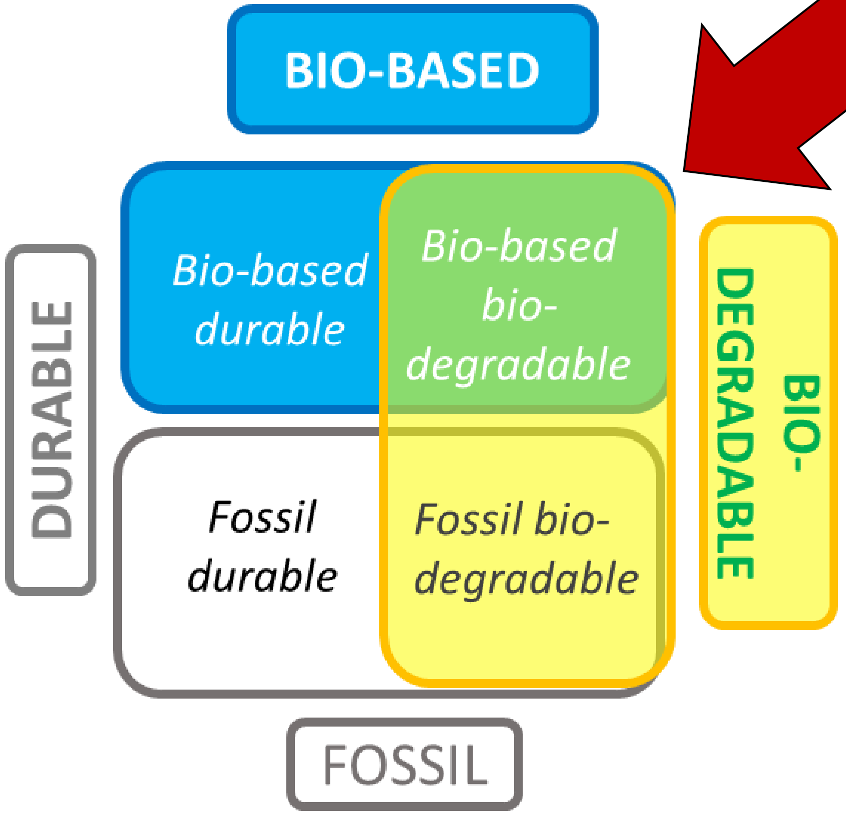
BASF
We create chemistry

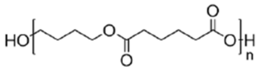
- ✓ the ideal blend component for bioplastics
- ✓ certified compostable and biodegradable
- ✓ elastic as well as water and tear resistant
- ✓ processable on conventional blown film plants (for polyethylene)
- ✓ printable and weldable
- ✓ suitable for food contact

Entirely Fossil-based!!!

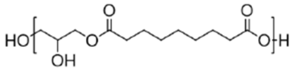
ıttps://plastics-rubber.basf.com/global/en/performance_polymers/products/ecoflex.html

Why eco-design of biodegradable bio-based polyesters?





poly(butileneadipate)
adhesives, coatings



poly(glycerolazelate)
cosmetic, dermatological formulations

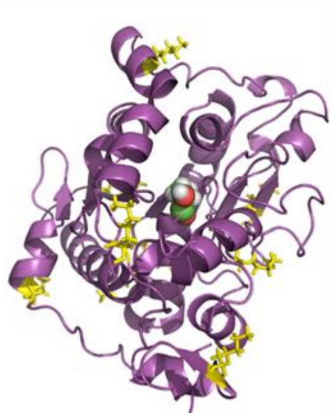
High risk of being dispersed in open environments because of their final use

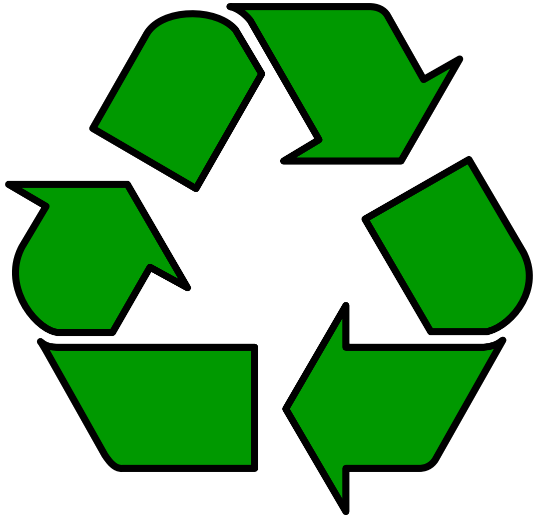
C. CALDEIRA, R. FARCAL, A. GARMENDIA AGUIRRE ET AL., *Safe and sustainable by design chemicals and materials. Framework for the definition of criteria and evaluation procedure for chemicals and materials*, 2022; EUR 31100 EN, Publications Office of the European Union, Luxembourg, 2022, ISBN 978-92-76-53280-4, doi:10.2760/404991, JRC128591.

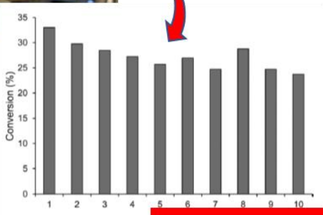
The process: enzymatic solvent-less polycondensation of bio-based monomers

- Selective
  Ok for multifunctional monomers
- Efficient under milder conditions (50-70° C)
  Ok for labile monomers
- No need of toxic metal catalysts
- Solvent-free synthesis feasible
- Low molecular weight products

Lipase B
Candida antarctica

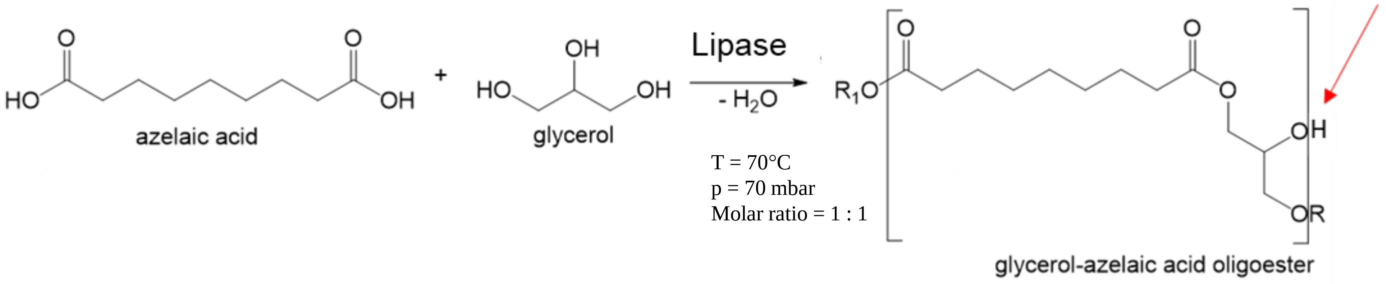






Enzyme recyclable

M_n 926 Da

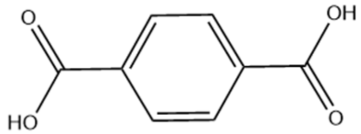


A. Guarneri et al. Adv. Synth. Cat., 2019, 361, 2559-2573 A. Pellis et al. Green Chem., 2017, 19, 490-502. A. Todea et al., *ChemSusChem,* 2022, 15 (9), e202102657

Enzymatic synthesis of 11 model copolymers and terpolymers with Mn < 1000 g/mol for studies of biodegradation and ecotoxicity: analysis from a molecular perspective

- **Overcoming factors such as the crystallinity, shape** and thickness of the debris
- Focus on the selection of **monomers** and the fundamental **chemical structure** of the polymer backbone.

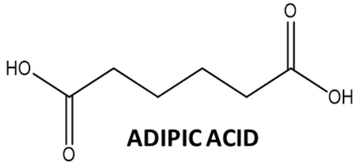
FOSSIL



TEREPHTHALIC

Aromatic TA *vs* FDCA

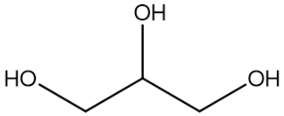
BIO-BASED



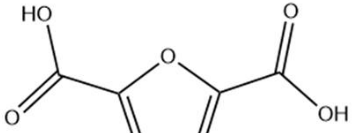
ADIPIC ACID

1,4-BUTANEDIOL

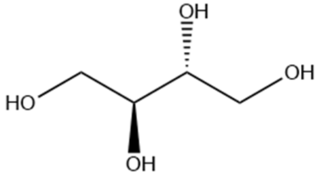
Linear aliphatic AA, BDO



GLYCEROL

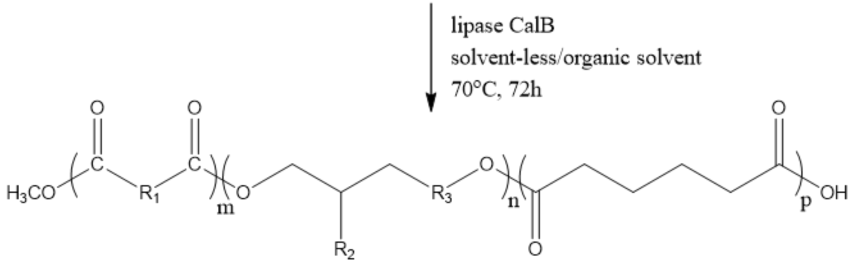


FURANDICARBOXYLIC ACID



ERYTHRITOL

Branched hydrophilic GLY, ERY



Todea et al., . Int. J. Mol. Sci. 2024, 25, 5433.
https://doi.org/10.3390/ijms25105433

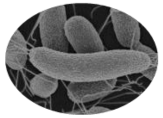
Ecotoxicity studies in sea and fresh water

EC20 and EC50 values from the ecotoxicity tests by using marine organisms (data are expressed as mg/L).

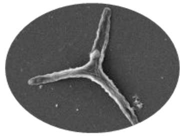
	Aliivibrio fischeri		*Phaeodactylum tricornutum*		*Paracentrotus lividus*	
Samples	EC_{50}	EC_{20}	EC_{50}	EC_{20}	EC_{50}	EC_{20}
BDO-FDCA-AA	**>100**	**95 (15 min); 98 (30 min)**	>100	>100	**74.0**	**46.3**
BDO-TA-AA	**71 (15 min); 75 (30 min)**	**32 (15 min); 40 (30 min)**	>100	>100	**64.5**	**26.4**
AA-GLY-ERY	>100	>100	>100	>100	>100	82.7
AA-GLY-FDCA	>100	>100	>100	>100	>100	>100
BDO-FDCA	>100	>100	>100	>100	**66.6**	**32.3**
GLY-FDCA	>100	>100	>100	>100	**74.3**	**35.3**
GLY-AA	>100	>100	>100	>100	**87.3**	**73.4**
AA-BDO	>100	>100	>100	>100	**87.3**	**73.4**
GLY	>100	>100	>100	>100	100.0	83.0
ERY	>100	>100	>100	>100	>100	>100
FDCA	>100	>100	>100	>100	>100	95.9
BDO	>100	>100	>100	>100	**92.9**	**78.2**
AA	>100	>100	>100	>100	>100	90.9
TA	>100	>100	>100	>100	>100	>100

Values of EC20 and EC50 (mg/L) for the two types of freshwater organisms studied

Sample	*Daphnia magna*		*Raphidocelis subcapitata*	
	EC_{50}	EC_{20}	EC_{50}	EC_{20}
BDO-FDCA-AA	>100	>100	>100	>100
BDO-TA-AA	>100	100 (48 h)	>100	>100
AA-GLY-ERY	>100	**40.9 (48 h)**	>100	>100
AA-GLY-FDCA	56.5 (48 h)	**27.9 (48 h)**	>100	>100
BDO-FDCA	>100	100 (48 h)	>100	>100
GLY-FDCA	>100	100 (48 h)	>100	>100
GLY-AA	>100	100 (24 - 48 h)	>100	>100
AA-BDO	>100	100 (48 h)	>100	**95.6**
GLY	>100	>100	>100	>100
ERY	**72.7 (24 h)**	<100	>100	>100
FDCA	>100	<100	>100	53.0
BDO	>100	>100	>100	>100
AA	**32.5 (48 h)**	**17.9 (48 h)**	>100	**97.3**
TA	>100	>100	>100	>100



Aliivibrio fischeri



Phaeodactylum tricornutum

Paracentrotus lividus

UNI EN ISO 6341:2012
UNI EN ISO 8692 (2012)
UNI EN ISO 11348-3 (2019)
UNI UN ISO 10253 (2016)
EPA/600/R-95-136/

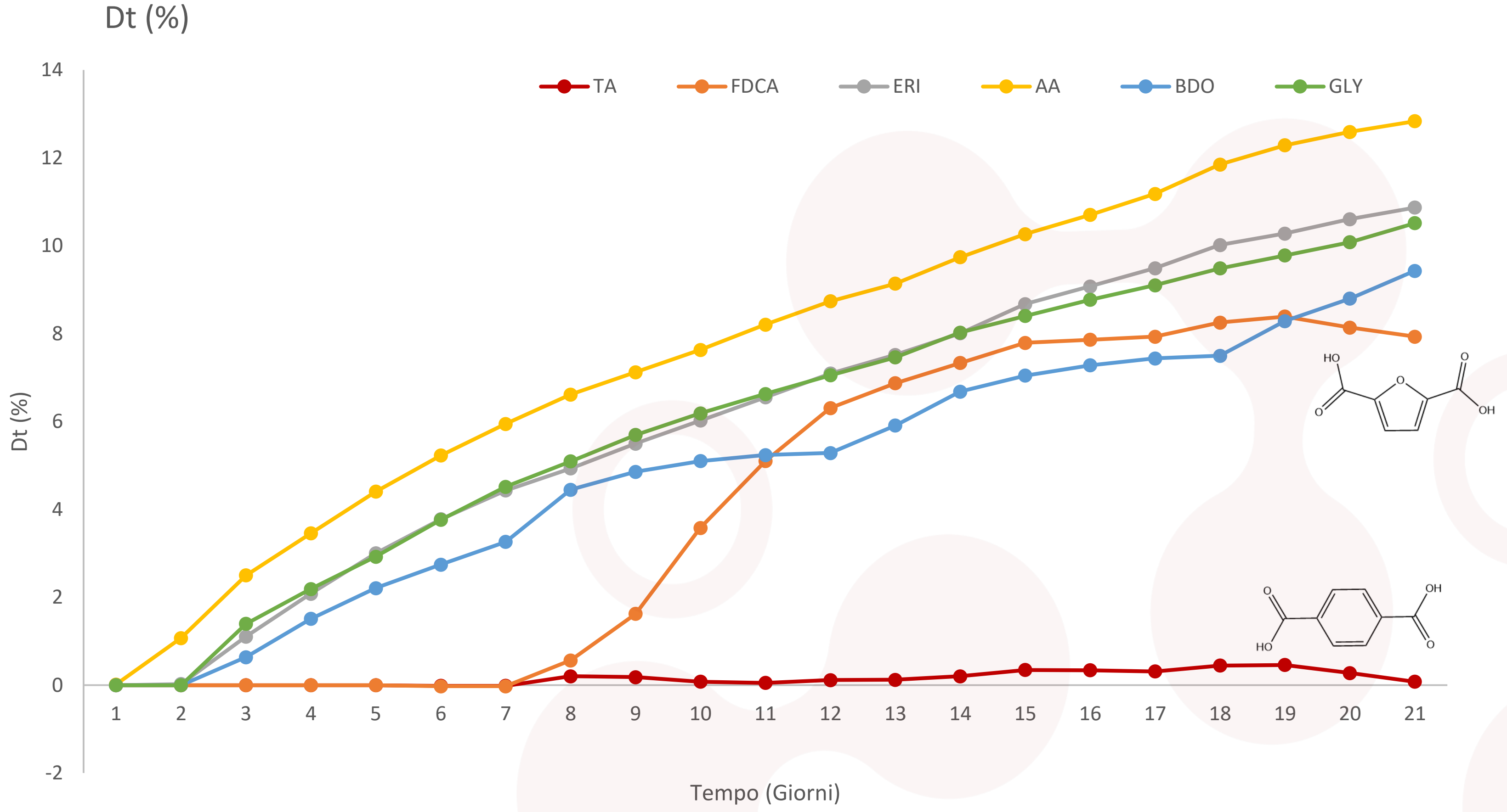
There are encouraging premises for the design of bio-based polymers and plastics which do not harm marine ecosystems.

Daphnia magna

Raphidocelis subcapitata

Todea et al., . Int. J. Mol. Sci. 2024, 25, 5433. https://doi.org/10.3390/ijms25105433

Marine biodegradation → Monomers

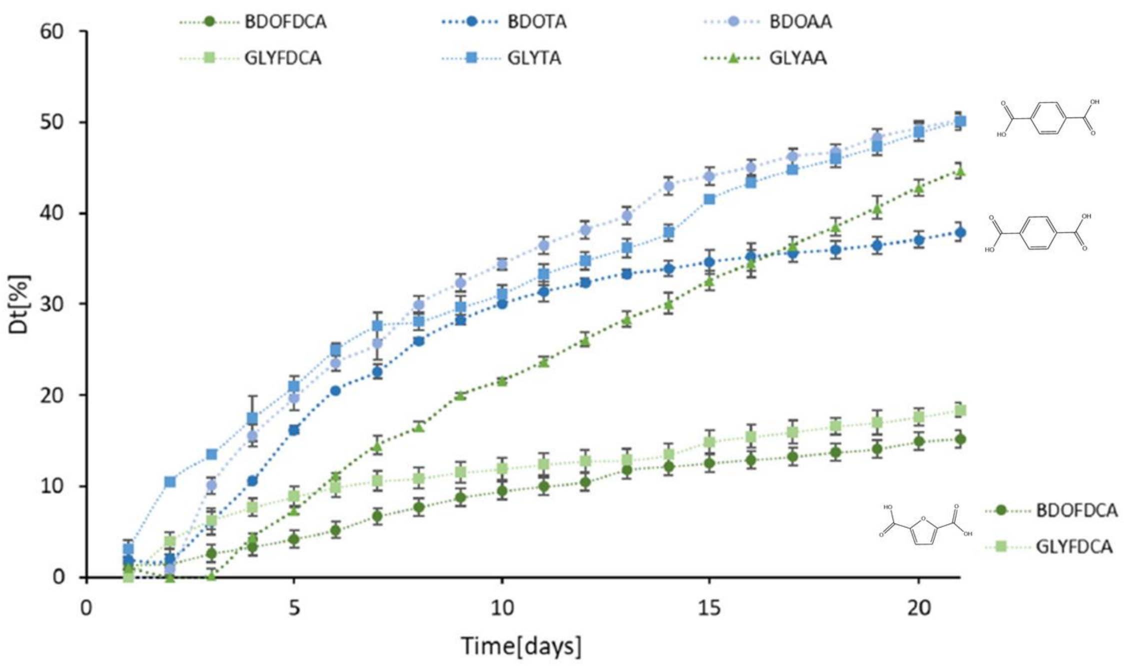


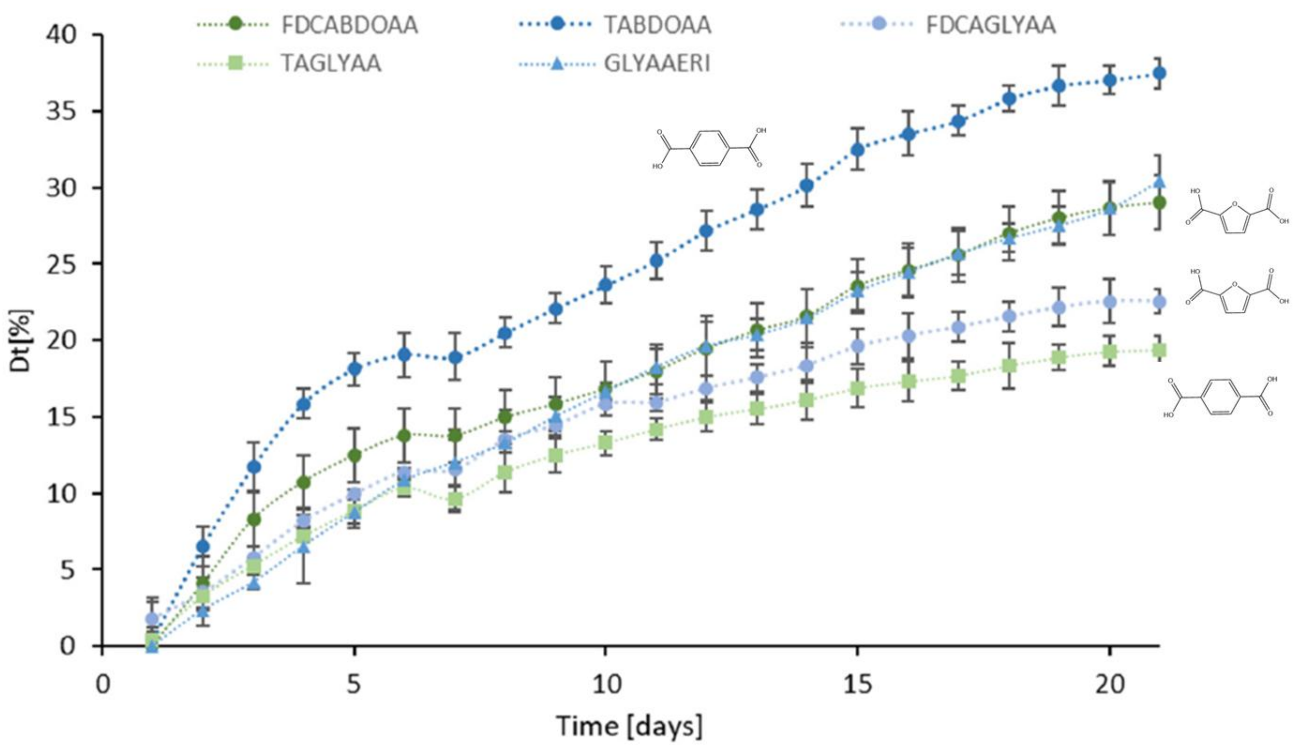
Calculated by measuring for 21-28 days biochemical oxygen demand (BOD) OECD 306 protocol (**sea inoculum)**

ISO 17556:2019

Understanding Marine Biodegradation of Bio-Based Oligoesters and Plasticizers. Polymers 2023, 15, 1536. https://doi.org/ 10.3390/polym15061536.

Marine biodegradation → Oligoesters





- negatively influenced by FDCA
- extended aliphatic portions lead to higher biodegradation

- TA-BDO-AA
- ERY increases the biodegradability

Todea et al., . Int. J. Mol. Sci. 2024, 25, 5433. https://doi.org/10.3390/ijms25105433

Physical-chemical properties correlation

Physical state	Product	T_g [°C]	T_m [°C]	ΔH_m [J/g]	T_c [°C]	Mn	D	Dt (%)
S	GLY-TA	-54.6	109.6	-14.66	90	960,2	1,21	**58,90**
S	BDO-AA	-	45.3	74.27	26.9	/	/	**49.95**
S	BDO-TA	-55.9	89.4	10.63	79.7	694,15	1,2	**46,69**
L	AA-GLY	-41.3	n.d.	n.d.	Am.	887,11	1,41	**46,68**
S	BDO-TA-AA	-21.6	4.5	5.059	96.9	1002,11	1,21	**36,42**
L	GLY-ERI-AA	-28.0	n.d.	n.d.	Am.	844,65	1,35	**34,41**
S	BDO-FDCA-AA	-43.4	74.4	7.154	Am.	844,12	1,06	**26,81**
L	GLY-FDCA-AA	-46.9	n.d.	n.d.	Am.	439,42	1,25	**21,85**
S	GLY-FDCA	-	105.2	93.49	86.7	551,1	1,69	**20,63**
L	GLY-TA-AA	-51.8	16.7 44.5	2.472 0.643	-	474,17	1,31	**18,76**
S	BDO-FDCA	-12.5	92.9 120	7.663 2.046	Am.	635,15	1,16	**17,29**

L= liquid, S=solid

Thermal properties affect biodegradability but they are not fully responsible for the observed variability

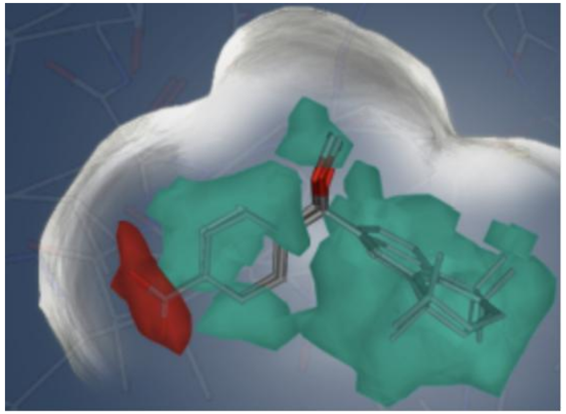
Biodegradability

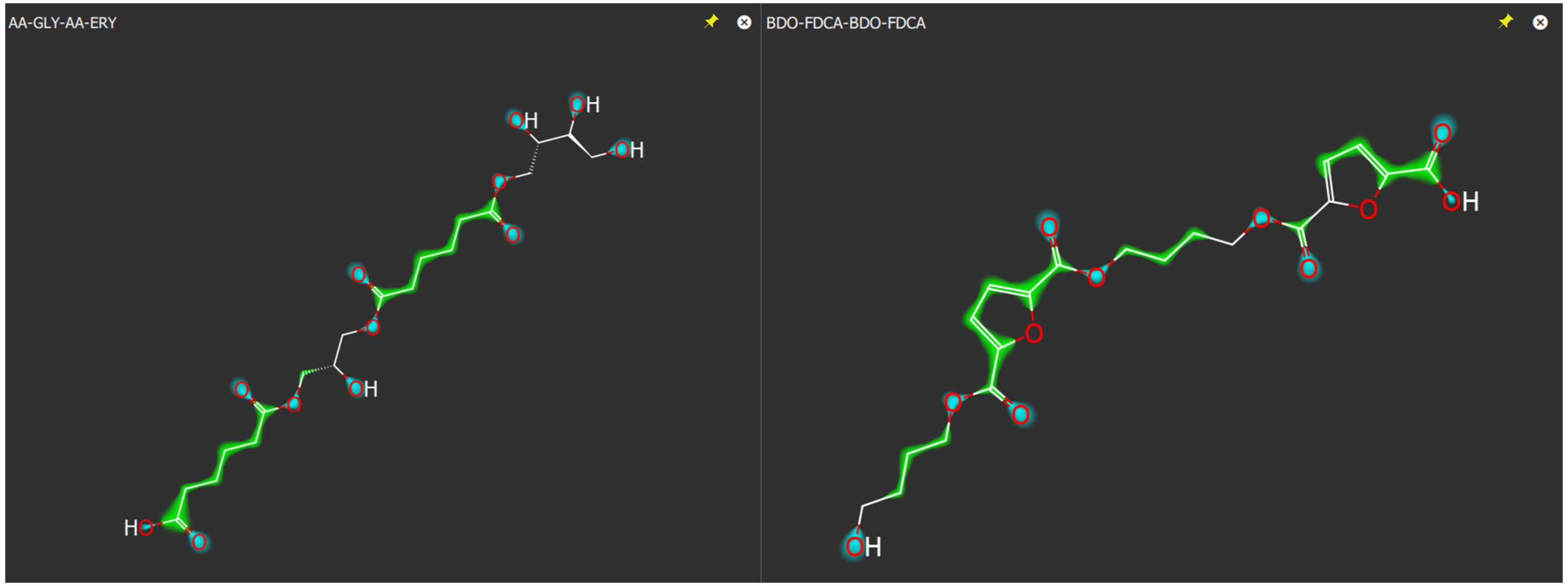
Computational models to correlate the structural and physical-chemical properties of oligoesters with their biodegradability

Prof. Emanuele Carosati

Descriptors based on Molecular Interaction Fields – MIFs

VolSurf[3]





Probes used for the calculation of the descriptors :
DRY (hydrophobic probe)
OH2 (water probe)
O (carbonyl probe)
N1 (amide nitrogen).

For more details on the computational data-analysis visit poster P7

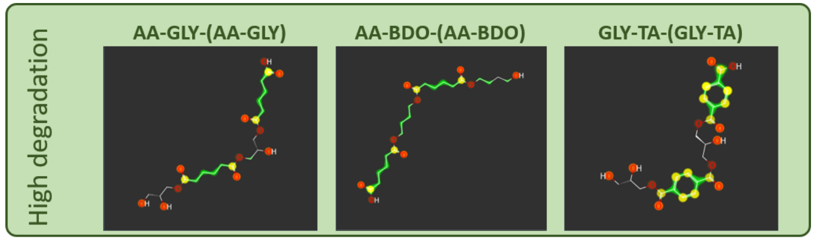
Todea et al., . Int. J. Mol. Sci. 2024, 25, 5433.
https://doi.org/10.3390/ijms25105433

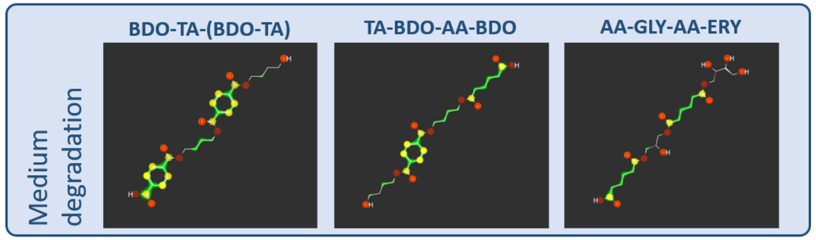
Computational analysis of tetramer structures using VolSurf³ molecular descriptors: Partial Least Square statistical analysis

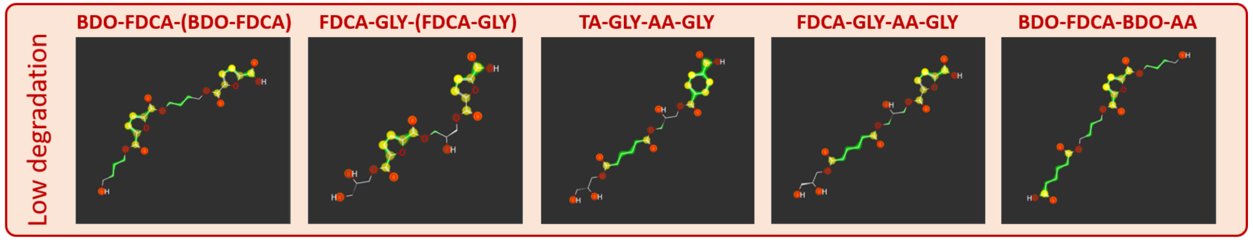
Chemical structures of the oligoesters.

yellow = apolar atoms,
red = polar atoms,
green = hydrophobic atoms

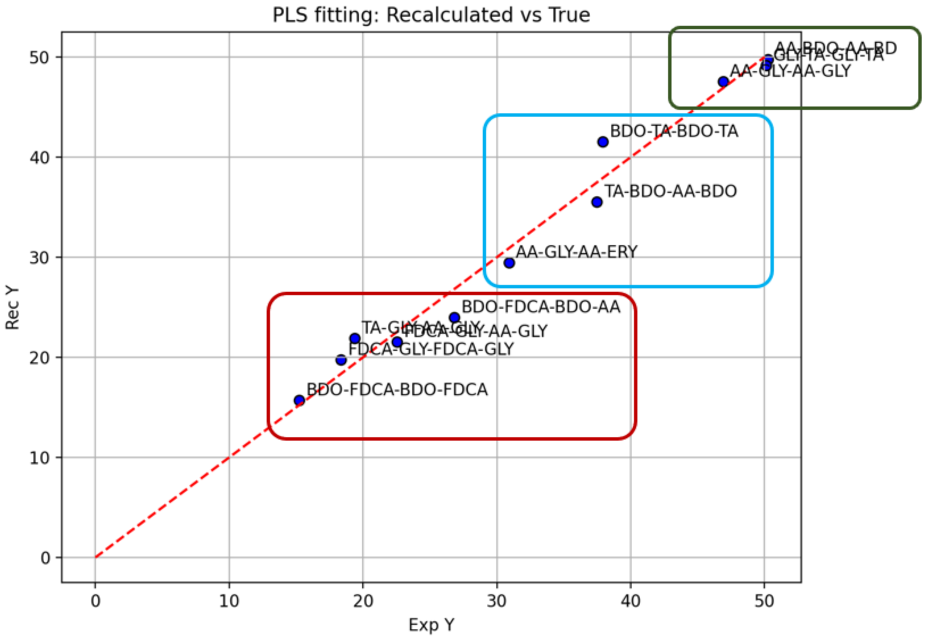
Exp Y







Partial Least Square (PLS) as regression method, with a dataset of 11 molecules. Model with five latent variables: $R^2 = 0.98$ and $Q^2 = 0.57$



PLS fitting graph

For more details on the computational data-analysis visit poster P7

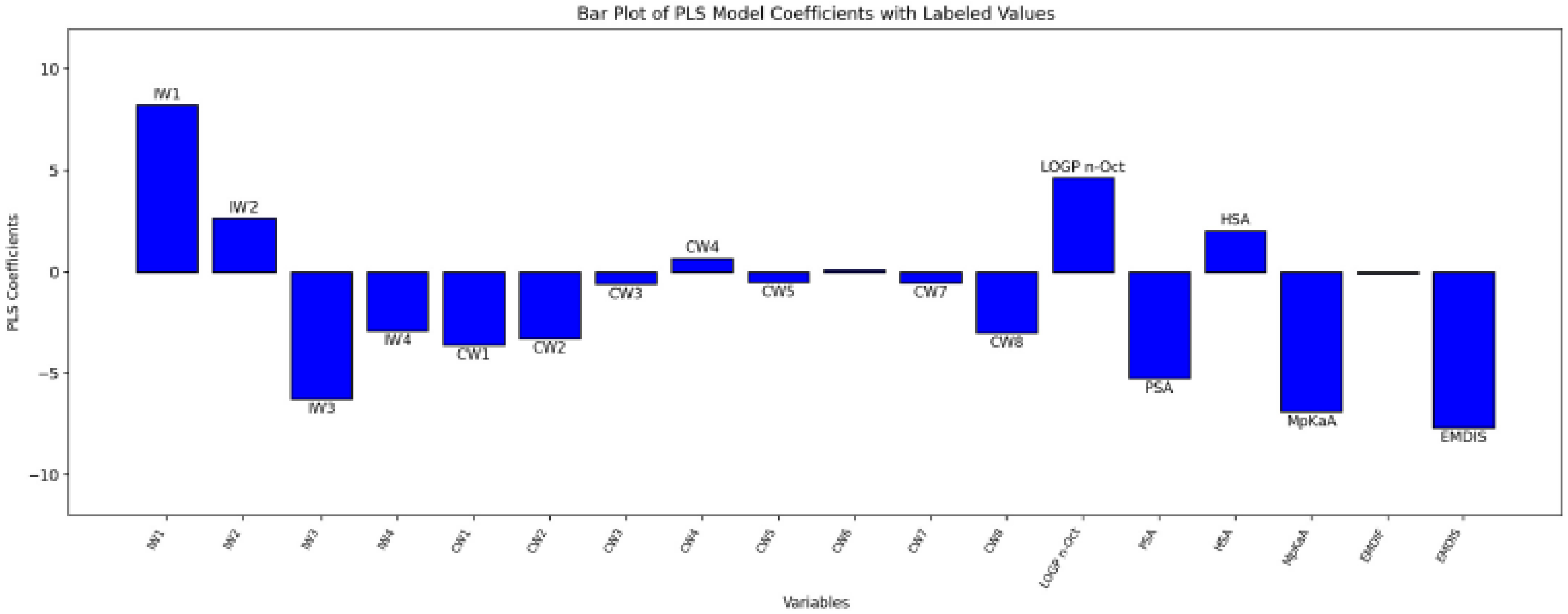
Todea et al., . Int. J. Mol. Sci. 2024, 25, 5433. https://doi.org/10.3390/ijms25105433

Computational analysis of tetramer structures using VolSurf[3] molecular descriptors

PLS coefficients:

- Positive values: direct relationship with biodegradability
- Negative values: indicate a direct relationship with stability

Biodegradability depends on the balance of both distance and volumes of hydrophilic and hydrophobic atoms



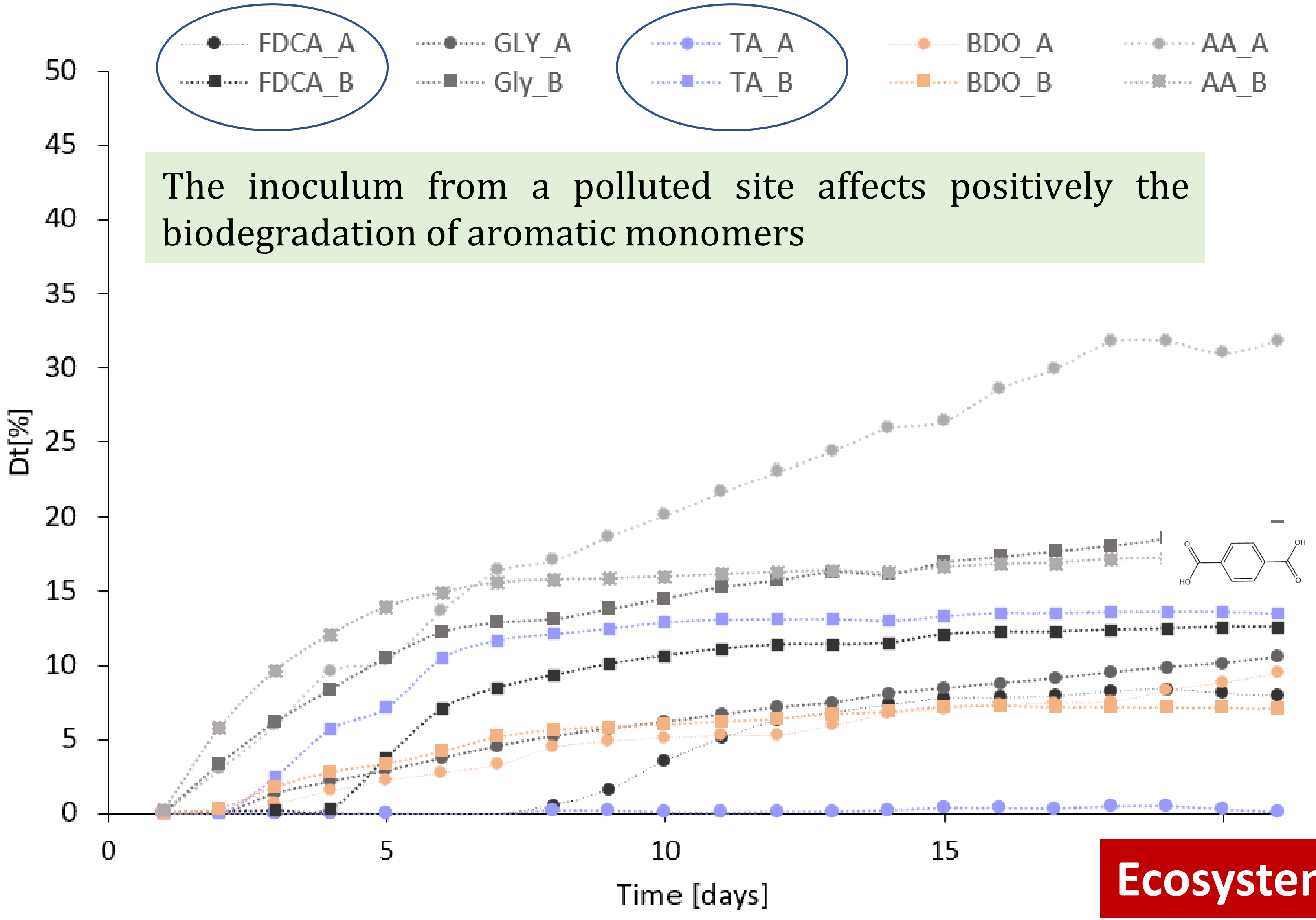
Todea et al., . Int. J. Mol. Sci. 2024, 25, 5433. https://doi.org/10.3390/ijms25105433

IW1: Variable derived from the calculation of hydrophilic interactions, highlighting the importance of the distance between hydrophilic and hydrophobic moieties.

EMDIS: distance between atoms with polar and apolar interactions.
Less biodegradable oligomers have larger distances between polar and apolar moieties.

IW3 and IW4 numerically describe the hydrophilic volumes when they are very close to each other: negative effect on biodegradability

Marine biodegradation with different inocula → Monomers



The inoculum from a polluted site affects positively the biodegradation of aromatic monomers

Area close to a sewer pipe, a water treatment plant, and an oil tanker terminal

Ecosystems adapt to chemical pollutants

Thank you for your kind attention!

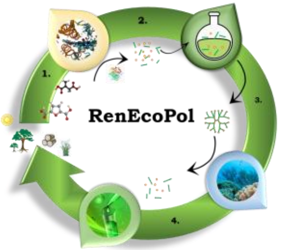
Acknowlegements

Softwares

Gabriele Cruciani
Lydia Siragusa

MOLECULAR DISCOVERY

Fundings



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Acque del Friuli

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