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ICCE 2023, 13 June 2023, Venice

What can we learn from biodegradation of natural polymers for regulation?

Stefan Hahn, Dieter Hennecke

« Four major challenges have been identified for assessing polymer biodegradation: lack of standardization, long duration required, demanding analytical methods, lack of a framework «

Albright and Chai
Environ Sci Technol 55 (2021),11476-11488

« RAC recommends that additional research is undertaken to explore and understand the applicability of REACH Annex XIII half life criteria to particulate materials «

ECHA/RAC/RES-O-0000006790-71-01/F („**RAC Opinion**“), 11. Juni 2020

Background

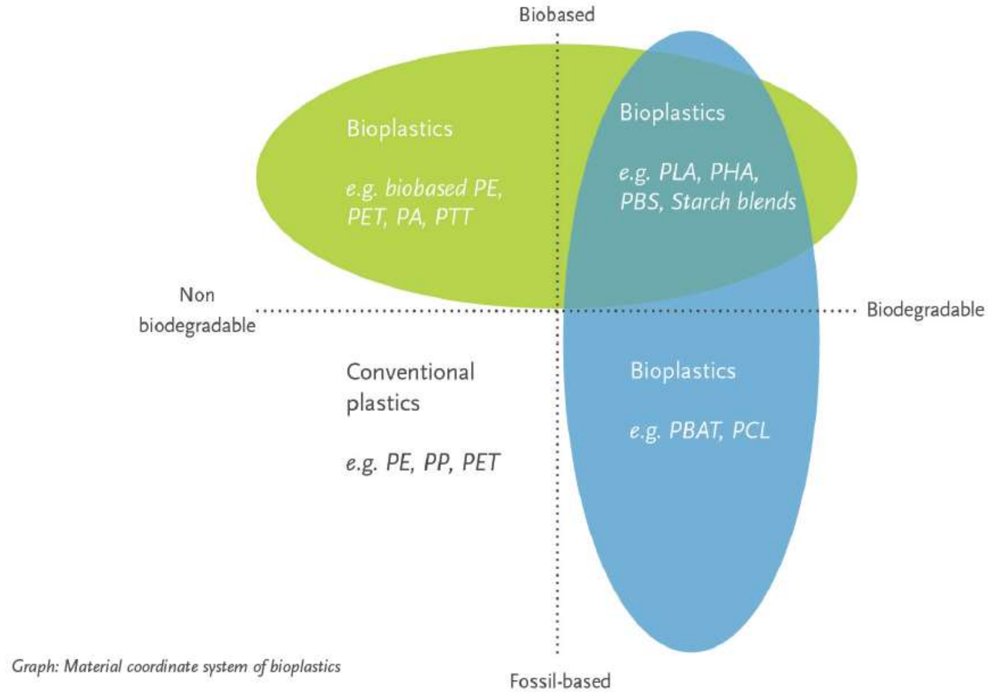
Types of polymers

Properties

- Structural
- Morphological
- PC data: water solubility, density, …
- Behaviour: thermoplastic, thermoset, elastomere

Groups

- Biodegradable and non biodegradable plastic
- Fossil-based and biobased



Material coordinate system of plastics according to European Bioplastics (2018)

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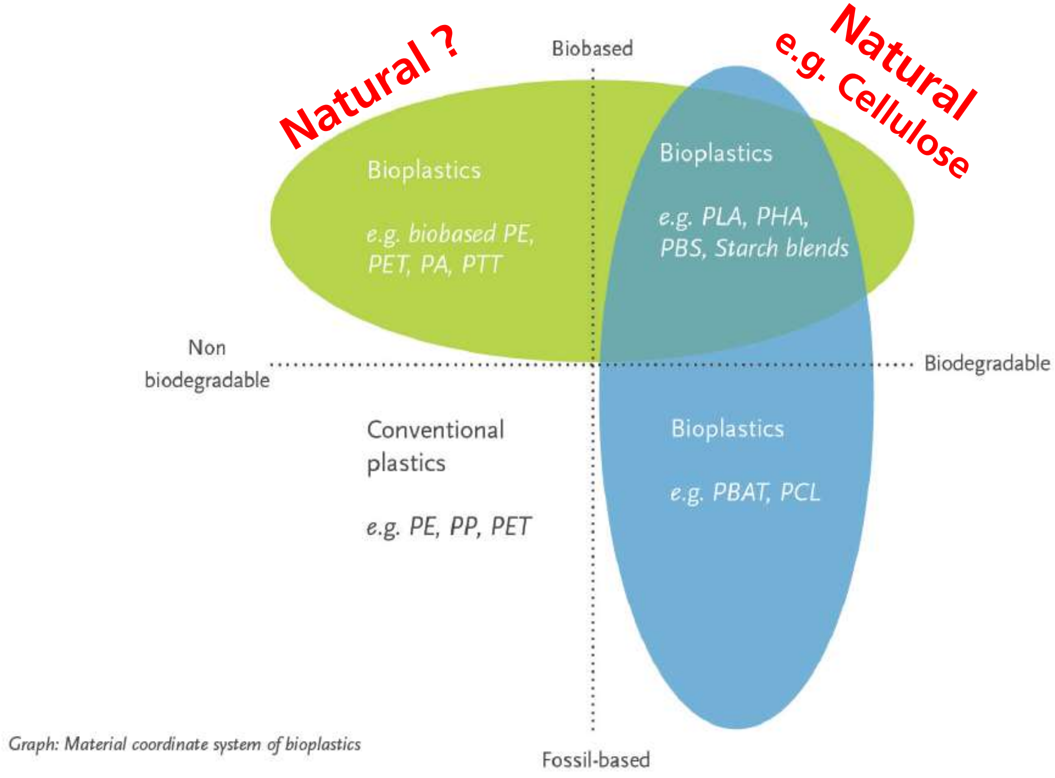


Material coordinate system of plastics according to European Bioplastics (2018)

Background

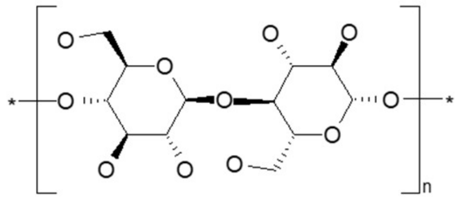
Natural polymers

Type and properties

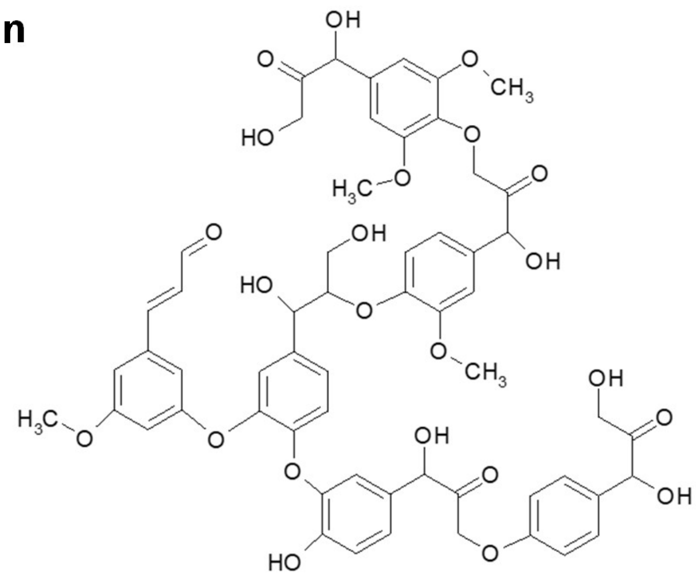
- Often polysaccharides with weak α-glycosidic bonds or stronger β-glycosidic linkages,
  - starch, cellulose, ...
- But also more complex structures:
  - hemicellulose, lignin, cutin, chitin,…,
- Natural rubber

- Crystalline, semi-crystalline or amorphous
- Often insoluble
- Hydrophilic but also hydrophobic

Cellulose



Lignin



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Environmental fate of polymers

Natural polymers

Occurrence and distribution

- Soil
  - Top soil
  - Amount and type depends on vegetation, climate, etc.
  - Humification, humic acids
  - Mineralization takes often several years

- Aquatic
  - Deposit to sediment
  - Particle tansport with sediment

Table: Components of natural materials (%dry materials)

	Wheat straw	Spruce	Birch
Lignin	11-26	29-34	24-26
Cellulose	32-45	38-47	35-44
Hemicellulose	20-45	18-22	26-30
Starch	0-3	-	-

adapted from Zhang L, Larsson A, Moldin A,Edlund U (2022) Comparison of lignin distribution, structure, and morphology in wheat straw and wood. Industrial Crops and Products, 187

Natural polymers

Information on degradation using standard tests (OECD, ISO, ASTM)

- OECD 301B (McDonough et al. 2017), 125 – 500 µm
  - Jojoba wax, beeswax > 60% in 28 days
  - Walnut shells < 10%

- Aquatic
  - ISO 14851, 14852 or 14853
  - Test period typically not exceeding 2 month
  - Cellulose as reference
    - validity criterion > 60% at the end
    - usually > 70% in 28 days

- Soil
  - ASTM 5998, ISO 17566
  - Cellulose as reference
    - ASTM > 70% in 6 month
    - ISO > 60% at plateau or at end (6 month)
  - e.g. Gomez and Michel (2013)
    - Other natural polymers or materials significantly lower degradation rate

Natural polymers

Information on degradation using non-guideline studies

Lignin

- e.g. Polman et al 2020, Thevenot et al 2010, Kögel-Knabner 2002
- Laboratory 19-60% degradation in up to 2 years
- Field studies: degradation up to 5 years
- Fungi

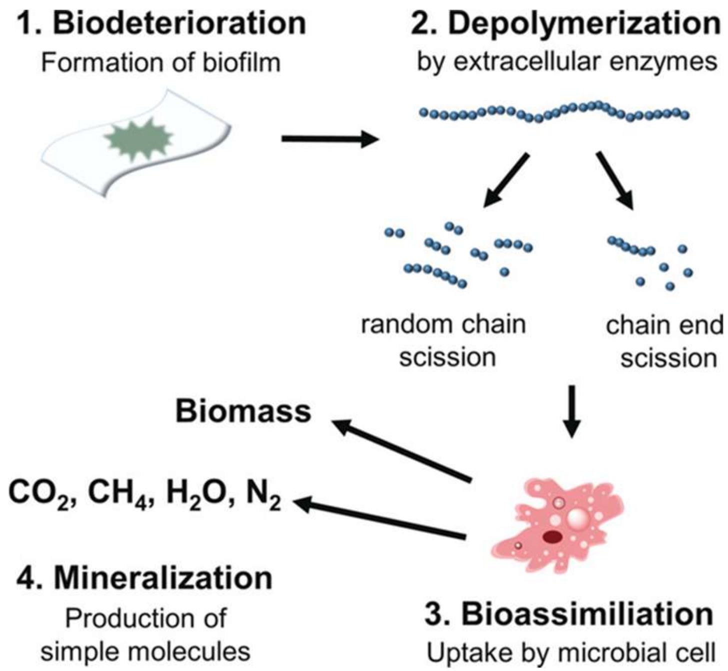
Cutin

- e.g. Kolattukudy 1981, Heredia-Guerrero et al 2017
- Extracellular polymer
- Enzymatic hydrolysis (cutinase) as an important pathway
- Fully hydrolyzed by soil microorganisms in a period of 3–8 months

Distribution and Degradation pathway of polymers

Processes for polymer (bio)degradation

- Natural and synthetic polymers undergo several processes
- Starting point of polymer fragmentation and degradation is often photolysis and/or hydrolysis
- Sequential degradation of chain length expected
- Four steps of polymer (bio)degradation:
  i. biodeterioration
  ii. depolymerisation
  iii. bioassimilation
  iv. mineralisation



Taken from:

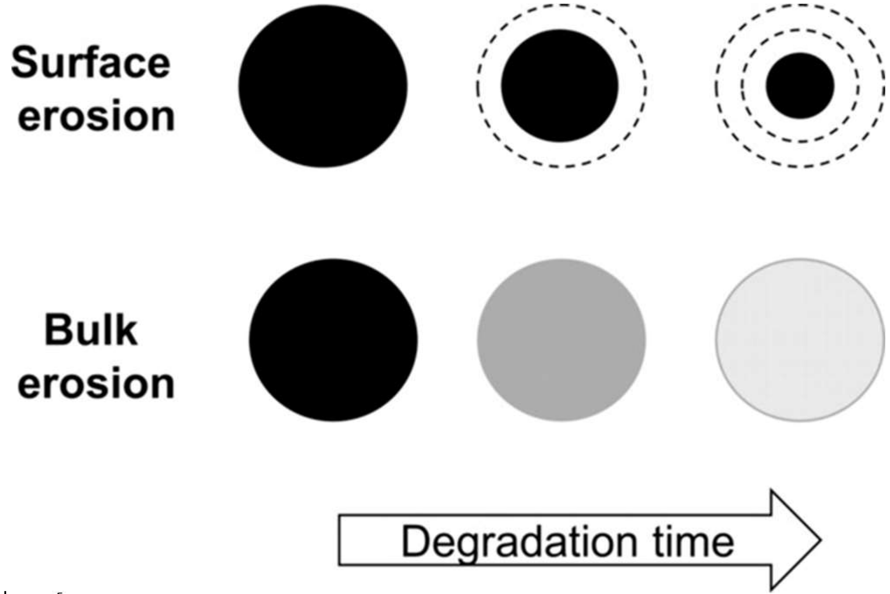
Haider TP, Volker C, Kramm J, Landfester K,Wurm FR (2019) Plastics of the Future? The Impact of Biodegradable Polymers on the Environment and on Society. Angew Chem Int Ed, Volume: 58, Issue: 1, Pages: 50-62, First published: 04 July 2018, DOI: (10.1002/anie.201805766) .

Environmental fate of polymers

Distribution and Degradation pathway of particles

Solid particles

1. Disintegration or fragmentation of particles
2. Change of surface properties
3. Surface erosion or bulk erosion
   - Bulk erosion, e.g. hydrolysis
     - ✓ Small catalysts (e.g., organic acids) or reagents (water) diffuse into polymer systems
     - ✓ The number of particles will change but not the total mass of the particles
   - Surface erosion, e.g. enzymatic degradation
     - ✓ The size of the particles will change but not the number of the particles



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Take Home Message

What can we learn from natural polymers?

Framework should include several building blocks

Weight-of-evidence (WoE) using ECHA template

1 Natural polymers:
- ✓ are considered as biodegradable
- ✓ having no concern for the environment
- ✓ building blocks of humus, which is crucial for soil functions

2 Persistency assessment:
- ✓ some natural polymers would have to be regarded as P/vP
- ✓ mineralization a meaningful endpoint?

3 Natural polymer degradation
- ✓ stepwise process, slowest step triggers mineralization
- ✓ depolymerisation an alternative endpoint for primary degradation?

4 To be considered
- ✓ processes relevant for polymer degradation in the environment are not considered in current standard degradation testing

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Acknowledgements

Research team
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Graham Whale (Whale Environmental Consultancy Ltd)
Chris Hughes, Megan Griffiths, Chesney Swansborough, Eleonore Delouvrier, Emma Pemberton, David Brown (Ricardo)

CEFIC LRI and the Monitoring team

Thank you for your attention!