Biodegradation and Compostability

Biopolymers
CHEM-E2155

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School of Chemical
Engineering

Schedule

Day	Subject of lecture	Discussion part
08 January	Introduction to the course	
15 January	Biopolymers overview	Reading 1
22 January	Biopolymers for packaging	Reading 2
29 January	Discussion day	Reading 3 & Assignment 1
05 February	Biodegradation 1	Reading 4
12 February	Biodegradation 2	Reading 5
26 February	Discussion day	Reading 6 & Assignment 2
04 March	Chitin, alginates and others	Reading 7
12 March	Proteins	Reading 8
19 March	Discussion day	Reading 9 & Assignment 3
25 March	TBD	Reading 10

Content

- **Definitions**
- **Biodegradation and composting**
- **Test Methods**
- **Photodegradation and Oxo-degradable Plastics**

- Degradation of Polymers
  (Bio-based,Synthetic & Modified Natural Polymers)
- Factors and mechanisms of Biodegradation
- Polymers as biomaterials

Next session

Learning Outcomes

After today’s course you

- are familiar with different standards for biodegradation and compostability
- can name different test methods
- know the difference between oxo-degradation and photodegradation

What is the definition of Biodegradation and composting?

Definitions

- ASTM D1566 **polymer**: “a macromolecular material formed by the chemical combination of monomers having either the same or different chemical composition”
- ASTM D1695a **plastic**: “a material that contains as an essential ingredient an organic substance of large molecular weight, is solid in its finished state, and, at some stage in its manufacture or in its processing into finished articles, can be shaped by flow.”
- **ASTM D883-93: degradable, biodegradable, hydrolytically degradable, and oxidatively degradable plastics (applicable to polymers)**

Source: Swift, G. 2000. Polymers, Environmentally Degradable. Kirk-Othmer Encyclopedia of Chemical Technology

Definitions used in relation to biodegradable plastics

DIN FNK 103.2	Biodegradable plastics[(1)]: if all its organic compounds undergo a complete biodegradation process. Environmental conditions and rates of biodegradation are to be determined by standardized test methods.
	Biodegradation[(3)]: process, caused by biological activity, which leads under change of the chemical structure to naturally occurring metabolic products.
ASTM sub-committee D20-96	Biodegradable plastics[(1)]: A degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae.
Japanese Bio-degradable Plastics Society	Biodegradable plastics [(1)]: Polymeric materials which are changed into lower molecular weight compounds where at least one step in the degradation process is though metabolism in the presence of naturally occurring organisms.
ISO 472	Biodegradable plastics[(1)]: A plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and the application in a period of time that determines its classification. The change in the chemical structure results from the action of naturally occurring microorganisms.
CEN	Biodegradable plastics[(1)]: A degradable material in which the degradation results from the action of micro-organisms and ultimately the material is converted to water, carbon dioxide and/or methane and a new cell biomass.
	Biodegradation[(2)]: Biodegradation is a degradation caused by biological activity, especially by enzymatic action, leading to a significant change in the chemical structure of a material
	Inherent biodegradability [(2)]: The potential of a material to be biodegraded, established under laboratory conditions.
	Ultimate biodegradability [(2)]: The breakdown of an organic chemical compound by microorganisms in the presence of oxygen to biodegradability carbon dioxide, water and mineral salts of any other elements present (mineralization) and new biomass or in the absence of oxygen to carbon dioxide, methane, mineral salts and new biomass.
	Compostability[(2)]: Compostability is a property of a packaging to be biodegraded in a composting process. To claim compostability it must have been demonstrated that a packaging can be biodegraded in a composting system as can be shown by standard methods. The end product must meet the relevant compost quality criteria.

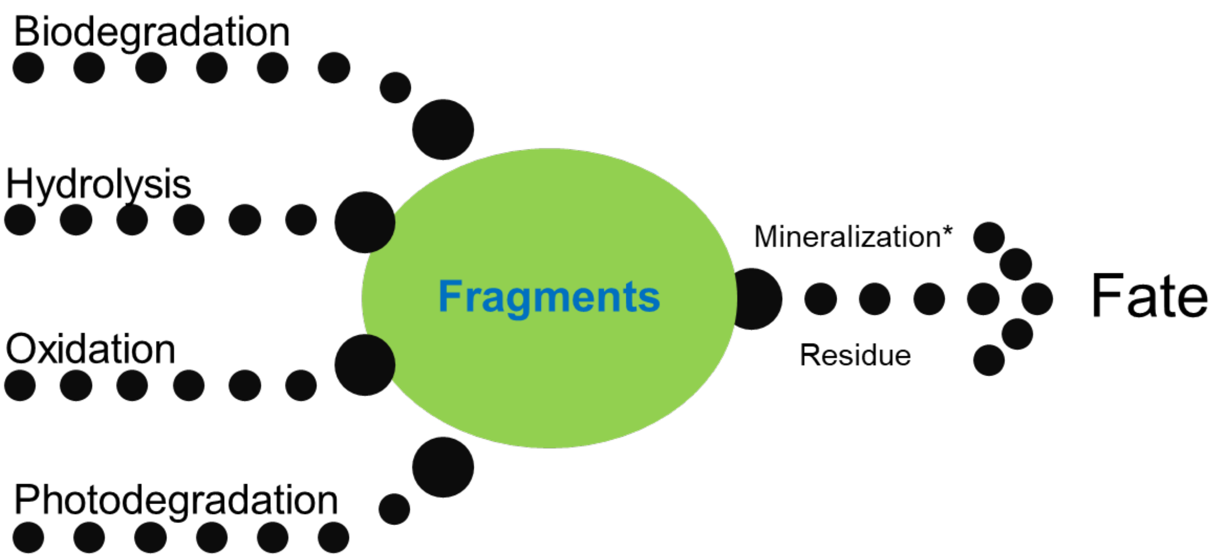
(1) Pagga, 1998
(2) Calmon-Decriaud et al.,1998
(3) DIN V 94900, 1998

- ***Degradable*** *plastic*: designed to undergo a significant change in its chemical structure under **specific environmental conditions**, resulting in a loss of some properties in a particular period of time.
- ***Biodegradable*** *plastic:* degradable plastic in which the **degradation results from the action of naturally occurring microorganisms** such as bacteria, fungi, and algae.
- ***Hydrolytically degradable*** *plastic:* degradable plastic in which the **degradation results from hydrolysis**.
- ***Oxidatively degradable*** *plastic:* degradable plastic in which the **degradation results from oxidation.**
- ***Photodegradable*** *plastic:* degradable plastic in which the **degradation results from the action of natural daylight**.

Definitions must be practical and descriptive in conveying the assurance that no harmful residues are left in the environment after degradation. Definitions, therefore, require elaboration in order to address this deficiency.

Source: Swift, G. 2000. Polymers, Environmentally Degradable. Kirk-Othmer Encyclopedia of Chemical Technology

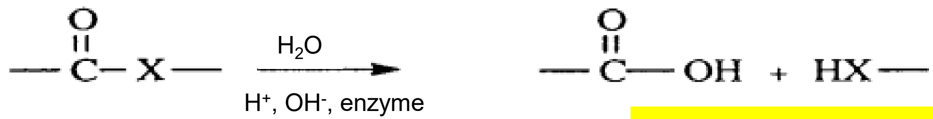
Biodegradation, hydrolysis, oxidation, and photodegradation, initially give intermediate products (fragments) that may biodegrade further to some other residue, biodegrade completely and be removed from the environment entirely and ultimately mineralized, or remain unchanged in the environment.



**slow process for polymeric materials and fragments: complete conversion to CO_2 or CH_4, water, and salts.*
In the cases where residues remain in the environment, they must be established as harmless by suitably rigorous fate and effect evaluations.

Adapted from: Swift, G. 2000. Polymers, Environmentally Degradable. Kirk-Othmer Encyclopedia of Chemical Technology

Examples of some hydrolyzable bonds

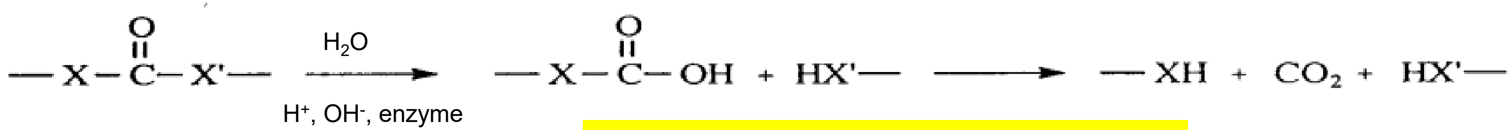


X = O, NH, S

Amide, ester

X = O, NH, S

Imide, Anhydride

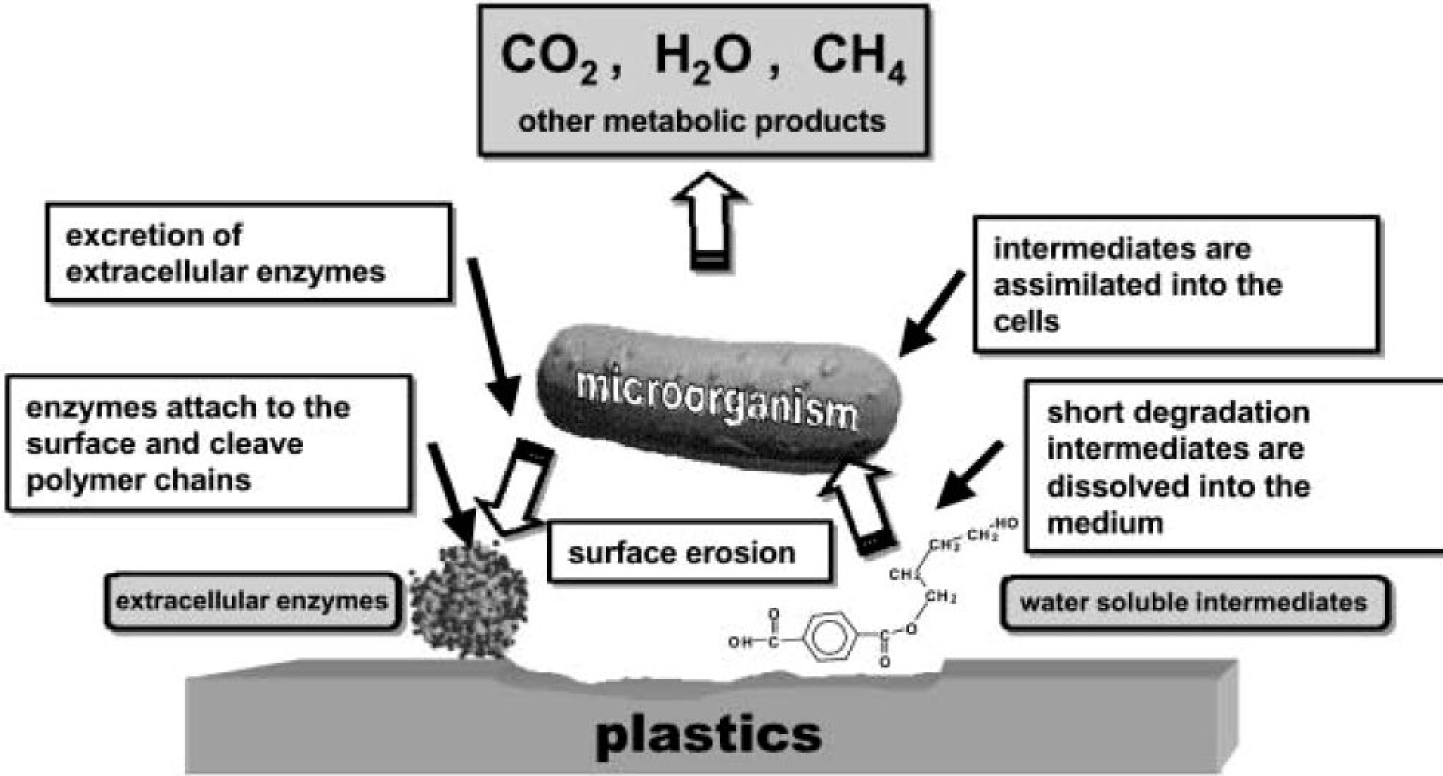


X, X' = O, NH, S

Urethane, urea, carbonate

Coury, A.J., Chemical and biochemical degradation of polymers, In Biomaterials Science (eds. Ratner, B.D. et. al.) Academic Press 1996, 64-73

General mechanism of plastics biodegradation



Müller, R-J, **Biodegradability of Polymers: Regulations and Methods for Testing** in **Biopolymers Online,** Online ISBN: 9783527600038, DOI: 10.1002/3527600035, pp. 365-388

Biodegradation

Aerobic biodegradation:

$$\text{Polymer} + O_2 \longrightarrow CO_2 + H_2O + \text{Biomass} + \text{Residue}$$

Anaerobic biodegradation:

$$\text{Polymer} \longrightarrow CO_2 \,/\, CH_4 + H_2O + \text{Biomass} + \text{Residue}$$

Most of the testing reported in the literature has been with **aerobic biodegradation** conditions (easier to do in the laboratory and relevant to **most disposal of polymers**).

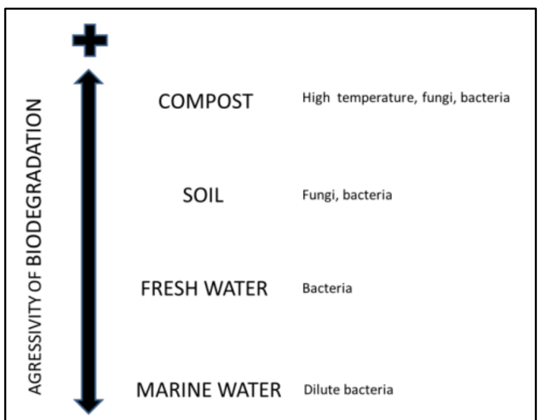
Anaerobic degradation: pertinent to **water-soluble polymers** that may enter anaerobic digestors in sewage treatment facilities

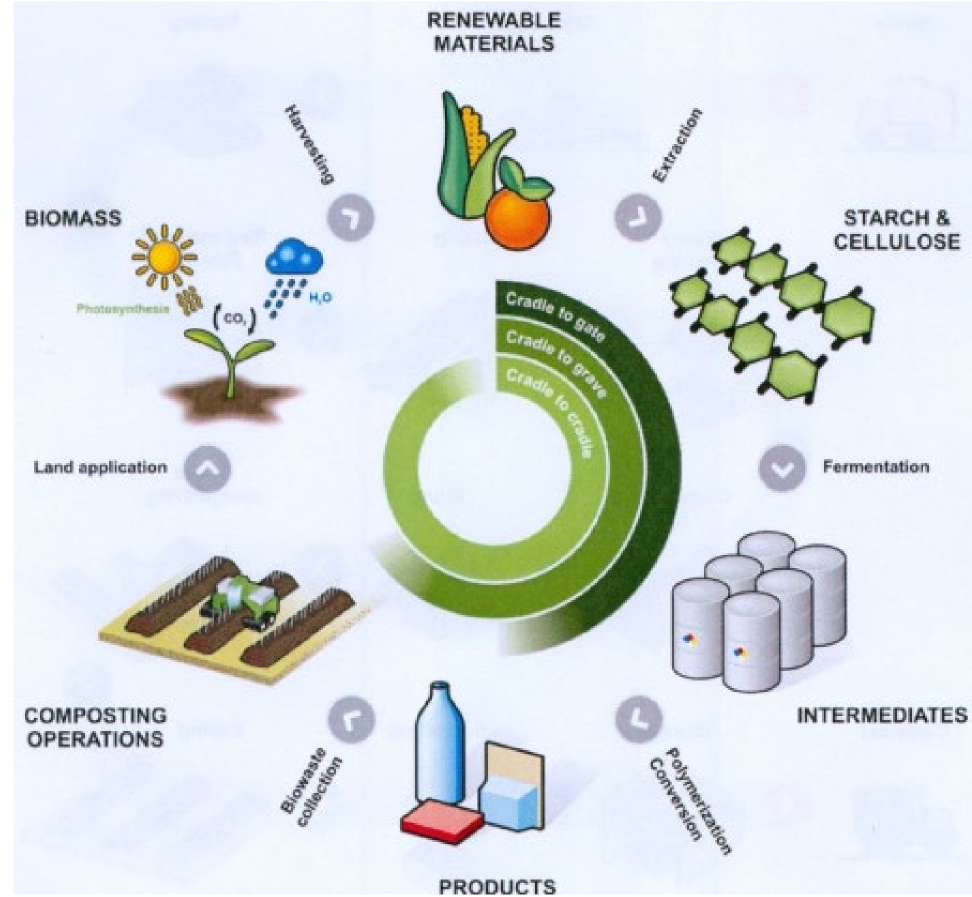
Current terminology on biodegradation vs. enzymatic degradation/decomposition can be
Found in: Vert et. al., Terminology for biorelated polymers and applications (IUPAC recommendations 2012), Pure Appl. Chem. (2012), Vol. 84, No.2, pp.377-410. http://pac.iupac.org/publications/pac/pdf/2012/pdf/8402x0377.pdf

Compositing

In landfills moisture and oxygen are minimized or absent, thus the materials are not readily decomposed.

In a compost operation biodegradable plastics can be converted by microbes into CO_2, water and humus in a matter of months.





- Moisture content
- Oxygen availability
- Temperature
- Type of microbiology
- Density of microbiology
- Salt concentration.

A biodegradable plastic is not automatically biodegradable in all environments

Kijchavengkul, T. and Auras, R., Perspective compostability of polymers, Polymer International 57 (2008) 793-804.

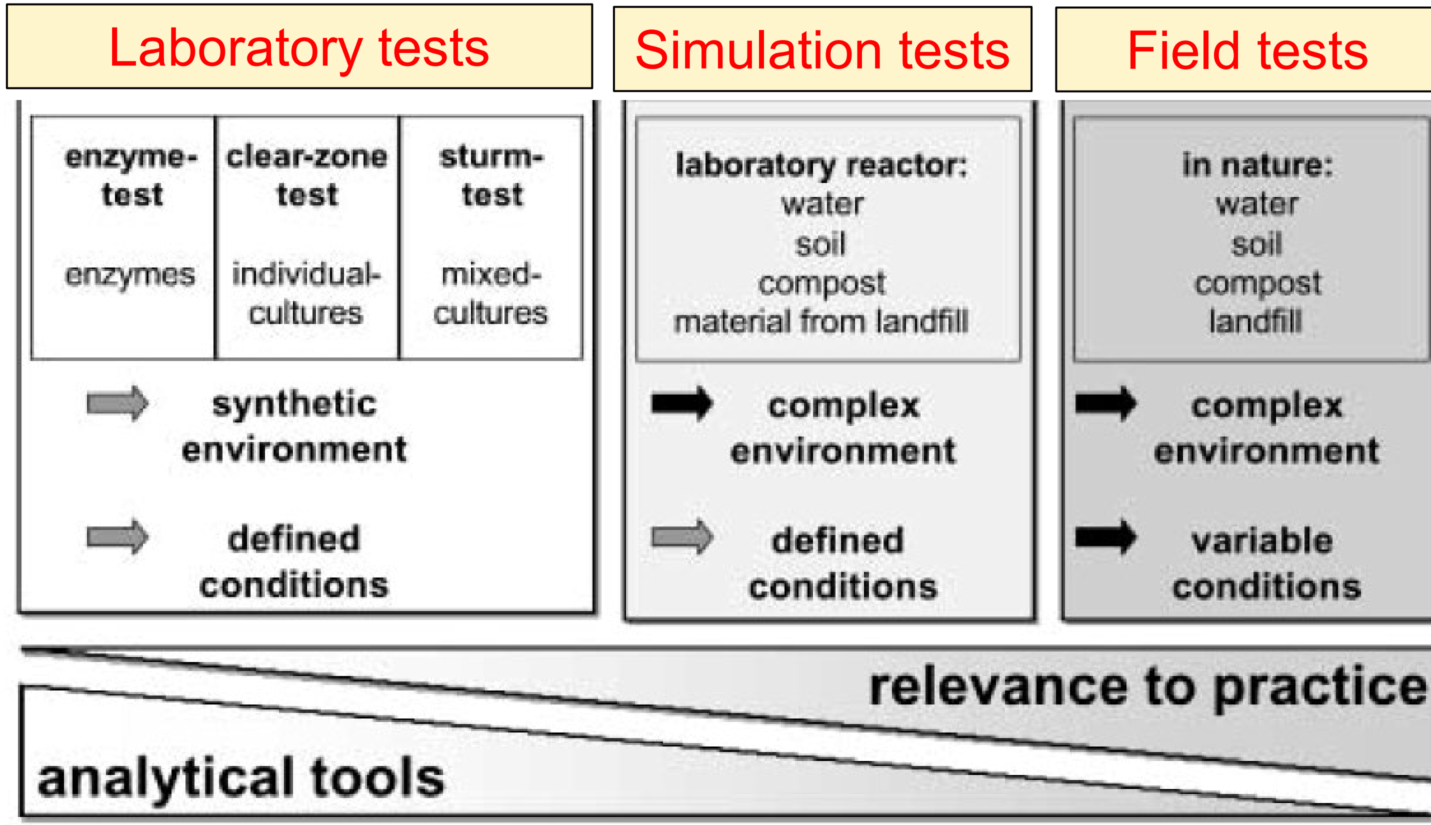
Test Methods

Biodegradation

- Early tests: related to microbial growth, weight loss, tensile changes, and other physical property losses = **indirect measurements of biodegradation** (Growth Ratings ASTM Tests G21-70 and G22-76)
- More recent tests: **quantitative** and include selection of environment to reflect probable disposal sites for a given polymer or plastic. Qualitative tests are still used for indicating the rate of disintegration of plastics (bearing on disposal methods as composting for compaction and volume reduction of the compost).
- Fungal organisms (***Aspergillus niger***, ***Aspergillus flavus*, *Chaetomium globosum*, and *Penicillium funiculosum*)** and bacterial standards (***Pseudomonas aeruginosa***) are suggested in protocols.
- After a suitable time period, growth is assessed:

Rating	Growth
0	no visible growth
1	< 10% of surface with growth
2	10–30% surface with growth
3	30–60% surface with growth
4	60–100% surface with growth

Tests for Biodegradability



Müller, R-J, **Biodegradability of Polymers: Regulations and Methods for Testing** in **Biopolymers Online,** Online ISBN: 9783527600038, DOI: 10.1002/3527600035, pp. 365-388

Sturm test, ISO 14852, ASTM D5209-92 based on carbon conversion

- The test item is placed in an aqueous mineral medium, spiked with inoculum and incubated under bath conditions
- The mineral medium provides the necessary nutrients and buffering capacity
- The inoculum can be either activated sewage sludge, compost eluate, soil eluate or a combination of these
- The test is run until a plateau in activity is reached; 4 weeks – 6 months

VTT Test arrangement

Biodegradation is calculated as a percentage of organic carbon converted into CO_2 compared to the theoretical value.

Adapted from: Minna Malin, course Lecture notes 2015

Aerobic biodegradation under controlled composting conditions

Disintegration and biodegradation have to be assessed based on ASTM D5338 or ISO 14855.

Materials are incubated with the compost mixture in bioreactors for 45 days or until reaching a plateau stage for **not more than 180 days at 58 ± 2 °C**

Humidified air is supplied to bioreactors, and the amount of CO_2 gas evolved is measured using either a cumulative method (titration), or direct measurement from the exhaust air (IR, GC)

Fraction of material with size greater than 2 mm should be ≤ 10 % of the original dry weight

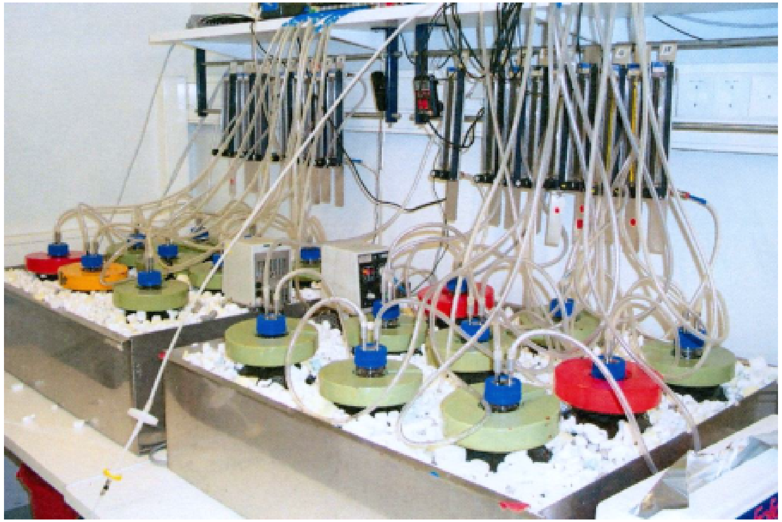


Photo from VTT / Venelampi O., Wikman, M., Itävaara, M.

The cumulative percentage of organic carbon converted into CO_2 compared to the theoretical value must be > 60% for homopolymer or random copolymer, and **90% for a material containing a block/graft copolymer or blend.**

Adapted from: Minna Malin, course Lecture notes 2015

Compostability

- **Natural, biological process by which organic material is decomposed into a soil-like substance, humus**
- Microorganisms (bacteria, fungi, antinomycetes) use organic matter as their food source, generate CO_2, and produce humus as an end product
- Requires availability of C, N, O and H_2O
- C:N ratio 30:1 is ideal for thermophilic microorganisms and fastens the composting process
- Large-scale commercial composting
- Small-scale backyard composting
- Proceeds in two stages: active composting stage (elevated temperature ~60° → strong microbial activity) and curing period

Norms related to industrial compostability

- EN 13432 (2000): Packaging –requirements for packaging recoverable through composting and biodegradation – Test scheme and evaluation criteria for the final acceptance of packaging
- EN 14955 (2007): Plastics – Evaluation of compostability – Test scheme and specifications.

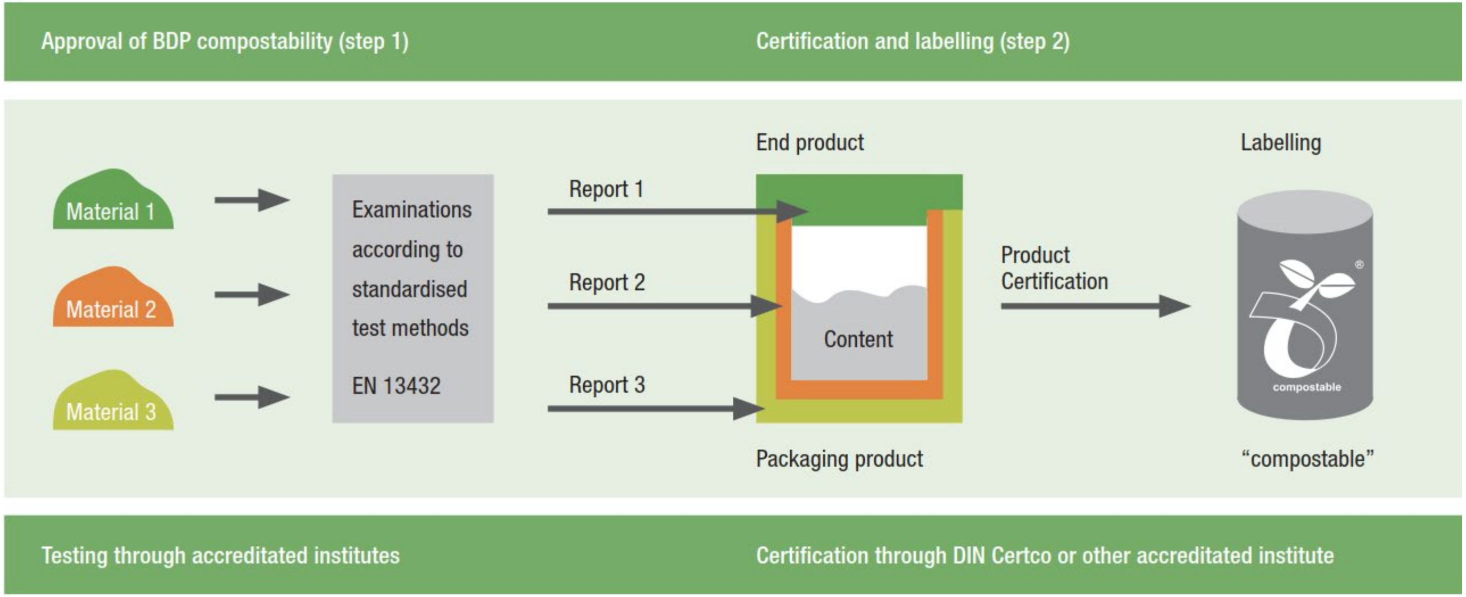
See also ASTM D 6400-12, ASTM D 6868-11 (USA), AS 4736 (Australia), ISO 17088, ISO 18606 (global)

Adapted from: Minna Malin, course Lecture notes 2015

Compostability

a property of a packaging to be biodegraded in a composting process. To claim compostability it must have been demonstrated that a packaging can be biodegraded in a composting system as can be shown by standard methods.

The end product must meet the relevant compost quality criteria (CEN)



Product certification guarantees that not only the plastic is compostable, but also all other components of the product, e.g. colors, labels, glues and residuals of the content.

Adapted from: Minna Malin, course Lecture notes 2015

Fact Sheet (Nov 2009): Industrial Composting, European Bioplastics e.V., 14 p.
http://en.european-bioplastics.org/wp-content/uploads/2011/04/fs/FactSheet_Industrial_Composting.pdf

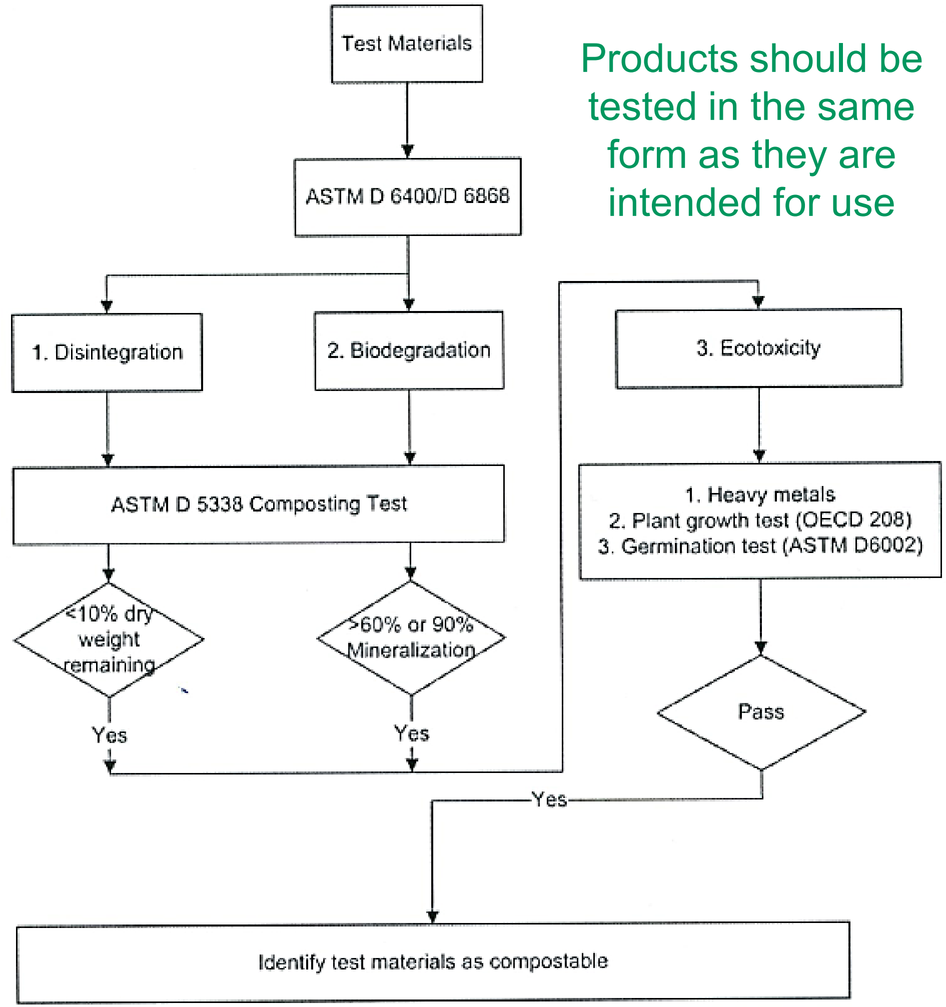
Compostable materials identification flow chart

EN 13432 criteria for compostability

- Characterization
- Biodegradability
- Disintegration
- Compost quality, ecotoxicity

All compostable plastics are bio-degradable, but not vice versa

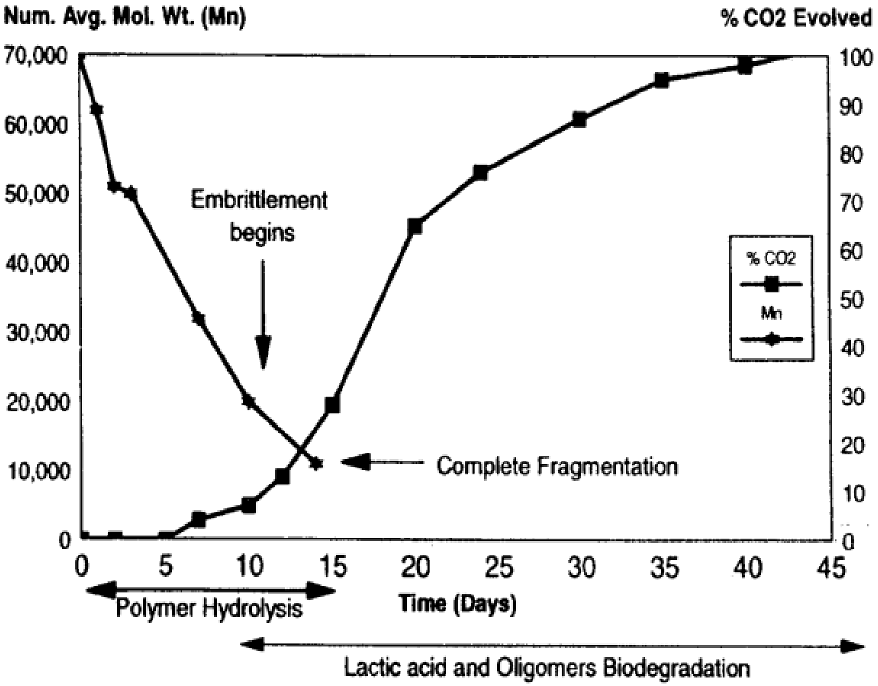
Polym. Int. 57 (2008), 793-804



Products should be tested in the same form as they are intended for use

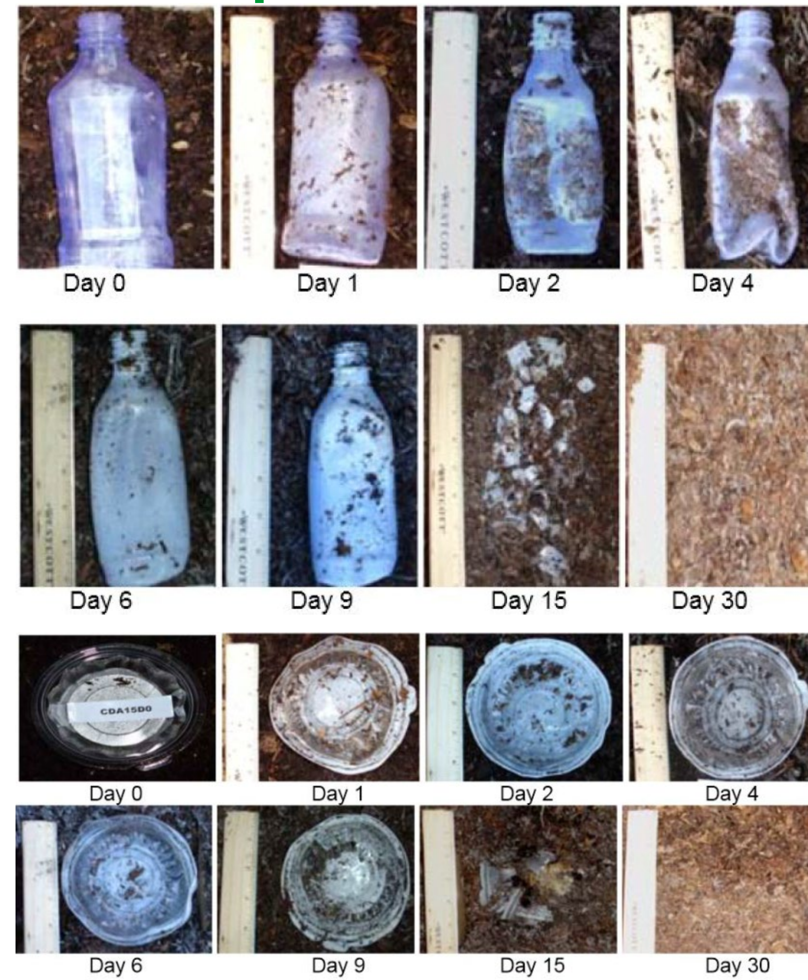
Adapted from: Minna Malin, course Lecture notes 2015

Case: Biodegradation of PLA in compost at 60°C



Adapted from: Minna Malin, course Lecture notes 2015

PLA containers exposed to compost conditions



Kale, G., Auras, R., Singh, S.P., Comparision of the degradability of poly(lactide) packages in composting and ambient exposure conditions, *Packag. Technol. Sci.* 20 (2007), 49-70.

Oxo-degradable plastics and photodegradation

Oxo-degradable Plastics

- The term was introduced by the industry and is being used for commercial reasons
- Non-biodegradable conventional polymers and polymer blends consisting of additives which would make the polymer degradable if exposed to oxygen, heat and/or light
- Plastics containing inorganic additives that should cause the plastic to degrade by a process initiated by oxygen
- Plastics containing organic additives that are claimed to be consumed by microorganisms during which these excrete acids and enzymes that should break down the plastic
- These polymers are claimed to disintegrate into small fragments, but are not biodegradable in the foreseen timeframe as set forth in the different standards e.g. on composting.

Deconinck, S. & De Wilde B., Benefits and challenges of bio- and oxo-degradable plastics. A comparative literature study. August 2013.

Effect of UV Degradation on Polymers

- Change in chemical structure
- Change on surface
- Embrittlement
- Generation of free radicals
- Change in molecular weight
- Loss in mechanical properties
- Impairment of transparency

https://polymer-additives.specialchem.com/selection-guide/light-uv-stabilizers-selection-for-polymers

Photodegradation

Test methods: combination of an exposure to some form of radiation and subsequent property loss measurement in another test, for example a tensile strength loss (ASTM D882-83), impact resistance loss (ASTM D1709-85), tear strength loss (ASTM D1922-67), molecular weight loss, friability, disintegration, brittle point, etc.

ASTM Standard Practices for Photodegradation	
D3826-91	degradation end points using a tensile test
D5071-91	operation of a xenon arc ARC-type exposure apparatus
D5208-91	operation of a fluorescent ultraviolet (uv) and condensation apparatus
D5272-92	outdoor exposure testing of photodegradable plastics

Source: Swift, G. 2000. Polymers, Environmentally Degradable. Kirk-Othmer Encyclopedia of Chemical Technology

Photodegradation Mechanisms

Chain scission promoted by natural daylight and usually oxygen to yield low molecular weight fragments that are **more susceptible to biodegradation** than the original high molecular weight polymer.

The polymers can be structurally similar to currently used environmentally stable polymers but have been modified during synthesis or post-treatment to **insert photochemically active groups**:

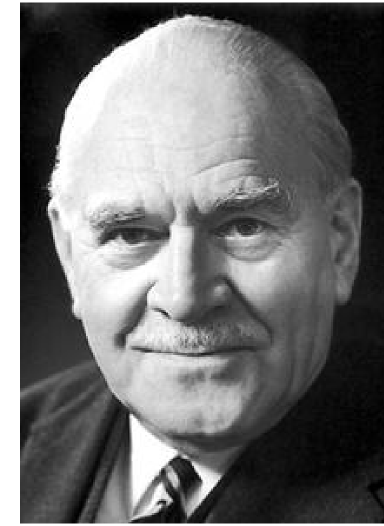
- Carbonyl functionality (main or side chain)
- External photosensitizers
- Pro-oxidants such as metal salts
- Benzophenone
- Ketones
- Ethers
- Mercaptans
- Polyunsaturated compounds

Complete environmental acceptability may be still lacking. It is not sufficient to expect low molecular weight fragments to be biodegradable; this must be demonstrated.

Source: Swift, G. 2000. Polymers, Environmentally Degradable. Kirk-Othmer Encyclopedia of Chemical Technology

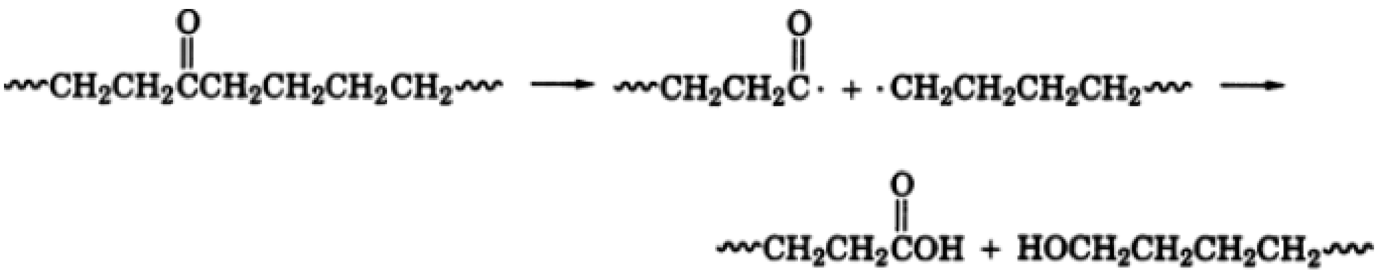
UV radiation: activated ketone functionalities can fragment by two different mechanisms: **Norrish types I and II**.

Degradation of polymers with the carbonyl functionality in the backbone of the polymer results in chain cleavage by Norrish I and II. If the carbonyl is in the polymer side chain, only Norrish II degradation produces main-chain scission



Ronald George Wreyford Norrish
1897 - 1978

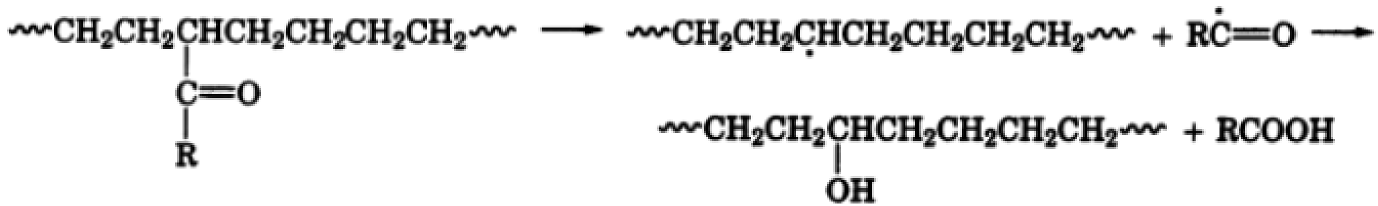
Norrish type I reaction for backbone carbonyl functionality:



Norrish type II reaction for backbone carbonyl functionality

Source: Swift, G. 2000. Polymers, Environmentally Degradable. Kirk-Othmer Encyclopedia of Chemical Technology

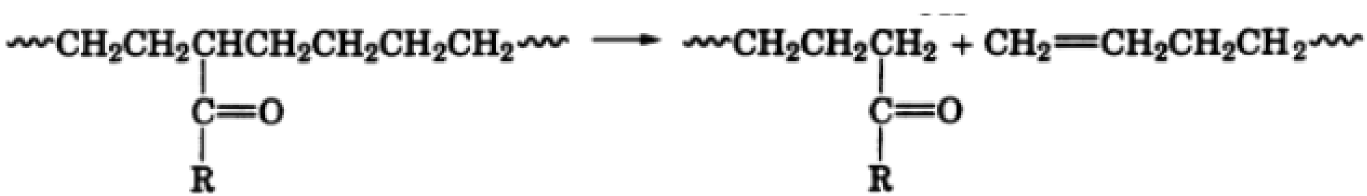
Norrish type I reaction for side-chain carbonyl functionality:



At room temperature: 15% of the chain scission of ethylene–carbon monoxide polymers. At 120°C: 59% of the degradation.

Norrish I reactions are independent of temperature and oxygen concentration at temperatures above the T_g of the polymer

Norrish type II reaction for side-chain carbonyl functionality



Source: Swift, G. 2000. Polymers, Environmentally Degradable. Kirk-Othmer Encyclopedia of Chemical Technology

Degradation of polyolefins such as polyethylene, polypropylene, polybutylene, and polybutadiene promoted by metals and other oxidants occurs via an oxidation and a photo-oxidative mechanism:

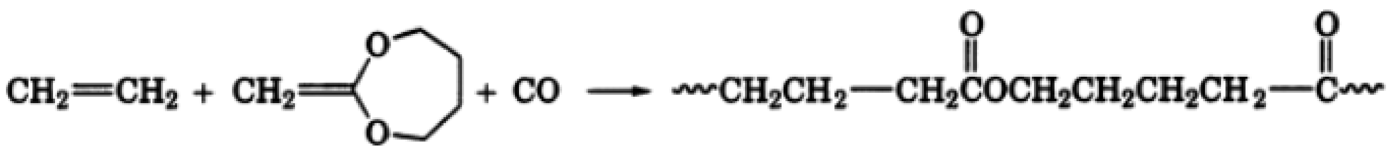
The reactant radical may be produced by any suitable mechanism from the interaction of air or oxygen with polyolefins to UV radiation.

These reaction intermediates abstract more hydrogen atoms from the polymer backbone, which is ultimately converted into a polymer with ketone functionalities and degraded by the Norrish mechanisms

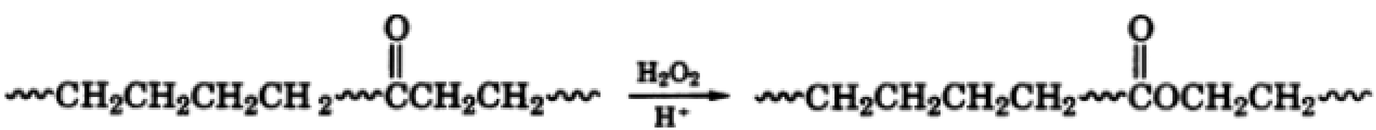
Source: Swift, G. 2000. Polymers, Environmentally Degradable. Kirk-Othmer Encyclopedia of Chemical Technology

Photodegradable polymers: additives for polymers to encourage more rapid biodegradation by decreasing MW.

Ex. dioxapane introduces an ester linkage into polyolefins during free-radical polymerization:
become susceptible to biodegradation



Ex. Baeyer-Villiger reaction, depending on the degree of conversion to polyester, the polymer becomes totally or partially degraded by a biological mechanism



ethylene–carbon monoxide polymer

acidic hydrogen peroxide

polyester-containing terpolymer

Source: Swift, G. 2000. Polymers, Environmentally Degradable. Kirk-Othmer Encyclopedia of Chemical Technology

Open positions

Students Wanted for Exciting Summer Jobs at the School of Chemical Engineering

5.12.2023

Application closes on	Unit	Job category
18.2.2024	School of Chemical Engineering	Students (assisting teaching and research)

https://www.aalto.fi/en/open-positions/students-wanted-for-exciting-summer-jobs-at-the-school-of-chemical-engineering-0

Reading 4 discussion

Title: Biopolymers Reuse, Recycling, and Disposal. Chapter 3: Reuse
From: Michael Niaounakis, 2013.

Discussion items:

- The 5 subchapters describe different aspects of polymer reuse. Discuss the pros and cons of each strategy and summarize them briefly.
- Which form(s) of reuse might be the most important one(s) and why?

Instructions:

Write your names and summary of your discussion in e.g., PowerPoint. Save the text as image file (.jpg) and upload it to the Padlet page:
https://padlet.com/michaelhummel/CHEME2155_2024