Biodegradation and Compostability

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- Degradation of Polymers
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- Factors and mechanisms of Biodegradation
- Polymers as biomaterials
Definitions

Biodegradation and composting

ASTM D1566 (A or B?): “a macromolecular material formed by the chemical combination of monomers having either the same or different chemical composition”

ASTM D1695a (A or B?): “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)

Definitions

- **ASTM D1566 polymer (A):** “a macromolecular material formed by the chemical combination of monomers having either the same or different chemical composition”
- **ASTM D1695a plastic (B):** “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)


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Definitions used in relation to biodegradable plastics

<table>
<thead>
<tr>
<th>Source</th>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td>DIN FNK 103.2</td>
<td>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.</td>
</tr>
<tr>
<td>ASTM sub-committee D20-96</td>
<td>Biodegradable plastics(^{(1)}): A degradable plastic in which the degradation results from the action of naturally occurring microorganisms such as bacteria, fungi and algae.</td>
</tr>
<tr>
<td>Japanese Biodegradable Plastics Society</td>
<td>Biodegradable plastics(^{(1)}): Polymeric materials which are changed into lower molecular weight compounds where at least one step in the degradation process is through metabolism in the presence of naturally occurring organisms.</td>
</tr>
<tr>
<td>ISO 472</td>
<td>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.</td>
</tr>
<tr>
<td>CEN</td>
<td>Biodegradable plastics(^{(1)}): A degradable material in which the degradation results from the action of microorganisms and ultimately the material is converted to water, carbon dioxide and/or methane and a new cell biomass.</td>
</tr>
<tr>
<td></td>
<td>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</td>
</tr>
<tr>
<td></td>
<td>Inherent biodegradability(^{(2)}): The potential of a material to be biodegraded, established under laboratory conditions.</td>
</tr>
<tr>
<td></td>
<td>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.</td>
</tr>
<tr>
<td></td>
<td>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.</td>
</tr>
</tbody>
</table>

---

\(^{(1)}\) Pagga, 1998  
\(^{(2)}\) Calmon-Decraud et al., 1998  
\(^{(3)}\) DIN V 84900, 1998
• **(A-E) 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.

• **(A-E) plastic**: degradable plastic in which the **degradation results from the action of naturally occurring microorganisms** such as bacteria, fungi, and algae.

• **(A-E) plastic**: degradable plastic in which the **degradation results from hydrolysis**.

• **(A-E) plastic**: degradable plastic in which the **degradation results from oxidation**.

• **(A-E) plastic**: degradable plastic in which the **degradation results from the action of natural daylight**.


---

• **(D) 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.

• **(C) Biodegradable plastic**: degradable plastic in which the **degradation results from the action of naturally occurring microorganisms** such as bacteria, fungi, and algae.

• **(B) Hydrolytically degradable plastic**: degradable plastic in which the **degradation results from hydrolysis**.

• **(E) Oxidatively degradable plastic**: degradable plastic in which the **degradation results from oxidation**.

• **(A) 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.

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 CO₂ or CH₄, 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.


**Examples of some hydrolyzable bonds**

A. Urethane, urea, carbonate
B. Imide, Anhydride
C. Amide, ester

\[
\begin{align*}
\text{C} - \text{X} & \quad \text{H}_2\text{O} \\
& \quad \text{H}^+, \text{OH}, \text{enzyme}
\end{align*}
\]

\[
\begin{align*}
\text{X} & = \text{O}, \text{NH}, \text{S}
\end{align*}
\]

(A-C)?

\[
\begin{align*}
\text{C} - \text{X} & \quad \text{H}_2\text{O} \\
& \quad \text{H}^+, \text{OH}, \text{enzyme}
\end{align*}
\]

\[
\begin{align*}
\text{X} & = \text{O}, \text{NH}, \text{S}
\end{align*}
\]

(A-C)?

\[
\begin{align*}
\text{X} - \text{C} - \text{X'} & \quad \text{H}_2\text{O} \\
& \quad \text{H}^+, \text{OH}, \text{enzyme}
\end{align*}
\]

\[
\begin{align*}
\text{X} & = \text{O}, \text{NH}, \text{S}
\end{align*}
\]

(A-C)?

Examples of some hydrolyzable bonds

C: Amide, ester

B: Imide, Anhydride

A: Urethane, urea, carbonate


General mechanism of plastics biodegradation

Biodegradation

**A. Aerobic Biodegradation**

Biodegradation: 

\[
\text{Polymer} + O_2 \rightarrow CO_2 + H_2O + \text{Biomass} + \text{Residue}
\]

**B. Anaerobic Biodegradation**

Biodegradation: 

\[
\text{Polymer} \rightarrow CO_2/CH_4 + H_2O + \text{Biomass} + \text{Residue}
\]

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

Compositing

Options for recovery:
- Composting
- Recycling
- Energy recovery incineration

Plastics used in packaging and agriculture are soiled with contaminants reducing the opportunities for recycling.

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 CO2, water and humus in a matter of months.

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:
  
<table>
<thead>
<tr>
<th>Rating</th>
<th>Growth</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>no visible growth</td>
</tr>
<tr>
<td>1</td>
<td>&lt; 10% of surface with growth</td>
</tr>
<tr>
<td>2</td>
<td>10–30% surface with growth</td>
</tr>
<tr>
<td>3</td>
<td>30–60% surface with growth</td>
</tr>
<tr>
<td>4</td>
<td>60–100% surface with growth</td>
</tr>
</tbody>
</table>

Tests for Biodegradability

• Any impurities in the plastic (plasticizers and solvents): interfere with the test (promotes growth, and false positive results).
• Soil burial (biodegradability of PCL): disappearance with time
• Clear zone method: biodegradation by the formation of a clear zone in an agar medium as the polymer is consumed
• Many of the quantitative tests: based on those of the detergent industry for water-soluble organic compounds (surfactants) (EPA & OECD)
• Analytical techniques for reactants and products; the polymer; oxygen uptake (biochemical oxygen demand, BOD) and the residue.

<table>
<thead>
<tr>
<th>Test number</th>
<th>Environment</th>
<th>Measurement</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASTM D5209-92</td>
<td>aerobic sewage sludge</td>
<td>CO₂</td>
</tr>
<tr>
<td>ASTM D5210-92</td>
<td>anaerobic sewage sludge</td>
<td>CO₂ and CH₄</td>
</tr>
<tr>
<td>ASTM D5247-92</td>
<td>aerobic specific microorganisms</td>
<td>molecular weight</td>
</tr>
<tr>
<td>ASTM D5271-93</td>
<td>aerobic activated sewage sludge</td>
<td>O₂ and CO₂</td>
</tr>
<tr>
<td>ASTM D5338-92</td>
<td>aerobic controlled composting</td>
<td>CO₂</td>
</tr>
<tr>
<td>ASTM D5437-93</td>
<td>marine floating conditions</td>
<td>physical properties</td>
</tr>
<tr>
<td>MITI Test</td>
<td>mixed microbial</td>
<td>O₂</td>
</tr>
</tbody>
</table>

Test number Environment Measurement
ASTM D5209-92 aerobic sewage sludge CO₂
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ASTM D5271-93 aerobic activated sewage sludge O₂ and CO₂
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ASTM D5437-93 marine floating conditions physical properties
MITI Test mixed microbial O₂

Currently the most important test norm is EN 13432, which refers to industrial composting.

Biodegradation curve

Biodegradation curve

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

Biodegradation is calculated as a percentage of organic carbon converted into CO2 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 CO₂ 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.

The cumulative percentage of organic carbon converted into CO₂ 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.

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.
Composting

- Natural, biological process by which organic material is decomposed into a soil-like substance, humus
- Microorganisms (bacteria, fungi, and 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$_2$O
- 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

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

Compostable materials identification flow chart

EN 13432 criteria for compostability

- Characterization
- Biodegradability
- Disintegration
- Compost quality, ecotoxicity

All compostable plastics are biodegradable, but the reverse is not true

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

What material type goes here?

Adapted from: Minna Malin, course Lecture notes 2015
Compostable materials identification flow chart

EN 13432 criteria for compostability

- Characterization
- Biodegradability
- Disintegration
- Compost quality, ecotoxicity

**All compostable plastics are biodegradable, but the reverse is not true**

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

Case: Biodegradation of PLA in compost at 60°C

*What materials are produced here?*

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 bottles and containers exposed to compost conditions

Plant growth test of lactic acid based poly(ester-urethanes)

Tuominen, J. et al., Biodegradation of lactic acid based polymers under controlled composting conditions and evaluation of the ecotoxicological impact, Biomacromolecules 3 (2002), 445-455.

Adapted from: Minna Malin, course Lecture notes 2015

Labeling and Certification

- The best known and most used certification system
- Test laboratories approved by DIN-Certo
- Polymeric materials, compostable materials, intermediates and additives / products, product ranges
- A few products, mainly biowaste bags, have been certificated
- Major difference with the other certification systems lies in the need for toxicological safety data on the material itself


Adapted from: Minna Malin, course Lecture notes 2015
Photodegradation and Oxo-degradable Plastics


What type of plastic? **Plastics**
- 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
- The term was introduced by the industry and is being used for commercial reasons, but is not yet standardized
- 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.
**Oxo-degradable Plastics**

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**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.

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**ASTM Standard Practices for Photodegradation**

<table>
<thead>
<tr>
<th>Standard</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>D3826-91</td>
<td>degradation end points using a tensile test</td>
</tr>
<tr>
<td>D5071-91</td>
<td>operation of a xenon arc ARC-type exposure apparatus</td>
</tr>
<tr>
<td>D5208-91</td>
<td>operation of a fluorescent ultraviolet (uv) and condensation apparatus</td>
</tr>
<tr>
<td>D5272-92</td>
<td>outdoor exposure testing of photodegradable plastics</td>
</tr>
</tbody>
</table>

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 these groups that can be classified as ______________?

- 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.*

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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.

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- 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.*
**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.

**Norrish type I** reaction for backbone carbonyl functionality:

\[
\cdots \text{C} \cdots + \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \longrightarrow \cdots \text{C} \cdots + \text{H}_2\text{O} + \text{CH}_2\text{OCH}_2\text{CH}_2\text{OH}.
\]

**Norrish type II** reaction for backbone carbonyl functionality:

\[
\cdots \text{C} \cdots + \text{CH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OH} \longrightarrow \cdots \text{C} \cdots + \text{H}_2\text{C} = \text{CHCH}_2\text{OH}.
\]


At room T: 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 I** reaction for side-chain carbonyl functionality:

\[
\cdots \text{C} \cdots + \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \longrightarrow \cdots \text{C} \cdots + \text{RCOOH}.
\]

\[
\cdots \text{C} \cdots + \text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{OH} \longrightarrow \cdots \text{C} \cdots + \text{RCOOH}.
\]

**Norrish type II** reaction for side-chain carbonyl functionality.

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.


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

Degradation of Polymers
Bio-based polymers
Synthetic Polymers
Modified Natural Polymers

Synthetic Polymers
They do not evolve naturally = enzymes available in nature for degrading natural polymers are not as useful for synthetic polymers.
The search for synthetic polymeric structures: minor modification of the non-degradables in use to structures that mimic nature.

Some guidelines on polymer structure:

- A higher hydrophilic/hydrophobic ratio (increase/reduce?) biodegradation.
- Presence of carbon chain polymers (increase/reduce?) biodegradation.
- Chain branching (increase/reduce?) biodegradation.
- Presence of condensation polymers (increase/reduce?) biodegradation.
- Lower molecular weight polymers (increase/reduce?) biodegradation.
- Crystallinity (increase/reduce?) biodegradation.
- Favorable polymer physical properties include water solubility and purity.

Environmental conditions to consider in evaluating biodegradability are temperature, pH, moisture, oxygen, nutrients, suitable microbial population (fungal, algae, bacterial), concentration, and test duration.
**Synthetic Polymers**

They do not evolve naturally = enzymes available in nature for degrading natural polymers are not as useful for synthetic polymers.

The search for synthetic polymeric structures: minor modification of the non-degradables in use to structures that mimic nature.

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- **Presence of carbon chain polymers** *(reduce)* biodegradation.
- **Chain branching** *(reduce)* biodegradation.
- **Presence of condensation polymers** *(increase)* biodegradation.
- **Lower molecular weight polymers** *(reduce)* biodegradation.
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- **Favorable polymer physical properties include water solubility and purity.**

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**Carbon Chain Backbone Polymers**

R: H (polyethylene), -CH₃ (polypropylene), carboxyl (poly(acrylic acid)), chlorine (poly(vinyl chloride)), phenyl (polystyrene) hydroxyl (poly(vinyl alcohol)), ester (poly(vinyl acetate)), nitrile (polyacrylonitrile), vinyl (polybutadiene), etc.

The functional groups and the molecular weight of the polymers, control their properties which vary in hydrophobicity, solubility characteristics, glass-transition temperature, and crystallinity.

Fungal and bacterial growth tests indicated that PE and other high molecular weight carbon chain polymers did not support growth.

Branching of hydrocarbon chains limits biodegradation and the MW cut-off for linear molecules appears to be in the 500 Da range.

<table>
<thead>
<tr>
<th>Compound</th>
<th>MW</th>
<th># Branches</th>
<th>Growth test *</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dodecane</td>
<td>170</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>2,6,11-trimethyldodecane</td>
<td>212</td>
<td>3</td>
<td>0</td>
</tr>
<tr>
<td>Hexadecane</td>
<td>226</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>2,6,11,15-hexadecane</td>
<td>282</td>
<td>4</td>
<td>0</td>
</tr>
<tr>
<td>Tetracosane</td>
<td>338</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Squalene</td>
<td>422</td>
<td>6</td>
<td>0</td>
</tr>
<tr>
<td>Dotriacontane</td>
<td>450</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>Hexatriacontane</td>
<td>506</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Tetraccontane</td>
<td>562</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Tetratetracontane</td>
<td>618</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

*ASTM tests G21-70 and G22-76. Higher numbers correlate with the susceptibility of the plastic to biodegradation.

Low MW Pyrolysis Products of HDPE and LDPE

<table>
<thead>
<tr>
<th>Pyrolysis T, °C</th>
<th>MW</th>
<th>Growth rating</th>
</tr>
</thead>
<tbody>
<tr>
<td>Control (HDPE)</td>
<td>123,000</td>
<td>0</td>
</tr>
<tr>
<td>400</td>
<td>16,000</td>
<td>1</td>
</tr>
<tr>
<td>450</td>
<td>8,000</td>
<td>1</td>
</tr>
<tr>
<td>500</td>
<td>3,200</td>
<td>3</td>
</tr>
<tr>
<td>535</td>
<td>1,000</td>
<td>3</td>
</tr>
<tr>
<td>Control (LDPE)</td>
<td>56,000</td>
<td>0</td>
</tr>
<tr>
<td>400</td>
<td>19,000</td>
<td>1</td>
</tr>
<tr>
<td>450</td>
<td>12,000</td>
<td>1</td>
</tr>
<tr>
<td>500</td>
<td>2,100</td>
<td>2</td>
</tr>
<tr>
<td>535</td>
<td>1,000</td>
<td>3</td>
</tr>
</tbody>
</table>

*ASTM tests G21-70 and G22-76. Higher numbers are considered to correlate with the susceptibility of the plastic to biodegradation.

Increase in degradation with lower MW:
- Transportation of polymer across cell walls is more likely
- Mechanism of biodegradation: Random or chain-end cleavage prior to entering the cell.
- Chain-end exo-biodegradation by β-oxidation

Individual oxidation steps are enzyme-catalyzed with a final hydrolysis to a two-carbon diminished chain and acetic acid, which is then presumably biodegraded.

Such a mechanism would explain the occurrence of slower biodegradation at higher MW, where there would be fewer chain ends.

The terminal groups found in oxidized and photodegraded polyethylene are oxygen-containing and these should expedite biodegradation via a β-oxidation mechanism.


---

**Poly(vinyl alcohol)**

Probably the only carbon chain polymer to be fully biodegradable.

**Biodegradation:** a random chain cleavage of 1,3-diketones formed by an enzyme-catalyzed oxidation of the secondary alcohol functional groups in the polymer backbone (observed as a reduction in aqueous viscosity of the polymer in the presence of soil bacteria).

*Pseudomonas* species (*): soil bacterium responsible for the degradation over a degree of polymerization range of 500–2000

Proposed oxidative endo mechanism:

*Also Flavobacterium, Acinetobacter and many others, as well as fungi, molds, and yeasts*

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Proposed oxidative endo mechanism:

\[
\text{CH}_2\text{CH} \quad \rightarrow \quad \text{C} \quad \rightarrow \quad \text{CH} \quad \rightarrow \quad \text{CH}_2
\]

(*) Also *Flavobacterium*, *Acinetobacter* and many others, as well as fungi, molds, and yeasts


---

Poly(vinyl acetate)
Precursor of PVA, hydrolyzed to less than 70% = non-biodegradable under conditions similar to those that biodegrade the fully hydrolyzed polymer

**Carboxylate derivatives** of poly(vinyl alcohol) are biodegradable and function in detergents as cobuilders

Vinyloxyacetic acid has been polymerized, eg, poly(vinyloxyaspartic acid), based on vinyl carbamates obtained from the reaction of vinyl chloroformates and amino acids such as aspartic and glutamic acids. **Both hydrolyze to poly(vinyl alcohol) and then biodegrade.**

High molecular weight poly(acrylic acid), polyacrylamide, and poly(vinylpyrrolidinone)

- They ozonize to oligomers with molecular weights less than 14 kDa and show an increased biodegradability, with the exception of PAM.

- Poly(acrylic acids) are not completely biodegradable above about a degree of polymerization of 6–8 (400–600 Da).

- Radical polymerization to synthesize biodegradable carboxylated polymers: combining low MW oligomers through degradable linkages and by introducing weak links into the polymer backbone.

- BASF and NSKK: patented acrylic oligomers chain-branched with degradable linkages.

- Grillo Werke: patented copolymers of acrylic acid and enol sugars.

- The degradability of these polymers has not been clearly established, but the branching is likely to be a problem.


Heteroatom Chain Backbone Polymers

Polyesters, polyamides, polyethers, polyacetals, and other condensation polymers.

- Their linkages are quite frequently found in nature - They are more likely to biodegrade than hydrocarbon-based polymers.

- Low melting, low MW aliphatic polyesters can be readily biodegradable.

- PCL: one of a few commercially available synthetic polymers that is biodegradable.

- Aliphatic polyesters (lipase hydrolysis): rate of production of water-soluble oligomers.

- As the aliphatic polyesters become more hydrophobic (acid or alcohol chain length extension): biodegradation rate is slower.

- Amorphous regions of polyesters are more readily biodegradable.

- Free-radical route to polyesters was used to introduce weak linkages into the backbones of hydrocarbon polymers and render them susceptible to biodegradability.

- Copolymerization of ketene acetals with vinyl monomers incorporates an ester linkage into the polymer backbone by rearrangement of the ketene acetal radical. The ester is a potential site for biological attack.


**Poly(lactic acid)**
Medical field: sutures and other biomaterials.

**Polyamides**
Stereocchemistry of the groups close to the amide linkages and the hydrophilic nature control biodegradability

Polyesteramides are difficult to hydrolyze chemically yet can be biodegraded rapidly at ambient conditions in the right environment. Polymers of nylon-6 are considered nonbiodegradable, oligomers and low molecular weight polymers of less than 157 (11 kDa) can biodegrade.

**Poly(ethylene glycol)**
Anaerobically degrades slowly (up to 2000 Da biodegrade). The biodegradation of poly(alkylene glycols) is hindered by their lack of water solubility, and only the low oligomers of poly(propylene glycol) are biodegradable. Polyether carboxylates have been evaluated as biodegradable detergent polymers.


---

**Modified Natural Polymers**

Blends with other natural and synthetic polymers, grafting of another polymeric composition, and chemical modification to introduce functional groups by oxidation, chemical reaction (esterification or etherification), etc.

Blending of polyethylene with starch and compatibilizers.

Biodegradation studies of starch blends have not been conclusive (biodisintegration would be a better term to describe these polymers).

Check: Water-sensitivity of manufactured articles, and the balance of this and biodegradation with the starch level in the product.

Others: Polyhydroxyalkanoates (PHA) with cellulose acetate, PHA with PCL, poly(lactic acid) with poly(ethylene glycol), chitosan and cellulose, poly(lactic acid) with inorganic fillers, and PHA and aliphatic polyesters with inorganics.

Graft sites for carboxylic monomers to produce detergent polymers (DP): without great success. The synthetic portion of the graft is not usually biodegradable, although MW limitations may help (DP< ca 6–8).

Acrylic grafts onto polysaccharides in the presence of alcohol chain-transfer: not completely biodegradable, nor were the ones based on initiation with Ce4+ and mercaptan. Protein substrates are expected to be similar to the starch grafts; the fundamental problem is the need to control acrylic acid polymerization to the oligomer range.

Simple chemical reactions on natural polymers are widely known to produce commercial polymers such as hydroxyethylcellulose, hydroxypropylcellulose, carboxymethyl cellulose, cellulose acetates and propionates. Their biodegradability is not at all well established.

Carboxymethylcellulose: has been claimed to be biodegradable below a degree of substitution of about 2, which is similar to that of cellulose acetate.

Attempts to more rigorously quantify biodegradation of the cellulose acetates and to establish a property–biodegradation relationship. Rhône-Poulenc indicates that cellulose acetate with a degree of substitution of about 2 is biodegradable.


The ampholytic product of the reaction of chitosan with citric acid is claimed to be biodegradable.

Carboxylated natural polymers have been known for many years, with the introduction of carboxymethylcellulose. This product has wide use in detergents and household cleaning formulations, although it is of questionable biodegradability at the level of substitution on cellulose required for performance.

Nevertheless, carboxylated polysaccharides are a desirable choice for many applications, and the balance of biodegradation with performance that is achievable has been recognized as an attractive possible goal met in this case with a high probability of success.

Three approaches have been employed: esterification, oxidation, or Michael addition of the hydroxyl groups to unsaturated carboxylic acids such as maleic and acrylic, with some attempts to react specifically at the primary or secondary sites.

Factors and mechanisms of Biodegradation

Adapted from Minna Malin, course Lecture notes 2015

Kijchavengkul, T. and Auras, R., Perspective compostability of polymers
Factors affecting biodegradation

Exposure conditions
- Abiotic
  - Temperature
  - Moisture
  - pH
  - UV radiation
- Biotic
  - Extracellular enzymes
  - Hydrophobicity
  - Biosurfactants

Polymer characteristics
- Flexibility
- Crystallinity
- Morphology
- Functional Groups
- Crosslinking
- Molecular Weight
- Copolymers
- Blend
- Tacticity
- Additives

Steps in Hydrolytic Degradation
- Water diffusion into the polymer
- Decrease in MW
- Change in physical properties
- Mass loss
- Formation of oligomers and monomers

Polymer characteristics
- Polymer structure and chain flexibility
- Copolymer composition
- Molecular weight and MW distribution
- Melting and glass transition T
- Hydrophilicity / Hydrophobicity
- Crystallinity
- Surface area (size and shape)

Backbone structure and side groups
- C-C backbones are normally stable
- Hetero-chain polymers, especially those having O or N in their backbones, are more susceptible to hydrolysis and biodegradation
- Aliphatic chains are more flexible than aromatic structures and thus more susceptible to hydrolysis and biodegradation
- Carbon double bonds in the polymer backbone increase the flexibility
- Bulky side groups limit chain flexibility

Adapted from: Minna Malin, course Lecture notes 2015
Crystallinity & Monomer solubility

<table>
<thead>
<tr>
<th>Monomer chain length (x)</th>
<th>Polymer</th>
<th>DSC analysis</th>
<th>Monomer solubility (mg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mw (x10^5) g/mol</td>
<td>Tmax (°C)</td>
<td>ΔH (J/g)</td>
</tr>
<tr>
<td>Adipic acid (PAA)</td>
<td>4</td>
<td>6</td>
<td>79</td>
</tr>
<tr>
<td>Pimelic acid (PPA)</td>
<td>5</td>
<td>22</td>
<td>72</td>
</tr>
<tr>
<td>Suberic acid (PSU)</td>
<td>6</td>
<td>23</td>
<td>76</td>
</tr>
<tr>
<td>Azelaic acid (PAZ)</td>
<td>7</td>
<td>37</td>
<td>72</td>
</tr>
<tr>
<td>Saeic acid (PSA)</td>
<td>8</td>
<td>466</td>
<td>89</td>
</tr>
<tr>
<td>Dodecanedioic acid (PDD)</td>
<td>10</td>
<td>353</td>
<td>95</td>
</tr>
<tr>
<td>Dodecanedicarboxylic acid (PDX)</td>
<td>12</td>
<td>24</td>
<td>94</td>
</tr>
</tbody>
</table>

Adapted from: Minna Malin, course Lecture notes 2015

Case: Polyesteramide, BAK® (Bayer)

Polyamide-6 based (caprolactam, butanediol, adipic acid): **ester content 35-40 wt.-%.** Application forms: films. Tm 116-137 °C.

Polyamide-66 based (hexamethylenediamine, butanediol, adipic acid): **ester content > 60 wt.-%.** Application forms: injection molded items, fibers. Tm 172 °C.
Stereostructure

Hydrolysis rate of the amorphous phase: DL > D ja L > L/DL

The ratio of the two stereo-isomers L(+) and D (-) in PLA determines the morphology of the polymer

Copolymer composition

Case: Aliphatic-aromatic copolyanhydride

CPP = 1,3-bis(p-carboxyphenoxy)propane
SA = Sebacic acid

<table>
<thead>
<tr>
<th>Polymer composition</th>
<th>T_m (°C)</th>
<th>T_g (°C)</th>
<th>ΔH (Cal / g)</th>
<th>Kiteisys %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Poly(SA), 100 %</td>
<td>86</td>
<td>60</td>
<td>37</td>
<td>66</td>
</tr>
<tr>
<td>Poly(CPP-SA) 4:96</td>
<td>76</td>
<td>42</td>
<td>25</td>
<td>47</td>
</tr>
<tr>
<td>Poly(CPP-SA) 13:87</td>
<td>75</td>
<td>47</td>
<td>21</td>
<td>40</td>
</tr>
<tr>
<td>Poly(CPP-SA) 22:78</td>
<td>66</td>
<td>47</td>
<td>15</td>
<td>30</td>
</tr>
<tr>
<td>Poly(CPP-SA) 31:69</td>
<td>66</td>
<td>40</td>
<td>5</td>
<td>11</td>
</tr>
<tr>
<td>Poly(CPP-SA) 41:59</td>
<td>178</td>
<td>4</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Poly(CPP-SA) 46:54</td>
<td>185</td>
<td>2</td>
<td>3</td>
<td>6</td>
</tr>
<tr>
<td>Poly(CPP-SA) 60:40</td>
<td>200</td>
<td>0</td>
<td>6</td>
<td>14</td>
</tr>
<tr>
<td>Poly(CPP-SA) 80:20</td>
<td>205</td>
<td>15</td>
<td>8</td>
<td>18</td>
</tr>
<tr>
<td>Poly(CPP), 100 %</td>
<td>240</td>
<td>96</td>
<td>27</td>
<td></td>
</tr>
</tbody>
</table>

In general, co-monomers increase irregularity of polymer chains, which usually reduce crystallinity and improve accessibility to water and microbes. Aromatic structures on the other hand increase rigidity of polymer chains, thus reducing degradability.
**Molar ratio**  
**Case of aliphatic-aromatic copolyanhydride**

---

**Aliphatic blocks degrade (faster/slower?) than aromatic blocks**

- Difference in the solubility of degrading monomers may induce porous areas on the surface of polymer.
- The solubility of monomers is dependent on polymer structure and pH.

---

*Adapted from: Minna Malin, course Lecture notes 2015*
Hydrophilicity - Hydrophobicity

- Hydrophilic polymers are more susceptible to hydrolytic degradation

- Hydrophilic polymers that contain hydrolysable bonds degrade homogenously (bulk degradation)

- Hydrophobic polymers that contain hydrolysable bonds degrade heterogeneously (surface erosion)


Crystallinity

The degradation of semi-crystalline polymers occurs in two stages:

(1) Water diffusion into the amorphous regions of the polymer and random chain scission → increase in crystallinity

(2) As hydrolysis advances, crystalline areas are attacked and eventually removed → decrease in crystallinity

Adapted from: Minna Malin, course Lecture notes 2015
**Abiotic conditions**

- Temperature
- Oxygen
- Water
- pH
- Light
- Salts
- Metal ions
- Nutrient content

---

**Temperature**

Rate of hydrolytic degradation increases as $T > T_g$

*Case of PGA filaments (T_g = 36 °C)*

---

Reed, A.M. and Gilding, K., Biodegradable polymers for use in surgery — poly(glycolic)/poly(lactic acid) homo- and copolymers, Polymer 22 (1981), 494-498
Salts

Salts are found in large quantities in biological media. In vitro and in vivo degradation rates may differ from each other.


Adapted from: Minna Malin, course Lecture notes 2015

<table>
<thead>
<tr>
<th>Ion</th>
<th>Plasma</th>
<th>Liquid in tissues</th>
<th>Intracellular liquid</th>
</tr>
</thead>
<tbody>
<tr>
<td>Na⁺</td>
<td>138</td>
<td>141</td>
<td>10</td>
</tr>
<tr>
<td>K⁺</td>
<td>4</td>
<td>4.1</td>
<td>150</td>
</tr>
<tr>
<td>Ca²⁺</td>
<td>4</td>
<td>4.1</td>
<td>40</td>
</tr>
<tr>
<td>Mg²⁺</td>
<td>3</td>
<td>3</td>
<td>40</td>
</tr>
<tr>
<td>Cl⁻</td>
<td>102</td>
<td>115</td>
<td>15</td>
</tr>
<tr>
<td>HCO₃⁻</td>
<td>26</td>
<td>29</td>
<td>10</td>
</tr>
<tr>
<td>PO₄³⁻</td>
<td>2</td>
<td>2</td>
<td>100</td>
</tr>
<tr>
<td>SO₄²⁻</td>
<td>1</td>
<td>1.1</td>
<td>20</td>
</tr>
<tr>
<td>Organic acids</td>
<td>3</td>
<td>3.4</td>
<td>—</td>
</tr>
</tbody>
</table>

SBF (mM)

142
5.0
2.5
1.5
147.8
4.2
1.0
0.5

Adapted from: Minna Malin, course Lecture notes 2015

Microorganisms

- Specific enzyme / mixed population
- Activity and amount of enzymes
- Endo-/Exoenzymes
- Exposure conditions

Case: Chain cleavage of PHA by exodepolymerases and endodepolymerases

Adapted from: Minna Malin, course Lecture notes 2015
**Enzymatic degradation mechanisms**

1) Extracellular degradation
2) Intracellular degradation

---


---

**Classification of enzymes**

- Proteins, over 2000 different kinds
- Endo/exoenzymes, molecular weight $5 \times 10^3 - 7 \times 10^6$ g/mol
- Complex, specific conformations, catalyze chemical reactions

<table>
<thead>
<tr>
<th>Enzyme class</th>
<th>Reaction catalysed</th>
<th>Reactive bonds</th>
</tr>
</thead>
<tbody>
<tr>
<td>Redox reactions</td>
<td>$\geq C=O$</td>
<td>$\geq C-NH_2$</td>
</tr>
<tr>
<td>Transfer of functional groups</td>
<td>One C-groups</td>
<td>Acetyl groups</td>
</tr>
<tr>
<td>Hydrolysis</td>
<td>Esters</td>
<td>Peptides</td>
</tr>
<tr>
<td>Addition to double bonds</td>
<td>$\geq C=O$</td>
<td></td>
</tr>
<tr>
<td>Isomerisation</td>
<td>Racemases</td>
<td></td>
</tr>
<tr>
<td>Formation of new bonds using ATP</td>
<td>$-C-O-$</td>
<td>$-C-S-$</td>
</tr>
</tbody>
</table>

Put choices in order:

A. Lyase
B. Isomerase
C. Hydrolase
D. Transferase
E. Oxidoreductase
F. Ligase

Adapted from: Minna Malin, course Lecture notes 2015
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| D Transferase | Transfer of functional groups | One C-groups
| C Hydrolase | Hydrolysis | Esters
| A Lyase | Addition to double bonds | -HC=CH-
| B Isomerase | Isomerisation | Racemases
| F Ligase | Formation of new bonds using ATP | -C-O-

Adapted from: Minna Malin, course Lecture notes 2015

Activity of enzymes and principle of function

- The conformational structure of the polypeptide is sensitive to changes in temperature, pH and osmolarity
- Optimal activity is also dependent on such cofactors as:
  - Inorganic metal ions (Fe$^{2+}$, Zn$^{2+}$, etc.)
  - Organic molecules (= coenzymes; NAD, FAD, ATP), which function as intermediate carriers of electrons or chemical groups that are transferred in the overall enzymatic reaction
- Enzymes lower the activation energy of the reactions and thereby increase the reaction rates
- Catalyze only single type of reactions without side reactions or by-products
- Function in dilute aqueous solution under moderate conditions of temperature and pH

Adapted from: Minna Malin, course Lecture notes 2015
Mechanisms of heterogeneous enzymatic reactions

**Adsorption – Chain scission**

- PHA depolymerase
- 2-Helix of P(R)-3HBI
- a) adsorption
- b) hydrolysis

**Concentration of the enzyme**

- Low concentration
  \[ R = k_4[E], \quad K[E] < 1 \]
- Optimum concentration
  \[ R = k_4/E, \quad K[E] = 1 \]
- High concentration
  \[ R = k_4/E, \quad K[E] > 1 \]

Adapted from: Minna Malin, course Lecture notes 2015

**Typical enzymes related to biodegradation of different main chain polymer structures**

<table>
<thead>
<tr>
<th>Main chain structure</th>
<th>Polymer</th>
<th>Corresponding enzyme responsible to the primary degradation</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C</td>
<td>C-C link</td>
<td>peroxidase oxidades lignin peroxidase dehydrogenase</td>
</tr>
<tr>
<td>C-O</td>
<td>C-O link</td>
<td>dehydrogenase oxidas peroxidase</td>
</tr>
<tr>
<td>OH</td>
<td>OH link</td>
<td>dehydrogenase oxidas peroxidase</td>
</tr>
<tr>
<td>C-O</td>
<td>C-O link</td>
<td>dehydrogenase oxidas peroxidase</td>
</tr>
<tr>
<td>O</td>
<td>O link</td>
<td>dehydrogenase oxidas peroxidase</td>
</tr>
<tr>
<td>C-N</td>
<td>C-N link</td>
<td>dehydrogenase oxidas peroxidase</td>
</tr>
<tr>
<td>O</td>
<td>O link</td>
<td>dehydrogenase oxidas peroxidase</td>
</tr>
<tr>
<td>N</td>
<td>N link</td>
<td>dehydrogenase oxidas peroxidase</td>
</tr>
</tbody>
</table>

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<th>Polymer</th>
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</tr>
</thead>
<tbody>
<tr>
<td>C-C-</td>
<td>C-C linkage</td>
<td>Oxidoreductase</td>
</tr>
<tr>
<td></td>
<td>polyethylene</td>
<td>peroxidase, lignin peroxidase, dehydrogenase</td>
</tr>
<tr>
<td></td>
<td>natural rubber</td>
<td></td>
</tr>
<tr>
<td></td>
<td>polyprene</td>
<td></td>
</tr>
<tr>
<td></td>
<td>lignin</td>
<td></td>
</tr>
<tr>
<td></td>
<td>OH</td>
<td>Dehydrogenase</td>
</tr>
<tr>
<td></td>
<td>poly(vinyl alcohol)</td>
<td>Oxidase, peroxidase</td>
</tr>
<tr>
<td>OH-OH</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>poly(ethylene glycol)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>poly(propylene glycol)</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ether linkage</td>
<td></td>
</tr>
<tr>
<td></td>
<td>polyesters</td>
<td></td>
</tr>
<tr>
<td></td>
<td>PHA, PCL, PLLA</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Ester linkage</td>
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<tr>
<td></td>
<td>polycarbonate</td>
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<td></td>
<td>Carbonate linkage</td>
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<td></td>
<td>poly(carbonate)</td>
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<td></td>
<td>Amide linkage</td>
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<tr>
<td></td>
<td>protein</td>
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<td>polylysine</td>
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<td></td>
<td>poly(glutamic acid)</td>
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<td></td>
<td>poly(aspartic acid)</td>
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<td>Urethane linkage</td>
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</tr>
<tr>
<td></td>
<td>polyurethane</td>
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</tr>
</tbody>
</table>


Homogenic bulk / Heterogenic surface degradation

- bulk erosion  
  e.g. aliphatic polyesters

- surface erosion  
  e.g. polyanhydrides, polyorthoesterers

**Autocatalytic hydrolysis**

Homogeneous specimen (> 2 mm)

Hydrolytic cleavage of ester bonds starts

Soluble oligomeric degradation products formed at the surface diffuse in the medium. Migration reverses the gradient of acidity and degradation becomes faster inside than at the surface.

As inner oligomers become small enough to be water soluble, they diffuse though the outer layer and dissolve in the medium. A hollow structure is formed.

Shell degrades at a much slower rate

**Steps of hydrolytic degradation**

- Water diffusion into the polymer
- Decrease in MW
- Change in physical properties
- Mass loss
- Formation of oligomers and monomers


Adapted from Minna Malin, course Lecture notes 2015
Hydrolytic degradation *in vitro*

**Analysis of the polymer:**
Visual evaluation (SEM)
Mass (weighing)
  - Mass loss
  - Water absorption
Molecular weight (SEC)
Mechanical properties (tensile-, compression tests)
Crystallinity changes (DSC)
Hydrophobicity (contact angle)
Structure (NMR, FTIR)

ISO 15814: 1999(E) Implants for surgery —
Copolymers and blends based on polylactide —
In vitro degradation testing

Relation between environment and aggressivity of biodegradation

Rate and degree of biodegradation are determined by various factors, which can be different from one environment to the other:
- Moisture content
- Oxygen availability
- Temperature
- Type of microbiology
- Density of microbiology
- Salt concentration.

Biodegradable plastic is not automatically biodegradable in all environments.

Polymers as biomaterials – requirements in medical applications

Minna Malin, course Lecture notes 2015

Biomaterial

"Synthetic material used to replace part of a living system, or to function in intimate contact with living system"

"A material intended to interface with biological systems to evaluate, treat, augment or replace any tissue, organ or function of the body"

"A substance which is used to direct the course of any therapeutic or diagnostic procedure in medicine"

Synthetic biomaterials:
- Metals
- Alloys and ceramics
- Polymers
- Composites

Joint replacements, bone plates and screws, dental root implants, pacers and suture wires, orthopedic implants, sutures, blood vessels, implantable ocular lenses, heart valves, surgical packaging, cannulae etc.

Williams D.F., On the nature of biomaterials, Biomaterials 30 (2009), 5897-5909

Link: Body Replacement Systems
Requirements for polymers in biomaterial applications

- Medical grade monomers
- FDA limits use of certain chemicals; use of toxic inhibitors and catalysts is problematic
- Remains (monomers, heavy metals, solvents) need to be analyzed
- Additional purification steps are needed
- Syntheses and packaging in clean conditions
- Suitable storage conditions

Raw material requirements

GLP, GMP

Requirements for raw material supplier

Requirements for device manufacturer

- Appropriate mechanical properties
- Processibility, sterilizability
- Controlled degradation (or stable): degradation time, degradation products matching indicated application

Master file for material family or single material:
- chemical and physical analysis
- initial information on biocompatibility

Certified quality system ISO 13485

Biocompatibility (ISO 10993), in vitro tests

* The ability of a material to perform with an appropriate host response in a specific situation*
- Requirements depend on target tissue and duration of the contact

ISO 10993: Biological evaluation of medical devices

- Chemical characterization of materials (ISO 10993-18)
- Identification and quantification of potential degradation products (ISO 10993-9)
- Cytotoxicity tests required (ISO 10993-5): counting of cell deaths and classification
- Genotoxicity (10993-3): needed for devices with longer contact

An example from ArtiVasc 3D-project. Materials synthesized at AALTO and tested at INNOVENT. Cell seeding with 3T3 cells on top of polyurethane materials. Viability and cell morphology checked after 1 and 4 days of incubation (FDA/GelRed® staining)

Control (glass) → Nice adhering cells/cell layers with typical cell morphologies
→ Some spherical cells, very few dead cells (< 5%, not shown)
→ Almost no living cells
→ Many dead cells
Biocompatibility (ISO 10993), *in vivo* tests

- **Sensitization and irritation** (ISO 10993-10):
  contact with skin or mucosal membrane (Guineapig or rabbit)

- **Toxicity** (10993-11):
  needed for implants or devices with longer contact (24 hours to 3 months),
  mouse is the most common test animal

- **Implantation** (10993-6):
  needed for implants and external communication devices with long contact,
  reference material with known tissue reactions needed,
  testing period should cover the degradation process of the material,
  minimum 3 parallel animals, 10 parallel samples

Requirements for long-term implantable devices:
*non-toxic, non-immunogenic, non-thrombogenic, non-carcinogenic, non-irritant*

Williams D.F., On the mechanisms of biocompatibility, *Biomaterials* 29 (2008), 2941-2953

Link: FDA regulations