Biodegradable Polymers: Synthesis, Properties and Current Challenges

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1. Overview on Biodegradable Polymers

Plastics World Production in 2016: 280 millions of tons

More than 95% derives from petrochemistry

World Production of Biodegradable Polymers

<table>
<thead>
<tr>
<th>Year</th>
<th>Production (t)</th>
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<tbody>
<tr>
<td>1990</td>
<td>500</td>
</tr>
<tr>
<td>2002</td>
<td>254,000</td>
</tr>
<tr>
<td>2017</td>
<td>882,000</td>
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(≈ 0.34% of the market in 2017)

Source: ADEME (Agence De l’Environnement et de la Maîtrise de l’Énergie)

Context: Expected decrease of petrochemical resources, waste production

Key Challenges: Development of alternative materials from renewable and natural resources that exhibit the essential properties of « classical » plastics (polyolefins) and may even outperform them.

Thus, the tremendous interest for biodegradable polymers from renewable resources over the last 15 years
Global Production of Bioplastics

Global production capacity of bioplastics (2017)

Bioplastics production: region by region

Global production capacity by region in 2017


* Production in Australia/Oceania is a small proportion relative to the global production capacity.
In 2017, only 43% of produced bioplastics are biodegradable
Biodegradability is one of the most important parameters to characterize the environment impact of organic products. It is directly related to the rate of decomposition under natural biological conditions.

Example: A dead tree leave is 100% biodegraded within a few weeks. In contrast, it would take 450 years to fully degrade a « PE-made leave » under identical conditions.
**Phase 1:** polymer breaking, biofragmentation
**Phase 2:** bioassimilation, mineralisation

**Important factors impacting biodegradation**
- Degree of polymerisation: a low molecular weight polymer favors biodegradation.
- Hydrophilic or hydrophobic character of the material
- The crystallinity of the polymer: the higher it is, the slower biodegradation is.
- Thickness of the material
**Definition:** A thermoplastic material is characterized by elastic and flexible properties above a glass transition temperature ($T_g$). Above a higher temperature ($T_m$), it melts.

- **Crystallinity** → Strength
- **Amorphous character** → Flexibility

**Ideal thermoplastic:** Low $T_g$ and high $T_m$ (large $T_g$-$T_m$ region)

Example: Polyethylene (PE): $T_g = -127 ^\circ C; T_m = 130 ^\circ C$

PLA (after extrusion): $T_g \approx 55 ^\circ C$, $T_m = 50 - 80 ^\circ C$
1) Cellulose-derived Biodegradable Polymers (BPs)

Applications: - paper, cellophane (cellulose sheets), viscose (cellulose fibers)

Limitations: - overall environmental impact similar to that of PE
- additional synthetic steps consume fossil resources
- limited biodegradability
2) Starch-derived Biodegradable Polymers (BPs)

Limitations:
- necessity to isolate from biomass
- limited processability

Products of current interest: Starch foam, biodegradable polyesters/starch blends.

Blends with biodegradable polyesters are completely compostable
(see the material under the tradename Mater-Bi produced by Novamont)

http://www.materbi.com/ing/html/index_home.html
Natural Polysaccharide:
- Excellent mechanical properties (crystallinity)
- Biodegradability and biocompatibility

Drawbacks:
- Insoluble at physiological pH
- Moderate processability

Important application in the biomedical area (implants)
- Excellent biocompatibility (better than synthetic biodegradable materials)
Microbially Synthesized Polyesters

Poly(3-hydroxybutyrate (PHB)
(stereoregular isotactic polymer)

PHB and PHVB may be produced by various bacteria by fermentation of carbohydrates under controlled nutrition conditions.

PHVB versus PHB:
- better thermoplastic processability and mechanical stability
Non-biodegradable Polymers from renewable feed stocks

**Bio-PE**

\[ \text{éthylène} \rightarrow \text{Poly(éthylène) (PE)} \]

Numerous applications

**Production of Bio-ethylene (200,000 t in 2017):**
- Dehydration of ethanol (from glucose fermentation)
- Biosynthesis from methionine (amino acid)

L-méthionine
(one of the eight amino-acids essential to mankind)
Bio-PET

\[
\text{Bio-EG} \quad \text{Polycondensation} \quad \text{Ethylene polyterephthalate (PET)}
\]

- Use of Bio-ethylene glycol (bio-EG): from bio-ethylene

Applications: bottles, textile (Tergal), transparent films, LCD screens
Production: 26% of all bioplastics
Aliphatic Polyesters

petrochemical origin

ε-caprolactone (production of 33000 t. in 2006)

ring-opening polymerization by a metal alkoxide species (M-OR)

poly(ε-caprolactone)

Used in blending with starch
Easy to process (low melting point)

polybutylenesuccinate (PBS)
Excellent mechanical properties
Applications: films, packaging
Production: 100,000 t in 2017

succinic acid

1,4-butanediol
Polybutylene adipate terephthalate (PBAT): Biodegradable co-polymeric material

Monomers:

Polybutylene adipate terephthalate (PBAT): a co-polymer as an alternative to low-density PE

Flexible, rigid and biodegradable material

Applications: packaging, coatings

Production in 2017: 100,000 t (5% of all bioplastics)
Biodegradable Polymers derived from renewable resources

- **Poly(glycolic acid) (PGA)**
  - Bio-synthesis from glucose
  - Extracted from corn or sugar beets

- **Poly(lactic acid) (PLA)**
  - Bio-synthesis from glucose
  - Extracted from corn or sugar beets
Present Limitations of these polymers

Their mechanical and thermal properties are not yet good enough to replace polyolefins (« classical » plastics)
**The case of Poly(lactic acid)**

**Industrial Production:** 200,000 t. in 2017 (from lactic acid)

*First and most important* BP from renewable raw resources to be produced on an industrial scale

**Structure of commonly commercialized PLA:** Highly Isotactic

![Structure of Poly(L-lactic) acid](image)

\[ \text{T}_g = 50 \text{ to } 55 \, \text{°C} \]
\[ \text{T}_m = 162 \, \text{°C} \]

Poly (L-lactic) acid

The stereoregularity of the PLA greatly improves its thermal and mechanical properties

**Current Applications (other than medical):** packaging, food containers, clothes
Life-cycle of polylactide

"Cradle to grave"

Composting

Fermentation

Polymerization

PLA products

PLA pellets

HO-CH-C-OH

CH₃
Industrial production of PLA

Starch (from corn) enzymatic hydrolysis → glucose

\[ \text{lactobacillus} \quad \text{ca. 3 days} \quad 90\% \text{ yield} \quad \text{up to} \quad 100 \text{ g L}^{-1} \text{ of product} \]

\[ \text{HO} - \text{CH}_3 \]
\[ \text{HO} - \text{CO} - \text{CH}_2 - \text{COOH} \]
\[ \text{CH}_3 \]
\[ \text{HO} - \text{CO} - \text{CH}_2 - \text{COOH} \]

\[ \text{l(+)-lactic acid (LA)} \]

\[ \text{separation and purification} \]
\[ 2 \text{ LA} + \text{Ca(OH)}_2 \rightarrow \text{Ca-lactate} + 2 \text{ H}_2\text{O} \]
\[ \text{Ca-lactate} + \text{H}_2\text{SO}_4 \rightarrow 2 \text{ LA} + \text{CaSO}_4 \]
\[ \text{or} \]
\[ \text{LA} + \text{NaOH} \rightarrow \text{Na-lactate} + \text{H}_2\text{O} \]
\[ \text{electrodialysis: Na-lactate} + \text{HCl} \rightarrow \text{LA} + \text{NaCl} \]

\[ \text{HO} - \text{CO} - \text{CH}_2 - \text{COOH} \]
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\[ \text{Sn}^{II}(\text{O}_2\text{CR})_2 \quad \text{200 °C} \quad \text{vacuum} \]

130 °C / 30 h diphenyl ether / molecular sieves azeotropic distillation

\[ \text{purification by recrystallization or distillation} \]
\[ > 99.9 \% \text{ l-lactide} \]

\[ \text{formation by partial racemization} \]

\[ \text{meso-lactide} \quad T_m 52 \degree \text{C} \]
\[ \text{D-lactide} \quad T_m 97 \degree \text{C} \]
\[ \text{l-lactide} \quad T_m 97 \degree \text{C} \]

 PLA \[ M_w \text{ up to} 3 \times 10^5 \text{ g mol}^{-1} \]

\[ T_m \sim 160 \degree \text{C} \]

Synthesis of poly(lactic acid) (PLA).
Sn(Oct)$_2$ as ROP initiator of lactide

Industrially used for the production of PLA

Mechanism:
Biodegradation of PLA

Via Chemical hydrolysis and subsequent enzymatic chain cleavage

First stage: 2 weeks hydrolysis at 60 °C

PLA degrades to water-soluble compounds
And lactid acid

Second stage: Enzymatic chain cleavage (several months)

Rapid metabolisation of these products into CO₂, H₂O and biomass by a variety of microorganisms
Stereochemistry of lactic acid and lactide

D(R)-lactic acid
R₁: H
R₂: CH₃

L(S)-lactic acid
R₂: H
R₁: CH₃

D-lactic acid + L-lactic acid (rac-lactic acid)

D,D(R,R)-lactide
R₁, R₃: H
R₂, R₄: CH₃

L,L(S,S)-lactide
R₂, R₄: H
R₁, R₃: CH₃

D,L(R,S)-lactide (meso-lactide)
R₁, R₄: H
R₂, R₃: CH₃

D,D-lactide + L,L-lactide (rac-lactide)

L = Levorotatory
D = Dextrorotatory
Better Control of the Chain length and of the Stereoregularity

- Improve mechanical and thermal properties
- Access to potentially interesting new BPs

\[ \text{isotactic} \]
\[ \text{syndiotactic} \]
\[ \text{heterotactic} \]

\[ T_m \sim 150 \text{ to } 230 \, ^\circ C \]

The only PLA commercially available
Some examples on effects from the repeating units in polylactide

<table>
<thead>
<tr>
<th>Repeat Units</th>
<th>Temperature 1</th>
<th>Temperature 2</th>
</tr>
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<tbody>
<tr>
<td>Poly(L,L-lactide)</td>
<td>53-64 °C</td>
<td>145-186 °C</td>
</tr>
<tr>
<td>Poly(meso-lactide)</td>
<td>40-50 °C</td>
<td>-</td>
</tr>
<tr>
<td>Poly(D,L-lactide)</td>
<td>45-55 °C</td>
<td>-</td>
</tr>
<tr>
<td>Poly(L-lactide-b-D-lactide)</td>
<td>53-64 °C</td>
<td>145-186 °C</td>
</tr>
<tr>
<td>Poly(L-lactide) / Poly(D-lactide) stereocomplexes</td>
<td>65-75 °C</td>
<td>220-230 °C</td>
</tr>
</tbody>
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