Hydrolytic Degradation of Polylactide and Production of Water-Soluble Hydrolyzate Species

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Polylactide (PLA)

- **Polylactide (PLA)** is an aliphatic polyester polymer derived from lactic acid. Controlled **stereochemistry** of lactides allows flexibility to control physical and mechanical properties.

- **Applications of PLA:**
  - Textile fibers
  - Rigid thermoforms
  - Food and beverage containers
  - Biocompatible medical devices
A Critical Property Limiting PLA Applications is Moisture Permeation

• Why is Moisture Sorption/Transport in PLA Important?

*Commercial PLA water bottle buckles due to water loss after storage in warehouse for several months!*

**Schematic of Moisture Transport Through Bottle Wall**

- Wall Collapse
- Clustering of Hydrophilic Groups?
- Crystalline Domains

**Water Loss from Biota PLA Bottle**

\[ y = -0.1454x + 5954.2 \]

- R² = 0.9978

**PLA bottle loses about 1 g water/week**
Mechanics of Moisture Transport in PLA

Hydrophilic Alcohol End-Group

Hydrophilic Acid End-Group

Hydrophobic Chain of Ester Linkages

Hydrolysis degrades PLA

+ H2O

scission of ester bonds with water

Lactic Acid

Lactic Acid Dimer

Polymer Fragments & Oligomers

High MW PLA is Moderately Hydrophobic (absorbs 0.5-1% water)

Hypothesis:

Hydrophilic end groups critical for moisture sorption and transport:

- end groups excluded from crystalline regions of PLA
- # end groups increases with degradation
Hypothesis: *Hydrophilic end groups* critical for moisture sorption and transport

- Observations **Consistent** with Hypothesis
  - Sorption insensitive to crystallinity
  - Sorption increases with degradation
- Observations **Inconsistent** with Hypothesis
  - Low MW PEP-PLA block co-polymer absorbs only 30% less moisture
  - Sorption in Low MW PLA insensitive to end group composition (similar sorption to high MW PLA)
Degradation in PLA

Hydrophilic Alcohol End-Group

Hydrophobic Chain of Ester Linkages

Hydrophilic Acid End-Group

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+ H2O

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Lactic Acid

Polymer Fragments & Oligomers

Lactic Acid Dimer
Degradation of PLA

• Why is Degradation important?
• Controlled Degradability of PLA Products
  – Minimize degradation during use
  – Maximize degradation during waste management (composting)
• Degradation is coupled to moisture sorption/transport
Experimental Methods for Monitoring Degradation of PLA

• Controlled Temp & RH
• Analysis
  – Weighing
  – Acid/Base Titration
  – HPLC & GPC
  – NMR (with D$_2$O)
  – Sorption Experiments
  – Thermal Mechanical Properties
Degradation of PLA Exposed to Humid Air

- Degradation of PLA in Controlled Environment
- Desiccator placed in oven at given temperature
- Water activity maintained via saturated salt solution in desiccator base
- Conditions studied:
  - 85% RH and 30°C, 65°C and 80°C
Moisture Gain of PLA @ 85% Relative Humidity

- **35°C >T<sub>g</sub>**: Diffusion-limited Absorption
- **80°C >T<sub>g</sub>**: Hydrolytic Degradation Prompts Additional Hydrolytic Sites

- **Amorphous & low-crystalline samples** absorb more water

Legend:
- 4032: Highly Crystalline PLA (■)
- 4042: Moderate Crystalline PLA (●)
- 4060: Amorphous PLA (◆)
- Stereocomplex: Mix of PLLA & PDLA (▲)
Comparison of Changes in Crystallinity at 85%RH
Two Temperature Regimes

80°C > T_g
Amorphous Regions of PLA degraded:
Crystalline Fraction Increases

35°C < T_g
~ Unchanged Crystallinity
Samples below T_g unsuceptable to hydrolytic
degradation of amorphous regions

Amorphous Sample (4060) @ 80°C:
Possible Crystalline Induction
Degradation of PLA

Results from RI-Detection SEC, Kolthoff Laboratory, Dr. Hillmyer
*Apparent Mn based on Polystyrene Standards

35°C < Tg
Crystal and Amorphous Samples:
No Hydrolytic Degradation

80°C > Tg
Crystal and Amorphous Samples:
Significant Hydrolytic Degradation

Rapid Degradation at 80°C
Possible Dominance of Random Chain-Scission

Figure 10: Degradation of PLA exposed to 85% relative humidity. Changes in molecular weight measured by GPC.
Effect of Degradation on Sorption

Degradation at 60°C

Degradation at 80°C

Degradation Causes Rapid Rise in Sorption

– After Induction Period
Degradation of PLA Immersed in Water

• Two time series of degradation experiments – varying degrees of degradation deionized and deuterated water

• Analysis of the hydrolyzate containing the degraded products
  – Weighing
  – Acid/Base Titration
  – HPLC & GPC
  – NMR (with D$_2$O)
Degradation of PLA – Monitored by Mass Changes & Acid-Base Titration

Days of Degradation at 80C

Mass Change (% of initial mass)

Mass Loss of PLA Pellets from Balance
Mass Lactic Acid in Hydrolyzate from Titration
Change in PLA Molecular Weight (Mn) from GPC

*Initial Mn ~ 100K at Day 0*
Degradation Reactions in PLA

Hydrolysis degrades PLA
By scission of ester bonds with water

Functional Group Kinetics

3 Functional Groups:

- Monomer = Lactic Acid (90 g/mol)
- End Group (81 g/mol)
- Chain Group (72 g/mol)

½ Oxygen Atom To Account For Sharing of Ester Bonds
Functional Group Kinetics for PLA Degradation

3 Functional Groups:
- Monomer = Lactic Acid (90 g/mol)
- End Group (81 g/mol)
- Chain Group (72 g/mol)

Random Scission Reaction:

\[
\begin{align*}
\text{End} & \quad \text{Chain} & \quad \text{Chain} & \quad \text{Chain} & \quad \text{Chain} & \quad \text{Chain} & \quad \text{End} \\
\end{align*}
\]

\[
2 \quad \text{Chain} + \ H_2O \rightarrow 2 \quad \text{End}
\]

End Scission Reaction:

\[
\begin{align*}
\text{Chain} & \quad \text{End} & \quad + \ H_2O \rightarrow \text{End} & \quad + \text{Monomer} \\
\end{align*}
\]

Molecular Weight:

\[
M_n = \frac{72 \cdot n_C + 81 \cdot n_E}{n_E / 2}
\]
Analysis of Extent of Random and End Scission Reactions

Extent of Reaction = % of Ester Bonds Cleaved

Days of Degradation at 80C

Extent of Degradation Reactions (%)
Degradation of PLA immersed in Water at 80°C

- Random scission increases slightly the first two days - ~1% random scission sufficient to more than half the Mn
  - Falling MW without Soluble Products (lactic acid)
- No change in polymer pellets mass until 2 days
  - End Scission Dominates after the first 2 days
- Falling pH after 2 days →Rapid End Scission
Conclusions

• A Critical Property Limiting PLA Applications is Moisture Permeation
• Degradation is Coupled to Moisture Sorption/Transport
• PLA is Moderately Hydrophobic
• Hydrolytic Degradation creates additional hydrolytic sites causing rapid rise in sorption – After Induction Period
• Functional Group Kinetics of PLA degradation indicate that end group scission dominates after the first 2 days creating an autocatalytic effect
• Random scission, albeit small (~1%), very active in the first two days causing more than 50% decrease in Mn