# Biodegradable PLA Elastomers Based on bis-Oxazoline Coupling

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Poly(lactic acid) [PLA] and poly(glycolic acid) [PGA], homopolymers and co-polymers, have long been accepted as preferred candidates for biodegradable plastic and polymeric coating applications. Such ready acceptance trades on these polyesters being susceptible to relatively facile hydrolytic degradation to their ultimate monomeric units, lactic and glycolic acids, both of which are functionally compatible with human metabolic processes. These polymers therefore result in being considered environmentally friendly". Lactic acid, is of course, a normal metabolite and precursor in the human body's glycogen - glucose energy cycle.

Further evidence of PLA's acceptance in biodegradable polymer applications would be Dow / Cargill's construction of production facilities with a capacity of 300 M/pa of PLA resin.

To support PLA's acceptability for these markets, as well as enhance value to the US Agricultural Industry, work at Argonne National Laboratory (ANL), starting about 15 years ago, was directed at developing low cost access to lactic acid , specifically through the intermediacy of normally low-value high carbohydrate food wastes, such as potato starch, which can be converted (saccharified) to glucose and then fermented to lactic acid. The traditional approach to high molecular weight (HMW) PLA has been by the self- condensation of lactic acid to a low molecular weight (LMW) PLA followed by "cracking" to the cyclic lactide. The cyclic lactide, intensively purified, can then be subjected to ring opening polymerization to HMW PLA. Work at ANL opted for a non-traditional approach to "modified" HMW PLA involving "stitching" together LMW macromeric PLA segments into a "modified" HMW PLA.

PLA by virtue of its high $T_g$ (ca 58 degree $^{o}$C) and low tensile extensibility (3-10%) was initially of low interest for a particular end product application, a biodegradable chewing gum base. Because of the degrees of freedom introduced by the "stitching" approach, it became apparent that by judicious choice of "stitching" agent and possibly by introduction of "foreign" flexibilizing segments custom tailoring of a modified HMW PLA could potentially lead to the desired biodegradable PLA elastomer. Work reported herein outlines the successful development of a biodegradable chewing gum base, involving the coupling of a modified PLA macromer with 1,3-phenylene bis-oxazoline.

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# Objectives: PLA Polymer Pgm

- I. High molecular wt PLA by a more cost effective route
- II. Specialized properties for PLA by copolymerization (eg: bio-photodegradable, controlled water sensitivity)
- III. PLA polymer blends and alloys for specialized applications (eg: water permeability, higher service temps

# Topics of Discussion

- Historical Perspective: ANL Program on Poly (lactic acid) {PLA}
- Lactic Acid source from fermentation of High Carbohydrate Food Wastes
- Polymerization of PLA:
  - Lactide Ring Opening
  - “Stitching” together Lactic Acid Macromers
    - Di-isocyanates
    - bis-oxazolines

# Argonne National Laboratory PLA

- The starch in High Carbohydrate Food Wastes can be hydrolyzed to Glucose.
- The Glucose can be fermented with bacteria to Lactic acid
- Research in conversion of Lactic Acid into “Environmentally Friendly” polymers and elastomers
- ANL, Du Pont / Con Agra, Coors, Dow Cargill

# Rationale for Coupling

- Lactide ring opening limits versatility
- Degrees of Freedom can be improved by stitching using various coreactants
  - Di anhydrides
  - Di isocyanates
  - bis-oxazolines
- Introduction of reactive macromers allow the development of specialized properties!

# Lactic Acid Recovery

- Agricultural High Carbohydrate Sources
  - Potato Processing byproducts
  - Cheese Whey
  - Grains – corn, rice
- Liquefaction ( amylase to amylose )
- Saccharification (amylose to glucose)
- Fermentation (glucose to lactic acid)

# Lactic Acid Isolation / Purification

- Isolation
  - Pervaporation
  - Osmotic Filtration
  - Acidification
- This yields the precusor to the macromer

# PLA Macromer

- Copolymerize Lactic Acid with Dimer Acid by condensation

# bis-Oxaziline Coupling

- React PLA Macromer with bis-Oxaziline in a melt state to produce the resulting modified HMW PLA

# Application Case Study

- Polymeric, biodegradable chewing gum base.
- Product approval under FDA review

# New Applications

- Biodegradable Adhesives
  - Hot melt label adhesives
  - Paper board laminates
- Edible food product coatings
  - Nuts
  - Cookies
- Biodegradable coatings for trays and cups

# Thermal Properties

- Low melting
- Low Tg
- Good Thermal Stability

# Benefits of Coupling Approach

- Improved hydrophillicity can be incorporated
- Improve biodegradation and compostibility in polymers

# Summary:

- Coupling mechanism offers custom designed improvements over traditional PLA ring opening polymerization