POLYMER (PLASTICS) DEGRADATION: POLYLACTIC ACID

Christine Schifone

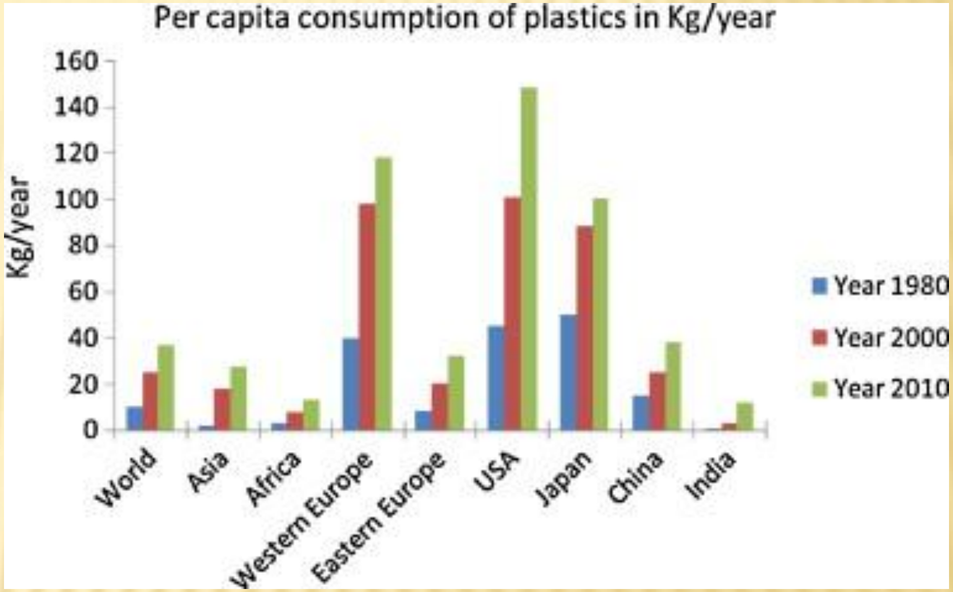
December 8, 2011

OVERVIEW

- Background
- Degradation processes
- Polylactic acid
  - Synthesis
  - Modification
  - Uses
- Conclusions

PLASTIC PRODUCTION

- Global production was 245MT in 2006
- Increases by almost 10% every year
- USA consumed 39MT in 2010
- 40% of plastic has a service life of less than 1 month



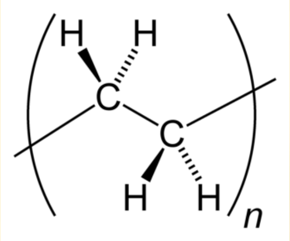
Panda D. *Achyut Thermolysis of waste plastics to liquid feul A suitable method for plastic waste management and manufacture of value added products-A world prospective* 6 July 2009. Renewable and Sustainable Energy Reviews

BACKGROUND CONT.

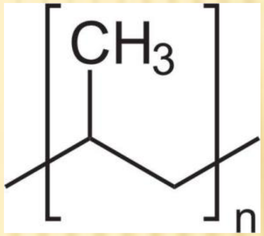
- Fossil fuels
  - However, uses less than other materials
- Waste accumulation
  - C-C backbone resist degradation
- Nurdles
  - Microplastic particles
  - May absorb organic pollutants
- Additive leaching (Plasticizers)
  - Phthalates disrupt the endocrine system and may be carcinogenic
- Toxic monomers (Vinyl Chloride)

COMMON PLASTIC POLYMERS

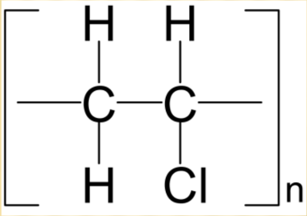
- Polyethylene (PE)
  - Most widely used plastic



- Polypropylene (PP)



- Polyvinyl chloride (PVC)



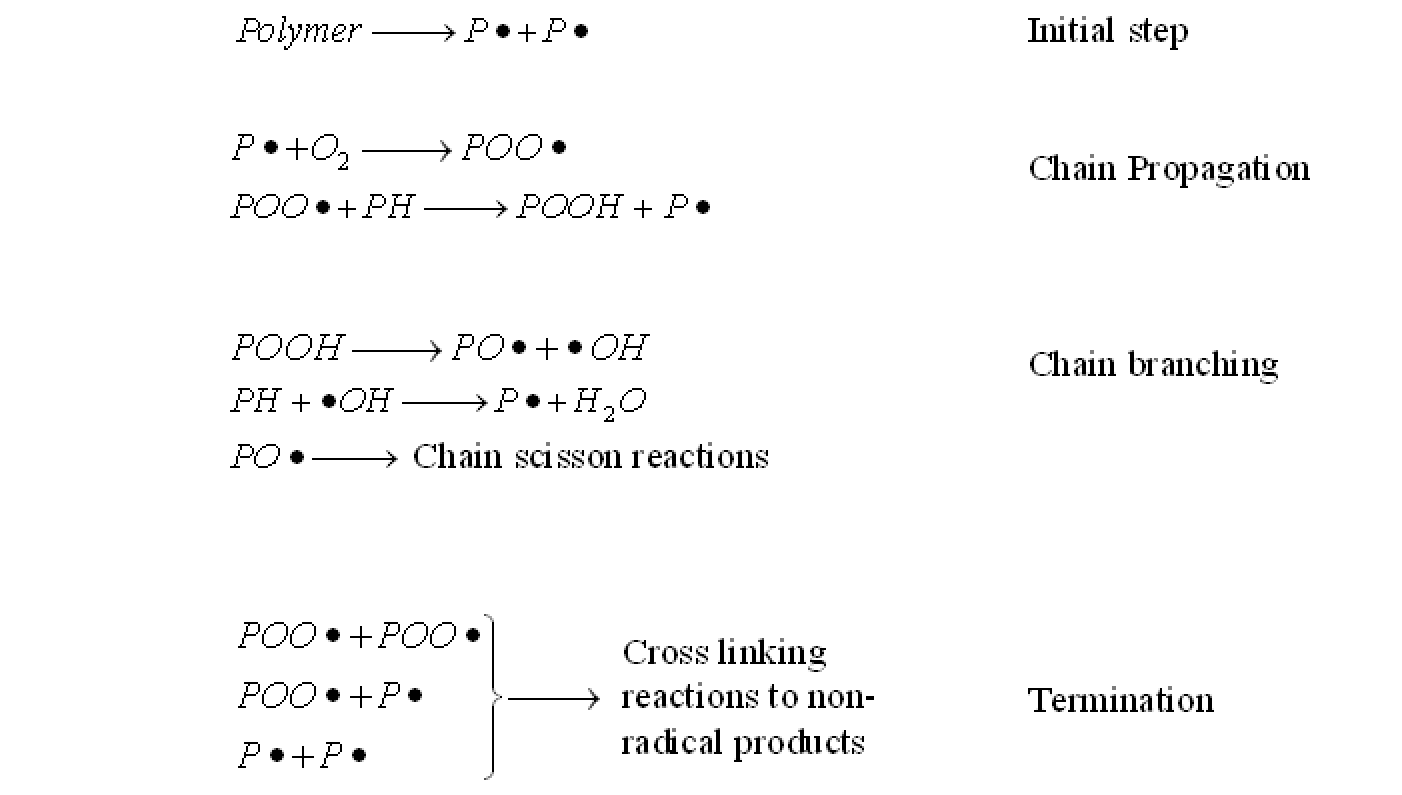
http://illumin.usc.edu/7/recycling-plastics-new-recycling-technology-and-biodegradable-polymer-development/

DEGRADATION PROCESSES

- Photo-oxidation
- Hydrolysis
- Thermal
- Mechanical stress
  - heating/cooling
  - freezing/thawing
  - wetting/drying
  - fungi
  - waves

http://www.dowcorning.com/content/publishedlit/01-1112-01.pdf

PHOTO-OXIDATION



Initial step

$$Polymer \longrightarrow P\bullet + P\bullet$$

Chain Propagation

$$P\bullet + O_2 \longrightarrow POO\bullet$$

$$POO\bullet + PH \longrightarrow POOH + P\bullet$$

Chain branching

$$POOH \longrightarrow PO\bullet + \bullet OH$$

$$PH + \bullet OH \longrightarrow P\bullet + H_2O$$

$$PO\bullet \longrightarrow \text{Chain scisson reactions}$$

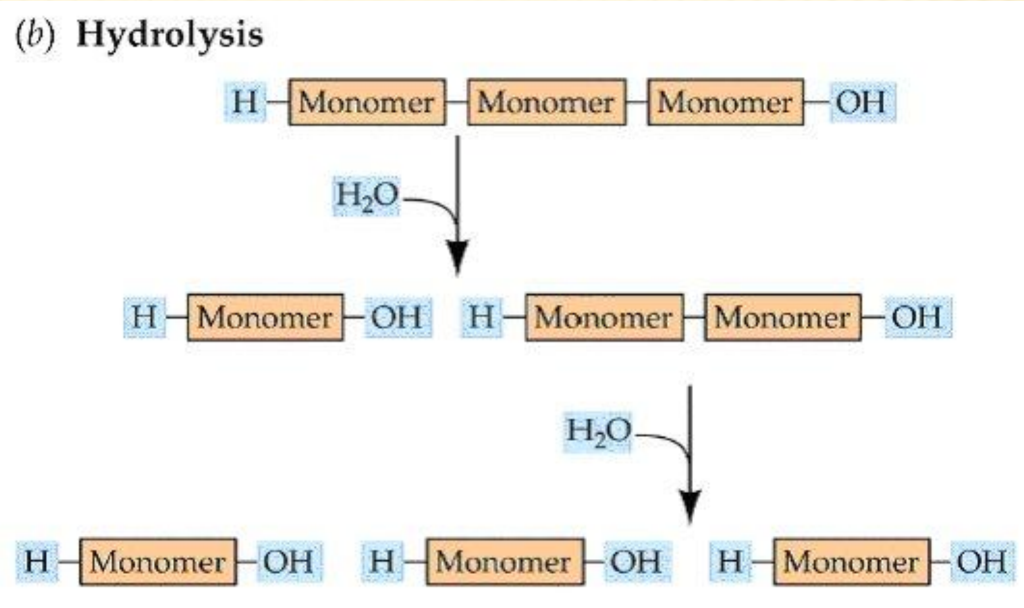
Termination

$$\left.\begin{array}{l} POO\bullet + POO\bullet \\ POO\bullet + P\bullet \\ P\bullet + P\bullet \end{array}\right\} \longrightarrow \text{Cross linking reactions to non-radical products}$$

http://en.wikipedia.org/wiki/Photo-oxidation_of_polymers

HYDROLYSIS

- Acid or base catalyzed



http://bcs.whfreeman.com/thelifewire8e/pages/bcsmain_body.asp?s=03000&n=00010&i=03010.01&v=chapter&o=|26000|&ns=0

BIODEGRADABLE POLYMER

- Linkages such as anhydride, ester, or amide bonds
  - Weakens backbone/ Increases hydrolysis
- Maintain good mechanical integrity until degraded
  - May need additives/fillers
- Controlled rates of degradation
  - percent crystallinity
  - molecular weight
  - hydrophobicity

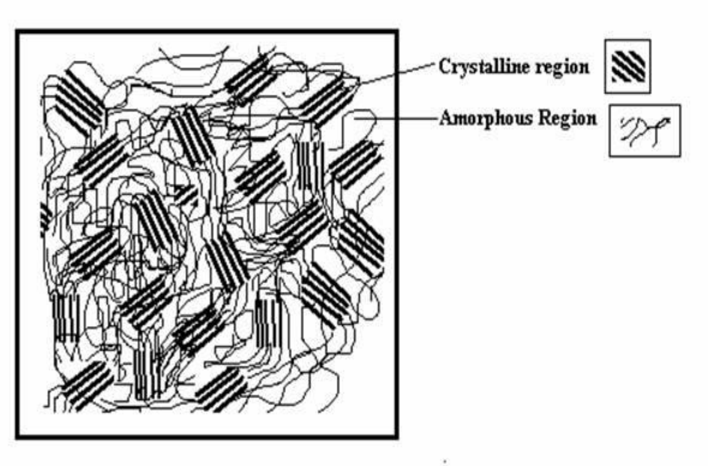
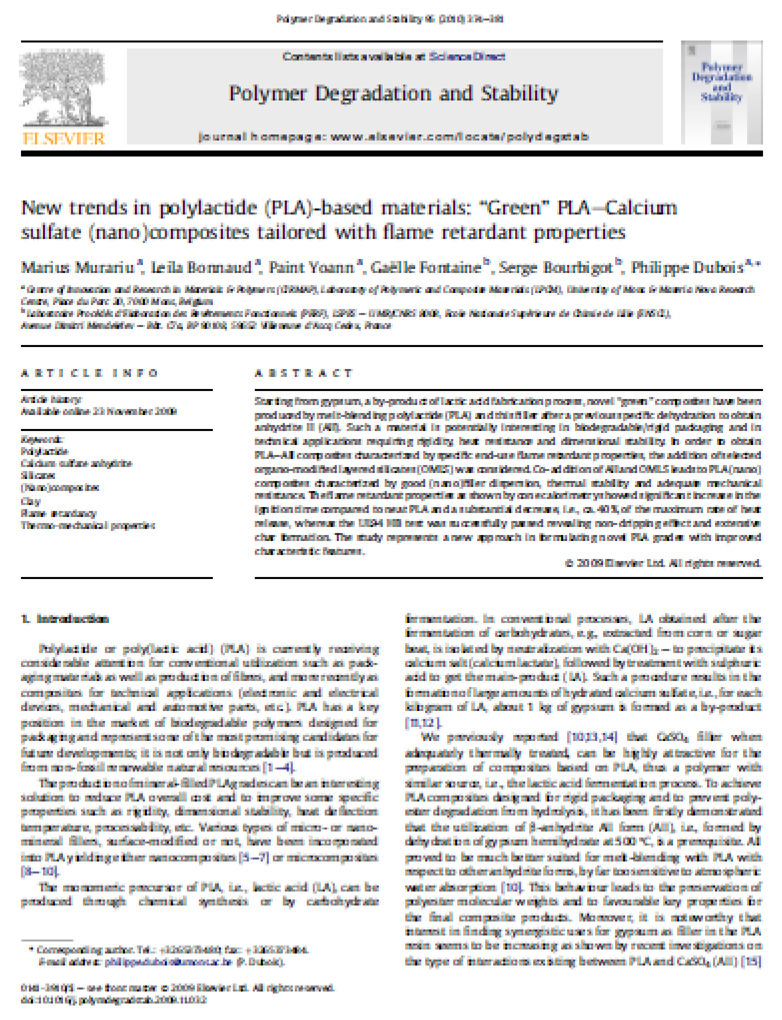


Fig 1. Mixed Amorphous Crystalline Macromolecular Polymer Structure

http://web.utk.edu/~mse/Textiles/Polymer%20Crystallinity.htm

ARTICLE TAKEN FROM ELSEVIER JOURNAL, *POLYMER DEGRADATION AND STABILITY*



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New trends in polylactide (PLA)-based materials: "Green" PLA–Calcium sulfate (nano)composites tailored with flame retardant properties

Marius Murariu[a], Leila Bonnaud[a], Paint Yoann[a], Gaëlle Fontaine[b], Serge Bourbigot[b], Philippe Dubois[a,*]

[a] *Centre of Innovation and Research in Materials & Polymers (CIRMAP), Laboratory of Polymeric and Composite Materials (LPCM), University of Mons & Materia Nova Research Centre, Place du Parc 20, 7000 Mons, Belgium*

[b] *Laboratoire Procédés d'Elaboration des Revêtements Fonctionnels (PERF), LSPES – UMR/CNRS 8008, Ecole Nationale Supérieure de Chimie de Lille (ENSCL), Avenue Dimitri Mendeleïev – Bât. C7a, BP 90108, 59652 Villeneuve d'Ascq Cedex, France*

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ABSTRACT

Starting from gypsum, a by-product of lactic acid fabrication process, novel "green" composites have been produced by melt-blending polylactide (PLA) and this filler after a previous specific dehydration to obtain anhydrite II (AII). Such a material is potentially interesting in biodegradable/rigid packaging and in technical applications requiring rigidity, heat resistance and dimensional stability. In order to obtain PLA–AII composites characterized by specific end-use flame retardant properties, the addition of selected organo-modified layered silicates (OMLS) was considered. Co-addition of AII and OMLS leads to PLA (nano)composites characterized by good (nano)filler dispersion, thermal stability and adequate mechanical resistance. The flame retardant properties as shown by cone calorimetry showed significant increase in the ignition time compared to neat PLA and a substantial decrease, i.e., ca. 40%, of the maximum rate of heat release, whereas the UL94 HB test was successfully passed revealing non-dripping effect and extensive char formation. The study represents a new approach in formulating novel PLA grades with improved characteristic features.

1. Introduction

Polylactide or poly(lactic acid) (PLA) is currently receiving considerable attention for conventional utilization such as packaging materials as well as production of fibres, and more recently as composites for technical applications (electronic and electrical devices, mechanical and automotive parts, etc.). PLA has a key position in the market of biodegradable polymers designed for packaging and represents one of the most promising candidates for future developments; it is not only biodegradable but is produced from non-fossil renewable natural resources [1–4].

The production of mineral-filled PLA grades can be an interesting solution to reduce PLA overall cost and to improve some specific properties such as rigidity, dimensional stability, heat deflection temperature, processability, etc. Various types of micro- or nano-mineral fillers, surface-modified or not, have been incorporated into PLA yielding either nanocomposites [5–7] or microcomposites [8–10].

The monomeric precursor of PLA, i.e., lactic acid (LA), can be produced through chemical synthesis or by carbohydrate fermentation. In conventional processes, LA obtained after the fermentation of carbohydrates, e.g., extracted from corn or sugar beat, is isolated by neutralization with $Ca(OH)_2$ – to precipitate its calcium salt (calcium lactate), followed by treatment with sulphuric acid to get the main-product (LA). Such a procedure results in the formation of large amounts of hydrated calcium sulfate, i.e., for each kilogram of LA, about 1 kg of gypsum is formed as a by-product [11,12].

We previously reported [10,13,14] that $CaSO_4$ filler when adequately thermally treated, can be highly attractive for the preparation of composites based on PLA, thus a polymer with similar source, i.e., the lactic acid fermentation process. To achieve PLA composites designed for rigid packaging and to prevent polyester degradation from hydrolysis, it has been firstly demonstrated that the utilization of β-anhydrite AII form (AII), i.e., formed by dehydration of gypsum hemihydrate at 500 °C, is a prerequisite. AII proved to be much better suited for melt-blending with PLA with respect to other anhydrite forms, by far too sensitive to atmospheric water absorption [10]. This behaviour leads to the preservation of polyester molecular weights and to favourable key properties for the final composite products. Moreover, it is noteworthy that interest in finding synergistic uses for gypsum as filler in the PLA resin seems to be increasing as shown by recent investigations on the type of interactions existing between PLA and $CaSO_4$ (AII) [15]

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[*] Corresponding author. Tel.: +32 65 37 3480; fax: +32 65 37 3484.
E-mail address: philippe.dubois@umons.ac.be (P. Dubois).

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Authors:
Marius Murariu, Leila Bonnaud, Paint Yoann, Gaelle Fontaine Serge Bourbigot, Philippe Dubois

From:
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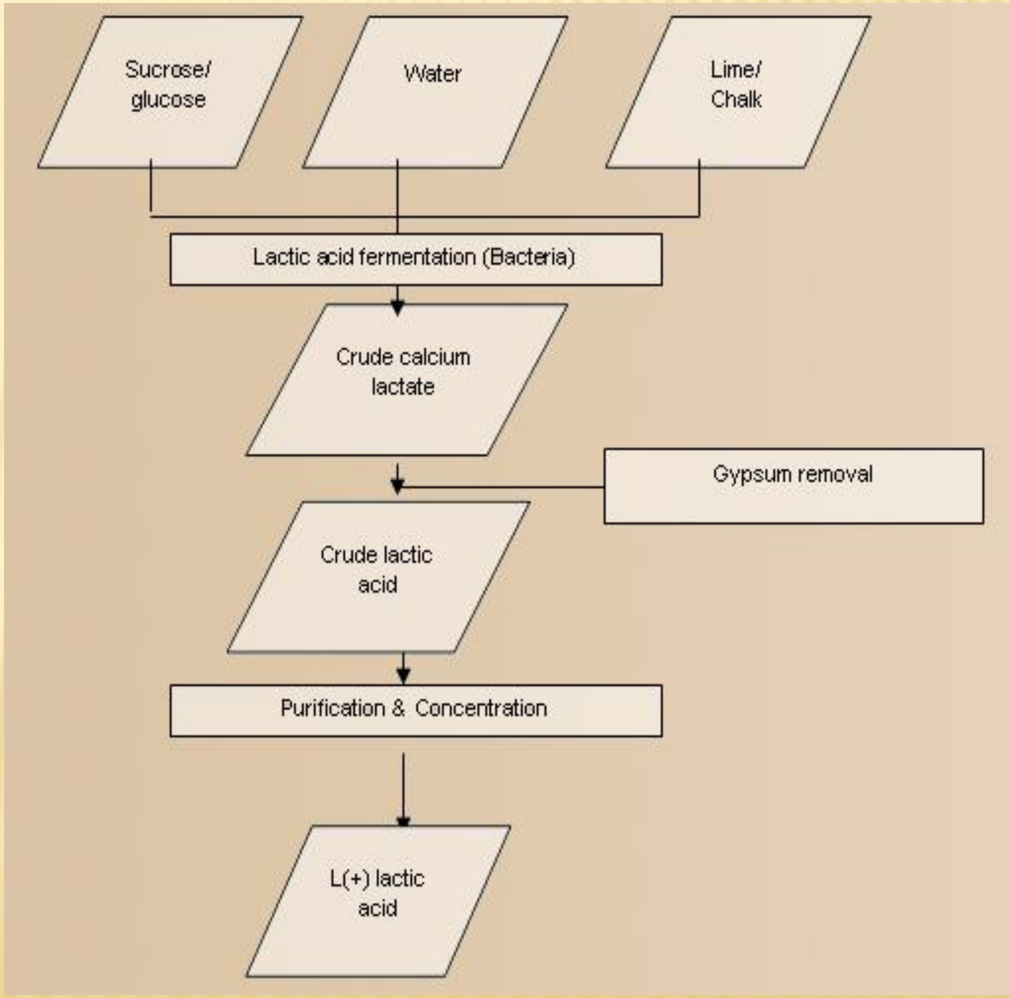
- Laboratory of Polymeric and Composite Materials (LPCM)
- University of Mons and Materia Nova Research

PLA USES

- Compost bags
- Food packaging
- Disposable tableware
- Biomedical applications
  - Sutures, stents, & dialysis media
  - Drug delivery devices
- As a fiber
  - Upholstery & disposable garments

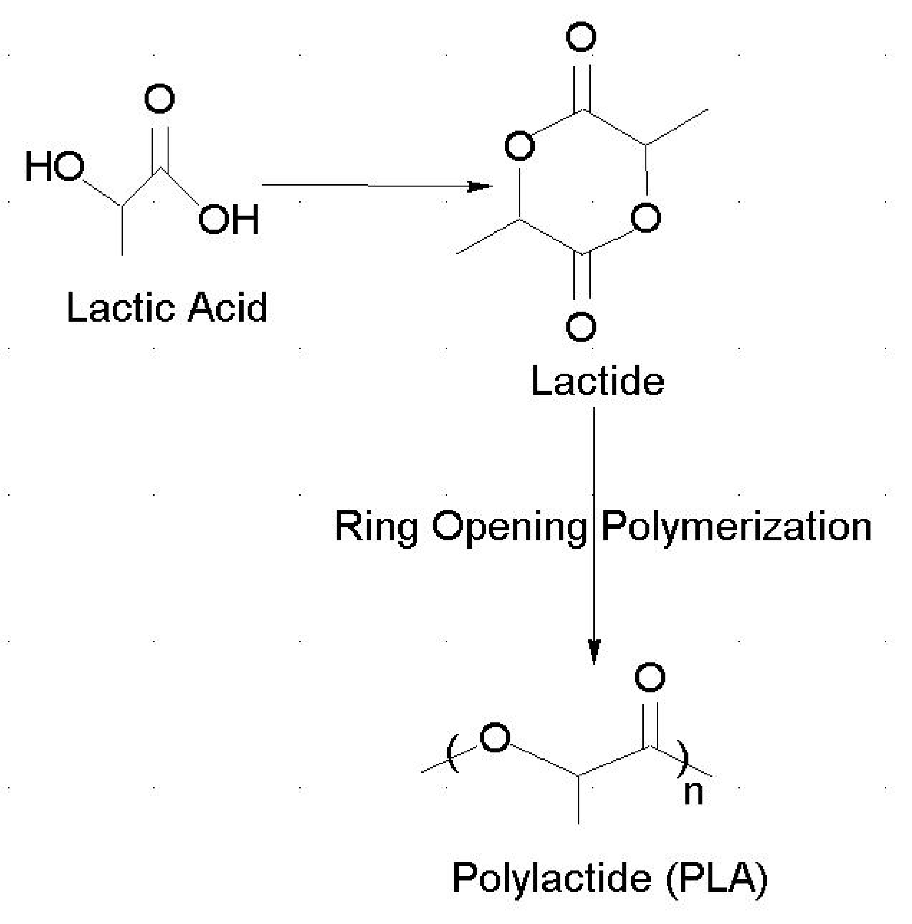
RENEWABLE LACTIC ACID SYNTHESIS

- Calcium Lactate precipitates and is treated with H_2SO_4
  - Prevents hydrolysis
  - Produces Lactic acid & $CaSO_4*2H_2O$(gypsum)
- $2\ CaSO_4 \cdot 2H_2O \rightarrow 2\ CaSO_4 + 2\ H_2O$ (released as steam) ~200°C
  - Obtain Anhydrite



POLYLACTIC ACID (PLA) SYNTHESIS

- Direct polymerization of LA produces water
- Lactides may be prepared by heating lactic acid in the presence of an acid catalyst
- Drop in polarity makes separation of lactides easier
- Lactides undergo ROP in the presence of a catalyst (Tin(II) 2-ethylhexanoate)



GLASS TRANSITION TEMPERATURE OF PLA

- A glass transition temperature between 60-65 °C
  - the reversible transition in amorphous materials (or in amorphous regions within semicrystalline materials) from a hard and relatively brittle state into a molten or rubber-like state

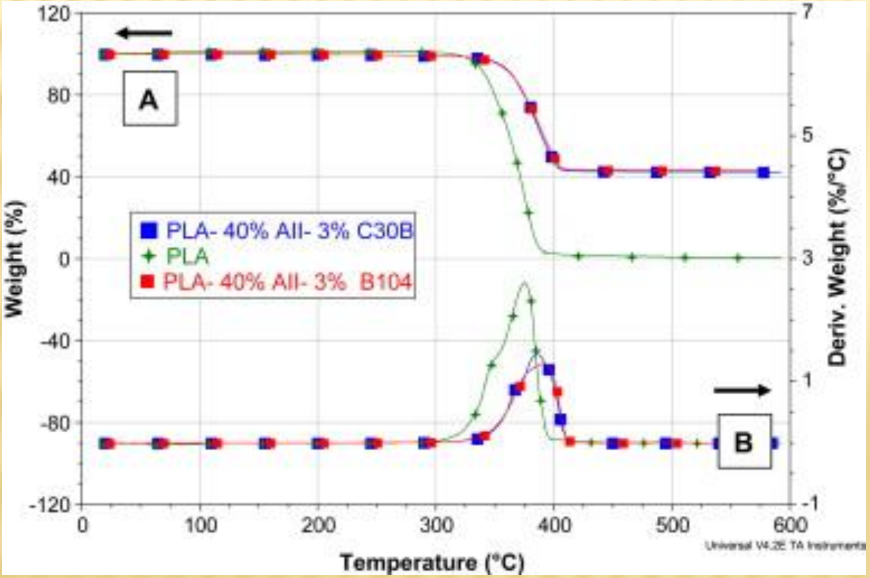
http://en.wikipedia.org/wiki/Glass_transition_temperature

MODIFYING PLA PROPERTIES WITH ANHYDRITE

- PLA and Anhydrite(AII) are melt blended to form a composite PLA-AII
  - High rigidity
  - Good thermal stability
  - Processing properties(less prone to hydrolysis)
- Cannot be recommended for applications where advanced flame retardant properties are required

ADJUSTING PLA-AII PROPERTIES WITH ORGANO-MODIFIED LAYERED SILICATES

- Organo-modified layered silicates (OMLS) were added via melt compounding
  - Increased thermo-mechanical properties
  - Flame retardant performance



Murariu, Marius *New trends in polylactide (PLA)-based materials: "Green" PLA–Calcium sulfate (nano)composites tailored with flame retardant properties* 23 November 2009. Polymer Degradation and Stability

PROPERTIES OF PLA BLENDS

Table 1

Evolution of PLA molecular weights and polydispersity indices upon melt-blending.

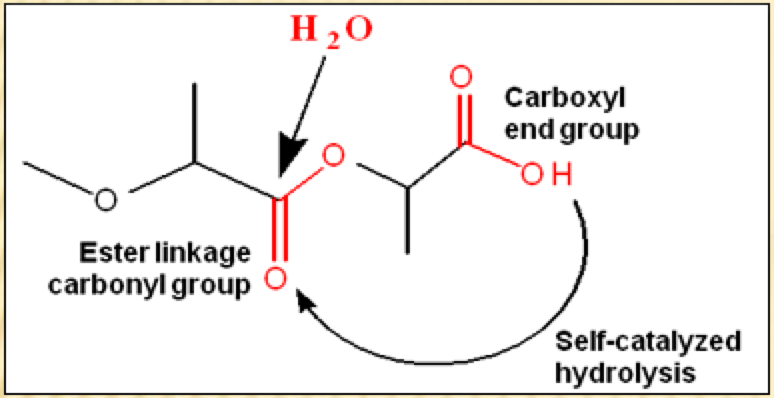
Sample (%, by weight)	Polydispersity index	Mn (PLA)	Crystallinity(%)
1 PLA (processed)	2.2	64 000	0.1
2 PLA-43% AII	2.3	59 000	2.0
3 PLA-40% AII-3% B104	2.0	57 000	0.6
4 PLA-40% AII-3% C30B	2.0	56 000	0.2

polydispersity index (**PDI**), is a measure of the distribution of molecular mass in a given polymer sample. The PDI calculated is the weight average molecular weight divided by the number average molecular weight

Number average molar mass or $M_{n,}$ total weight of all the polymer molecules in a sample, divided by the total number of polymer molecules in a sample

http://en.wikipedia.org/wiki/Polydispersity_index

PLA DEGRADATION



- Depends on the conditions
  - Temperature, humidity, light, & fillers
- PLA with no fillers can degrade within days or weeks
- PLA with fillers a few years (3-5)

http://illumin.usc.edu/7/recycling-plastics-new-recycling-technology-and-biodegradable-polymer-development/

12 PRINCIPLES OF GREEN CHEMISTRY

- **1.Waste Prevention**
- 2. Atom Economy
- 3. Less Hazardous Chemical Process
- 4. Designing Safer Chemicals
- 5. Safer Solvents and Auxiliaries
- **6. Energy Efficiency**
- **7. Renewable Feedstocks**
- 8. Reduce Derivatives
- 9. Catalysis
- **10. Design for Degradation**
- **11. Real-time Analysis for Pollution Prevention**
- 12. Safer Chemistry for Accident Prevention

Anastas and Warner "Green Chemistry: Theory and Practice" Oxford University Press, 1998

CONCLUSIONS

- Plastics derived from fossil fuels are unsustainable
- Accumulation of plastics causes harm to the environment and may leach toxic substances
- Challenges in designing renewable and biodegradable polymers
  - Cost
  - Maintaining mechanical and thermal properties
  - Controlling the rate of degradation

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THANK YOU

- Any Questions?