PLA - A Renewable/Sustainable Packaging Option

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Abstract

NatureWorks PLA (Polylactide) is providing an annually renewable resin based option for a number of packaging applications. As our company has developed a film/sheet partner network, we are providing "supply chain" based solutions to assist customers. As companies begin their journey towards sustainable/renewable packaging, they are finding PLA packaging based materials to be an excellent choice for fresh cut produce and food applications. The ability of PLA to be processed on most conventional packaging process equipment combined with its combination of desirable properties such as high clarity, stiffness and printability are affording leading brand owners an opportunity to utilize more responsible and globally available packaging choices.

Introduction

PLA is providing the packaging industry with a renewable sustainable option for a variety of uses. Many of these uses include flexible films made from PLA resin. The combination of desirable properties such as high clarity, stiffness and excellent printability combined with the ability to process PLA on conventional in many cases existing assets provides an opportunity for market leaders to bring innovative and more environmentally friendly packaging options to market.

Conclusions

Naturework's PLA is a versatile new industrially compostable polymer that is made from 100% renewable resources like corn, sugar beets or rice. Today, PLA begins with corn. All free energy consumed by biological systems arises from solar energy that is trapped by the process of photosynthesis. The basic equation of photosynthesis is:

$$H_2O + CO_2 \xrightarrow{\text{light}} CH_2O + O_2$$

In this equation, (CH2O) represents carbohydrate, primarily sucrose and starch. All the carbon, hydrogen and oxygen in the starch molecule as well as in the final polylactide molecule have their origin in water and carbon dioxide. After harvesting, the corn is transported to a corn wet mill where the starch is separated from the other components of the corn kernel (proteins, fats, fibers, ash and water) and converted via enzymatic hydrolysis into dextrose. Dextrose is fermented into lactic acid at near neutral pH. Via acidulation and a series of purification steps the lactate salt fermentation broth is then purified to yield lactic acid. The first generation of PLA is produced from the annually renewable resource corn, the cheapest and most widely available raw material in the USA rich in starch. In other parts of the world, locally available crops such as rice, sugar beets, sugarcane, wheat and sweet potatoes can be used as a starch/sugar feedstock.

There are two major routes to produce polylactic acid from the lactic acid monomer: direct condensation polymerization of lactic acid and ring-opening polymerization through the lactide intermediate. The first route involves the removal of water by condensation and the use of solvent under high vacuum and temperature. With this route only low- to intermediate molecular weight polymers can be produced mainly because of the presence of water and impurities. Other disadvantages of this route are the relatively large reactor required and the need for evaporation, recovery of the solvent and increased color and racemization. Natureworks uses the second route: ring-opening polymerization through the lactide intermediate [1]. In the first step of the process water is removed under mild conditions without the use of a solvent to produce a low molecular weight prepolymer. This prepolymer is then catalytically depolymerised to form a cyclic intermediate dimer referred to as lactide which is then purified to polymer grade using distillation [2]. The purified lactide is polymerized in a solvent free ring-opening polymerization and processed into polylactide pellets [3]. By controlling the purity of the lactide it is possible to produce a wide range of molecular weights.

Because there are four unique groups attached to the central carbon atom, lactic acid is a chiral molecule. Chiral molecules exist as ‘mirror images’ or stereoisomers. The optically active lactic acid has an ‘‘l’’ and ‘‘d’’ stereoisomer. ‘‘l’’ and ‘‘d’’ are also referred to as R and S. d=R=right handed and l=S=left handed. Chemically synthesized lactic acid gives the racemic mixture (50% d and 50% l). Fermentation-derived lactic acid typically consists of 99.5% of the l-isomer and 0.5% of the d-isomer. Production of the cyclic lactide dimer results in three potential forms: the d,d-lactide (called d-lactide), l,l-lactide (called l-Lactide) and l,d or d,l lactide called meso lactide. Meso lactide has different properties from d and l lactide. The d and l lactide are optically active, but the meso is not. Before polymerization the lactide stream is split into a low d lactide stream and a high d/meso lactide stream. Ring opening polymerization of the optically active types of lactide can yield a ‘family’ of polymers characterized by the molecular weight distribution and by the amount and the sequence of d-lactide in the polymer backbone. Polymers with high l-lactide levels can be used to produce crystalline polymers while the higher-d-lactide materials are more amorphous, idea for heat seal layers with low seal activation temperatures.

PLA polymers will process on conventional extruders using general purpose screws with L/D ratios from 24:1 to 30:1 and compression ratio of 2.5:1 to 3:1. Smooth barrels are recommended. PLA resins will process on conventional cast tenter equipment. In-line drying is required for PLA resin extrusion. A moisture content of less than 0.025% (250ppm) is recommended to prevent viscosity degradation. Typical drying conditions are 4 hours at 175ºF (80ºC) or to a dew point of -30ºF (-35ºC), with an airflow rate greater than 0.5 cfm/lb of resin throughput.

Processing Temperature Profile		
Melt Temperature	410ºF	210ºC
Feed Throat	113ºF	45ºC
Feed Temperature	355ºF	180ºC
Compression Section	375ºF	190ºC
Metering Section	390ºF	200ºC
Adapter	390ºF	200ºC
Die	375ºF	190ºC
Screw Speed	20-100 rpm	
MD Draw Temp.	140-160ºF	60-70ºC
TD Draw Temp.	160-175ºF	70-80ºC
Heat Set Oven	205-285ºF	120-140ºC

PLA physical properties are highly dependant on the grade of PLA as well as the specific processing conditions. For flexible films produced using semi-crystalline grades of PLA, physical properties vary with the amount of orientation as well as the heat treatment steps. PLA films that are biaxially oriented and heat set can be produced to provide service temperatures up to 150ºC. In addition to improved heat performance, orientation can also improve tensile properties. In general, increased film orientation results in improved film toughness providing higher strength and elongation. The use of amorphous (high D content) grades offer the ability to have heat seal layers with low seal activation temperatures (~80ºC).

Inherent PLA properties such as high clarity, stiffness and the ability to accept conventional inks provides a natural fit for a number of film applications. The increased stiffness offered by PLA often allows article down-gauging not only in films but in many rigid applications offering improved system cost and reduced waste. The crisp nature of PLA films offers interesting market opportunities for fresh food applications like salads where package characteristics may suggest improved product freshness.

PLA inherent barrier properties provide excellent large molecule barrier performance resulting in aroma and flavor barrier with a non flavor scalping material. PLA is also an excellent barrier for oils and greases. PLA does not generally provide sufficient barrier performance for small molecules. For oxygen or moisture sensitive products especially with extended shelf life barrier enhancement is typically required. For fresh vegetables and produce, PLA barrier is generally too high to prevent direct use without perforation or use of a breathable patch to provide the optimum atmosphere for these products. PLA packaging has been found to be readily fit in most standard systems to improve barrier performance either though the use of multilayer constructions with other polymers of application of various surface treatments to improve barrier performance.

PLA films also provide an excellent surface for printing and graphics. The high natural surface energy combined with excellent ink receptivity allows PLA to be used on conventional equipment using standard inks.

PLA also provides a number of end of life options. PLA offers traditional end of life options such as landfill and incineration but also fits well within standard mechanical recycle systems as well as provides an easy option to chemically recycle via hydrolysis to lactic acid. However, the big difference between PLA and other packaging materials is the option for industrial composting. With the increased focus on the environment, many countries are finding this a highly desirable attribute.

In summary, PLA in a variety of forms has been shown to be an excellent material for packaging food products. From rigid parts to flexible films the ability to process PLA on conventional existing equipment combined with a number of desirable material properties has allowed companies to take use a more responsible packaging material.

References:

[1] Gruber P, O'Brien M. Polylactides ''NatureWorksTM PLA.
In: Doi Y,Steinbuchel A, editors. Biopolymers in 10 volumes, volume 4, polyesters III applications and commercial products. Weinheim: Wiley-VCH; 2002 [ISBN 3-527-30225-5]. p. 235–49.

[2] Gruber PR, Hall E, Kolstad J, Iwen M, Benson R, Borchardt R.
US Patents: 5,142,023; 5,247,058; 5,247,059; 5,258,488; 5,274,073; 5,357,035; 6,005,067.

[3] Gruber P, Kolstad J, Hall E,Eichen-Conn R, Ryan C.
US Patents: 5,338,822; 5,446,123; 5,539,081; 5,763,564; 6,143,863.

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PLA

A Renewable Sustainable Packaging Option

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What is PLA?

PLA is an aliphatic polyester polymer made from lactic acid

- Lactic acid is a natural product
- It is found in the body, yogurt, & many other foods

What is PLA?

Lactic acid is made from fermentable sugars

- Sugars are found in plants
- Our company today uses sugar from corn to make lactic acid

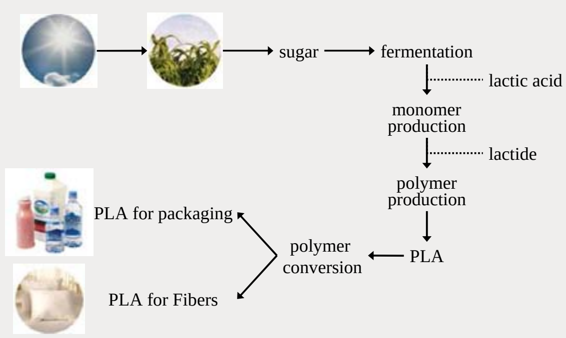
What is PLA?

Sugars are made from CO_2 via photosynthesis

– Photosynthesis involves carbon

light
$H_2O + CO_2$ --------> $CH_2O + O_2$

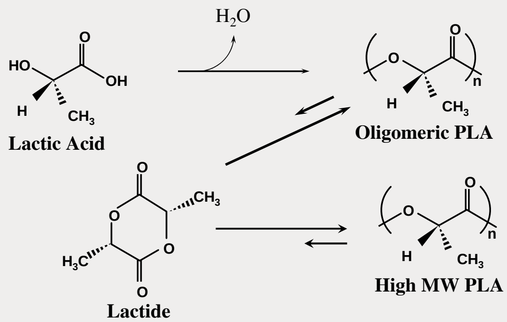
Where it Comes From



Why Corn?

- No. 2 Field corn is the least expensive and most abundant source of commercially available sugar
  - Stable supply
  - Stable price
- Even at full global capacity, we will use less than 1% of the annual U.S. corn crop
- PLA does not contain genetic material based on its manufacturing process

PLA Chemistry



PLA Resin Grades

- Multiple commercial grades available
- Viscosity and crystallization characteristics primary differentiators
- Grades designed for specific applications

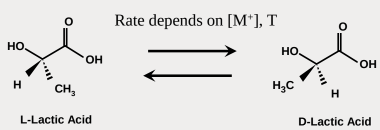
PLA Grades

- Packaging
  - 2002D Thermoforming, amorphous parts
  - 3051D Injection Molding
  - 4032D Film, higher heat resistant
  - 4042D Thermoforming, amorphous parts, Film

PLA Grades

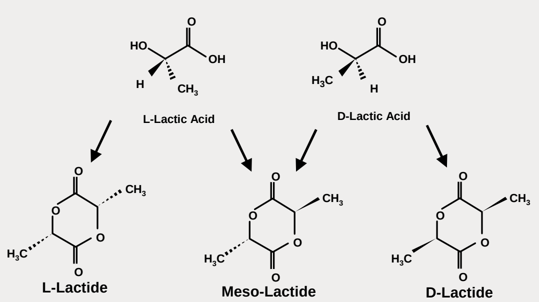
- Packaging (cont)
  - 4060D   Film, amorphous sealant
  - 7000D   Bottles
- Fiber - Wipes
  - 6201D   Staple and Filament

Lactic Acid Racemizes When Heated



Implications:
- *Only one type of lactic acid is needed*
- *Careful process control is needed to prevent too much isomerization*

LA Makes Multiple Monomers



PLA’s Inherent Properties

•Food safe natural-based
•Excellent clarity & gloss
•Excellent resistance to food fats/oils
•Aroma barrier
•High modulus > APET
•Good practical toughness > GPPS
•Toughness & crystallinity increase with orientation
•Good printability

PLA’s Inherent Properties

•Moisture breathability
•Wicking
•Low flammability
•Low soot (<0.01%)
•Low smoke
  86% less than polyester
•UV resistance
•Industrially Compostable
•Readily recycled via regrind or hydrolysis back to lactic acid

PLA Extrusion

- PLA can be processed on conventional extruders
  - general purpose screws
  - 24:1 to 30:1 L/D
  - Smooth barrels
- Requires resin drying to prevent hydrolysis
- Requires purging prior to use

PLA Film Processing

- Can be processed on conventional cast tenter equipment
- Tensile properties dependant on film orientation

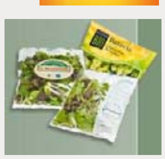
Flexible Films

- PLA is highly desirable for a number of applications
- Converters note high clarity, gloss, stiffness, printability, twist retention and excellent flavor and aroma barrier properties

Today's Range of Flexible Films

- Converters note high clarity, gloss, stiffness, twist retention and barrier properties:
  - **Packaging films for fresh food**
    - **Lidding**
    - **Produce bags**
  - **Window films for bread bags and bakery boxes**
  - **Labels films**
    - **PSA**
    - **Shrink**
    - **Cut & Stack**
  - **Overwrap films**
  - **Twist wrap**




Today’s Flexible Films

- Packaging films for fresh food
  - Window films
  - Labels (PSA Shrink Cut & Stack)
  - Twist wrap
  - Lidding films for trays
  - Produce bags

PLA Film Availability

- Full range of standard films commercially available
- Standard gauges from 0.8 mil and up
- Available in mono and multi-layer structures design for specific applications

Typical PLA Film Properties

	Blown	Tentered
Ultimate Tensile Strength MD/TD (PSI)	8,000 8,000	11,000 13,000
Elongation to Break (%)	5 3	45 33
Modulus (PSI)	396,000 320,000	385,000 410,000
Haze	< 4	2 – 3
Gloss (60°)	125	100

PLA Film Properties

- Tensile properties highly dependent on orientation
- Service temperature dependent on PLA grade and downstream processing
- Amorphous grades for heat seal offer low activation seal activation temperatures (From 80ºC)
- Semi-crystalline grades offer increased temperature capabilities when oriented and heat-set (up to 150ºC)

PLA Films Barrier Properties

- High barrier to aromatic compounds and most non-polar solvents
  - Oils and greases
  - Flavors and odors
- Amorphous nature makes it ideal for heat sealing
- Relatively poor barrier to water vapor, oxygen and carbon dioxide
- Ideal candidate for non-scalping heat seal layer

PLA Permeability vs. Common Polymers

Resin	OTR	WVTR	N_2	CO_2
PLA	**38-42**	**18-22**	**9.5**	**201**
PET (OPET)	3-6.1	1-2.8		15-25
HDPE	130-185	0.3-0.4		400-700
PP	150-800	0.5-0.7		150-650
Nylon 6	2-2.6	16-22		10-12
EVOH	0.01-0.16	1.4-6.5		
PVC	4-30	0.9-5.1		4-50

Note: Units are ml mil/100 sq. in day for Oxygen and CO_2; for water vapor transmission rate are in grams mil/100 sq. in day

PLA Films Barrier Fresh Fruit/Produce

•PLA film O_2 and CO_2 barrier is generally too high for direct use with extended shelf life "live" applications requiring respiration

•PLA film can be modified to overcome this attribute with perforation (micro/macro), breathable patches or other standard industry practices to increase respiration

PLA Films Barrier Other Applications

•For applications requiring increased moisture or gas barrier options include:

- •Barrier Coatings
  - •Most coating technologies directly applicable
- •Multilayer structures
  - •Choice of barrier polymer determines performance

PLA Films Printability

•Printable using conventional inks and dyes

•High natural surface energy

•Excellent print receptivity and ability to provide crisp and bold text/graphics

PLA Films Printability

Ink	Chemistry	Use	Print Method
Hydrokett 3000	WB-Acrylic	Surface and reverse print	Flexo
Hydorfilm 4000	WB-Acrylic	Surface and reverse print	Flexo
Polygloss	SB	Surface print	Flexo and Rotogravure
Pyroflex	SB-Nitrocellulose	Surface print	Roto
NuLam	SB-Polyamide	Reverse print/lamination	Flexo and Rotogravure
UVAROLID	UV-Acrylate	Surface print	Indirect offset

WB = Water based
SB = Solvent based

Additional PLA Benefits

- Inherent stiffness provides “crispy” package found to enhance customers perception of product freshness
- Inherent stiffness often allows down gauging vs incumbent materials to reduce total packaging costs

Today’s Range of Food Packaging

- Processed on existing equipment
- Excellent clarity, gloss and stiffness
  - Produce packaging
  - Food service items
    - Cups Plates Bowls
- Unique differentiation & positioning tool at POS

Food Packaging - continued

•Dairy packaging
Yogurt/Desserts

•Meat packaging
Fresh/Case-ready

•Foamed/Expanded
Trays/Clamshells



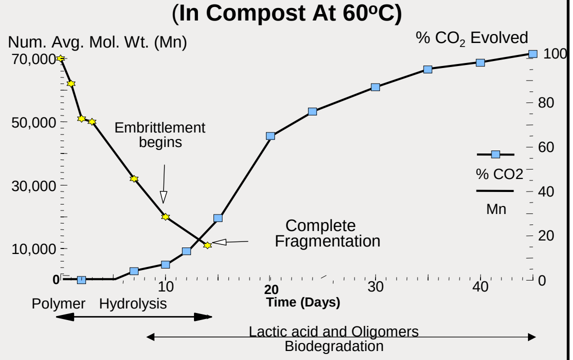

The Key Differences
Where it Comes From

- Non-crude-oil derived
- Comes from Renewable/Sustainable resources
- Price stability versus today’s crude oil derived plastics

The Key Differences
Where it Goes

PLA	Traditional Plastics
•Landfill	•Landfill
•Incineration	•Incineration
•Recycle Mechanical/Chemical	•Recycle
•Compost Organic Recycling	

Biodegradation Mechanism For PLA
(In Compost At 60ºC)



Renewable Resource-based Materials Can Compete With and Displace Petroleum-based Materials

- Roughly equivalent function
  Will be better over time
- Competitive price/value
  Lower costs, stable feedstock
- Minimum environmental footprint (long-term)

Thank You

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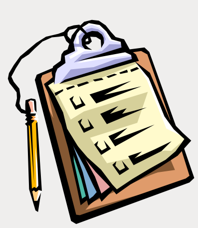

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