

Bioprocessing – No Longer a Field of Dreams

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Summary: A Field of Dreams was a movie about baseball. The theme was “Build it and They Will Come.” Bioprocessing as an industry has been waiting for someone to step up to the plate and build a large business, based on the technology. The large business was necessary to bring about a revolution to move the Chemical and Plastics Industries towards a new business model, based on more sustainable practices. By providing a unique combination of properties in fiber and packaging applications, PLA was the obvious first choice for companies looking to make bioprocessing a commercial reality.

Keywords: biopolymers, fibers, films, polylactide (PLA), recycling, renewable resources, sustainability

What is PLA?

PLA is the first product to be commercialized in the plastics industry on such a scale, based on renewable resources. Starches are extracted from common agricultural products such as corn or sugar beets. They are then converted by hydrolysis to sugars such as dextrose. Dextrose is utilized by microorganisms that ferment them to lactic acid, the starting material for the PLA production process.

PLA can be produced from lactic acid by direct coupling, using isocyanates. Typically, isocyanates are hazardous chemicals that aren't accepted as safe to use, or for the environment. Although direct condensation allows for easy use of a wide range of potential comonomers, producing polymers of useful molecular weights requires production in a solvent system, in order to handle the increasing viscosity as molecular weight increases.^[1] This then means the extra burden of removing the residual solvent to purify the polymer. So far, this has limited polymer produced in this fashion to applications that don't involve food contact. Alternatively, using the lactide intermediate route, PLA with high molecular weight can be produced without the use of solvents (see Figure 1).^[2]

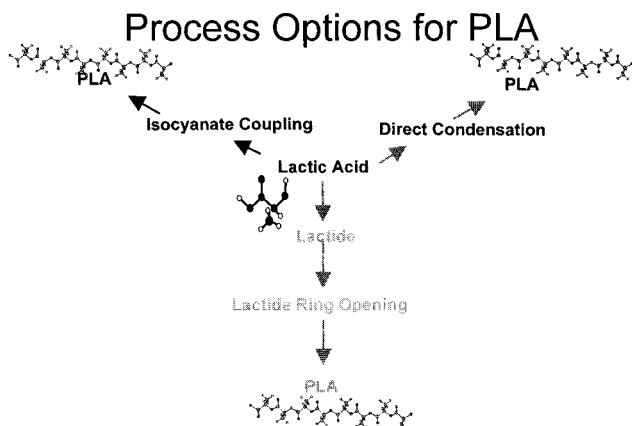


Fig. 1. Process options for PLA production.

LA Makes Multiple Lactide monomers which give rise to a family of polymers

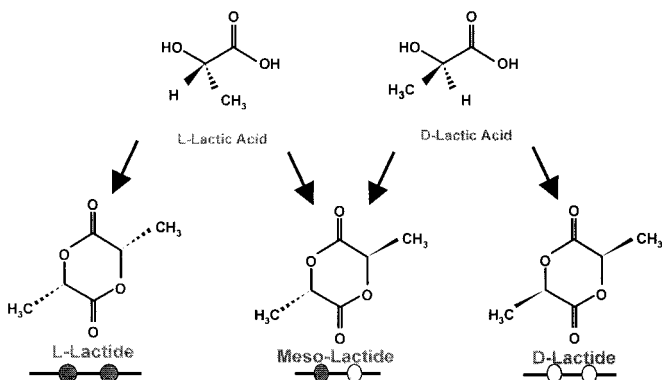


Fig. 2. Multiple lactide monomers arising from combining optically active lactic acid units.

The lactide route also allows for better control of the polymer properties by controlling the optical sequence of the polymer chains. For these reasons, the first commercial PLA process has utilized the lactide route. Since lactic acid is an optically active molecule, forming the

cyclic dimer, lactide, allows for the production of three different stereoisomers. D-lactide and L-lactide maintain the stereoactivity of the two lactic acid units they are comprised of. Meso-lactide, made up of one L and one D-unit, is optically inactive (see Figure 2).

Reducing the optical purity from nearly perfect to about 10-12% D allows a family of polymers to be produced with a range of crystalline melting points from about 130°-172°C. Lower melting components are useful for binding or sealing in fibers or films.^[3]

Whatever the production route, PLA is used in typical conversion processes to produce fiber, sheet or films (see Figure 3).

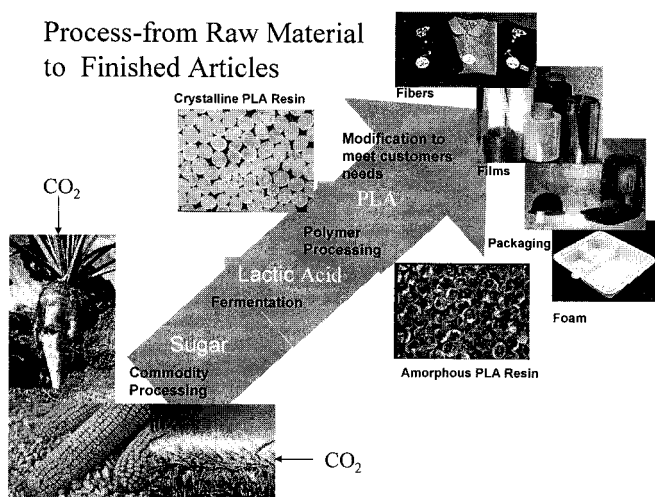


Fig. 3. Producing fibers, packaging and films from annually renewable resources.

Renewable Resource Base

When people consider sustainable materials, one of the most important aspects is the renewable resource base. In its first commercial generation, PLA is being produced from corn. Although lactic acid is produced globally from sugar beets and could also be produced from wheat, casava, or other starch sources, corn is the most economically sensible option, initially. However, technology is being developed which will allow biomass to be used as the feed source. By-products like corn stover, which are not fully utilized today could conceivably

be used as the feed material for lactic acid production. Although petrochemical resources could be used as the feedstock for PLA, there are important benefits which only the natural route provides. The precise control of the stereochemistry of the polymer chains is only possible using the natural route, since the microorganisms which produce lactic acid produce primarily one type of optically active form. Petrochemical-based lactic acid is of the racemic variety. Racemic mixtures will only allow for production of amorphous polymers, not the crystalline ones necessary to be used in heat-stable fiber and biaxially-oriented films.

Need for a More Sustainable Alternative

While population growth and increases in GDP are creating an increased demand for plastic, petrochemical resources and in some cases natural materials are not meeting the demand. For example, cotton production is not expected to meet the increased fiber demand as more people use more clothing. This increased demand will only be met through other fibers like polyester or new alternatives (see Figure 4). Continued depletion of the earth's fossil resources will eventually limit the earth's ability to meet the demands.^[4]

The World Fiber Market is Expected to Grow

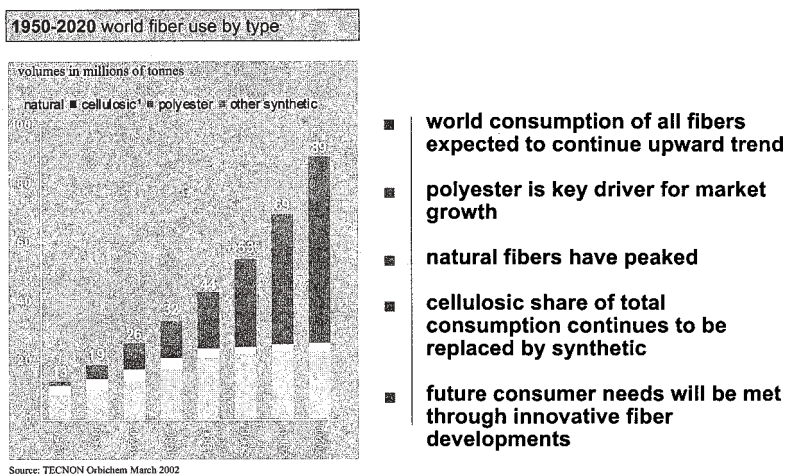


Fig. 4. Cotton alone cannot meet the world's increasing demand for fibers.

Sustainability

Sustainability, in a single word explains the reason there is a significant market developing for PLA. Although Sustainability is somewhat complex to define, it obviously involves reducing the impact on the environment of the production of what people need and want. However, true sustainability also involves other aspects, which allow for a longer-term improvement. People often use the phrase “Triple Bottom Line,” to include economic viability and social impact with the obvious environmental piece.^[5]

Economic Viability

Clearly, companies trying to manufacture more sustainable products will not stay in business long-term, if they can't make money at the same time. It is only when products are commercially produced that the impact can be felt. Actually, economic viability can be extended to include price and performance. Consumers want products that perform at least as well as incumbents, but offer a sustainability advantage. However, they are not typically willing to pay more unless a product performs better than what they are used to.

Environmental Impact

The environmental impact portion of sustainability is the obvious part that most people discuss when looking at plastics in their applications. It involves not depleting the earth's ability to provide the same products for future generations. It not only involves using renewable resources, but also includes recycling processes, energy use, by-products of manufacturing and effects along the whole chain from resource to end-user, along with disposal methods. Traditional polymer recycling brings articles back to the melt state after their use. However, recycled polymer typically is not as pure and useful as “virgin” polymer. Thermal degradation occurs with all plastics to some extent, each time the material is melt processed. With some polymers, it is thermal oxidative degradation or crosslinking. With others, it is hydrolysis. In any case, traditional recycling is simply delaying the point at which the polymer reaches the end of its use and needs to be disposed of. Traditional disposal is then done, either landfilling or incineration. In more complete, non-traditional recycling, work has been done with nylon, trying to return carpet fibers to caprolactam, but costs of separation and recovering the

monomer have been prohibitive. With PLA, a more complete recycling loop can be performed. PLA can be brought back to the lactide intermediate. But more importantly, it can be hydrolyzed completely back to lactic acid. This means the recycling will allow articles to be produced in successive recycling steps that are as useful as in their first use. A key difference with PLA is that when the useful life is over, PLA adds the disposal option of composting, which is not an option for other synthetic polymers. Under very specific composting conditions-high temperatures and humidities, typically around 60°C, with 90% relative humidity, the PLA articles will degrade first by hydrolysis, then by microbial action, eventually degrading simply to carbon dioxide and water.^[6]

Social Impact

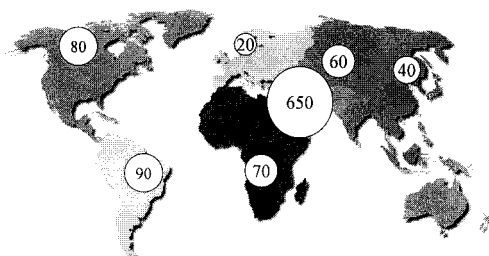
Not only do sustainable products have an environmental and economic impact, but there is also necessarily a positive social impact. Products need to improve the quality of life for the consumers, the producers and the people affected by the production facility. Human resources must be viewed in the same way as natural resources in that abusing them will result in depletion of the resource. In thinking about sustainability, it is important to consider all three components of “The Triple Bottom Line.”

Limited Supply of Petroleum Resources

As previously stated, sustainability is the driver that explains the need for PLA. Although petrochemicals provide the resource for traditional synthetic packaging and fiber articles, there is evidence that the world's oil reserves are inadequate to keep pace with the growth in demand. Even considering all projected reserves of oil, production is expected to peak in the next 20 to 75 years. This is assuming zero growth in demand! Assuming a more realistic demand increase of 1-3%, production will peak sooner.^[7] As resources become scarce and reserves are used up, it becomes increasingly difficult to recover the oil and production will decrease. Furthermore, it is important to consider also where the oil reserves are located. Obviously, the concentration of oil reserves is in the middle east, with smaller reserves around the Pacific Rim and in the U.S.. Hubbart has predicted that peak production will be very close in time to the point at which 50% of the world's supply is depleted.^[8] Considering this, as the

reserves are depleted, very little will be available in some of the areas of highest demand (see Figures 5 and 6). Clearly, the resource for packaging and fibers must change!^[9]

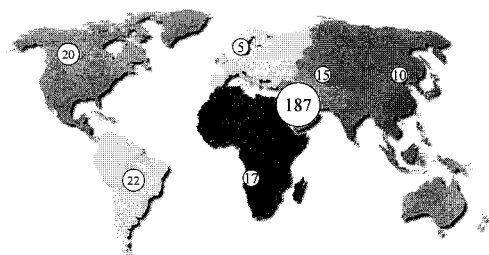
Billions of Barrels of Known Oil Reserves Today



Source: DOE-EIA

Fig. 5. Known oil reserves today.

Future Look: 50% Evenly Depleted



Source: DOE-EIA

Fig. 6. Oil reserves when 50% Depleted.

Performance of PLA

PLA polymer provides performance advantages in fiber and packaging applications. PLA film has FDA approval for food contact. PLA films do not contain any hormone mimics. PLA can be converted into film on standard processing equipment. The films have excellent gloss and clarity. The unique modulus of the films gives good twist and dead-fold properties. While PLA films do not provide the moisture vapor and oxygen barrier necessary for some types of food packaging, they do provide good barrier for certain flavors and aromas. They also provide good oil and grease resistance. With a range of melting temperatures possible through control of the stereochemistry, a broad range of 100% PLA heat-seal performance packages can be produced.

In fiber applications, end users take advantage of the loft and resilience of PLA fibers. PLA fibers wick moisture well, without absorbing large amounts of water. PLA burns with very low energy and under conditions of complete combustion, very little smoke is produced and no toxic chemicals are released. PLA fibers do not cause allergic reactions. Like other synthetic fibers, PLA fibers do not support bacterial growth. Due to a unique absorption spectrum, PLA fibers are naturally resistant to degradation by UV light. PLA fabric retains its strength in a similar way to acrylic, but does not yellow like acrylic or polyester. Lastly, PLA fibers give similar or better protection against stains, when compared with nylon.

PLA is Being Commercialized

Part of making PLA economically viable is producing it at low cost. To do so, the fermentation that supplies the lactic acid for polymer production and the polymer production must be done at large scale, to minimize manufacturing cost. This is why the first commercial PLA plant was built to produce 140,000 metric tons per year, while the lactic acid plant is scaled to 180,000 Metric Tons per year. The PLA plant has been operating since November, 2001 and the lactic acid plant is starting in the 1st quarter of 2003. As these plants move to full production capacity, the cost to produce PLA will come in line with more traditional performance polymers. Several packaging applications have been commercialized using PLA in Europe and Japan, including Dunlap Golf Ball sleeves in Japan and deli-food packages in grocery stores in Europe. In fiber applications, the largest launch to date has been Pacific

Coast Feather's launch of their natural balanceTM line of sleep products. Including pillows, comforters, mattress pads and fiber beds, consumer interest in the line of products has far exceeded expectations. End-users seem very positive about the performance of high-end synthetic fibers derived from annually renewable resources. Equally receptive have been grocery and electronics purchasers in Europe and Japan who have welcomed deli-trays and mini-disk packages, even blister packs for the popular WalkmanTM radios.^[10]

Renewable Resources can be Used to Make a Range of Chemicals and Polymers

The fermentation process used to produce lactic acid actually is more meaningful than just for PLA. Successful large-scale production of lactic acid and lactide makes it possible to produce a whole range of monomers for polymers other than PLA and a wide range of chemicals, all from renewable resources. For example, propylene glycol, propylene oxide, acrylic acid, all are possible from lactide. Lactate ester solvents have also been produced and are actually moving to the market, being produced from lactide. Interestingly, the purity of ethyl lactate produced from lactide, rather than from petrochemicals, is significantly more pure and is thus better suited for demanding electronics cleaning. See Figure 7 for the range of products that can be produced from lactide.

What Role Does Cargill Dow Play?

Cargill Dow, a joint venture formed in 1997 has as its mission to "Produce products which meet the needs of the world today, without compromising the earth's ability to meet the needs of tomorrow." This means taking a constantly reflective approach on sustainability and taking continued steps to reduce the impact of producing polymers and chemicals on the earth.

Conclusions

PLA polymer has moved bioprocessing forward, from the "Field of Dreams" stage to one where polymers for packaging and fibers, along with a wide range of chemicals can be produced from annually renewable resources. Since PLA is now being produced at commercial-scale, it can become an increasingly viable alternative to petrochemical

incumbents. The unique chemistry of PLA provides a set of performance characteristics that fiber and packaging applications will benefit from. As Cargill Dow, converting customers and end-users make PLA fibers and packaging a success, the bio-industrial revolution will boom. Companies will commonly produce products that make people's lives better, while reducing the impact making those products have on the earth.

Many Chemicals Can Be Made

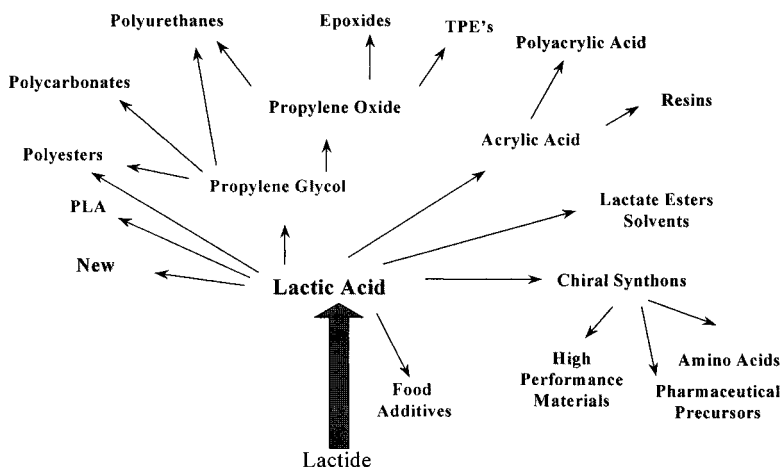


Fig. 7. Range of chemicals that can be produced from lactide.

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