Polylactic Acid : A Product of Bioengineering Technology

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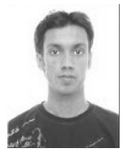
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Abstract

Our ecosystem is now considerably disturbed and is slowly being damaged as a result of the problems arising out of the usage of nonbiodegradable synthetic materials. Regular depletion of the petrochemical feedstock is leading to, more and more attention being focussed on synthesizing material from annually renewable resources. Polylactic acid is one such material. It is derived from corn, and it finds application in the field of textiles, pharmaceuticals, and plastics.

1. Introduction

Bioengineering technology is the biochemical transformation of agricultural feedstock, its by-products, and wastes into useful synthetic material. An important advantage of bioengineered material is that they lead to conservation of energy and provide additional markets for the by-products and wastes of the farming industry.

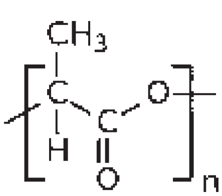
Till a few years back most of the commercialised synthetic polymers were derived from fossil resources. The mass production and consumption of these materials led to two serious problems namely

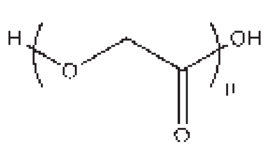
- Exhaustion of natural resources: This problem occurs as synthetic materials are dependent on fossil resources such as petroleum for their production.
- Generation of nonbiodegradable waste material: This problem takes place because the synthetic materials drop out of material circulation (carbon circulation) as they are not biodegradable.

Polylactic acid (PLA) is considered as a biodegradable and a compostable (reverted to lower-molecular-weight carbohydrates, carbon dioxide, and water by natural fermentation) polymer which is obtained from annually renewable plant resources. Thus its production and consumption does not cause any of the above mentioned problems. Moreover, PLA has a wide range of packaging, film, pharmaceutical and fibre application, leading to products that can ultimately biodegrade into H_2O, CO_2, and in some cases into biomass.

2. Polylactic Acid:

Chemical structure of poly(lactic acid) (PLA) and poly(glycolic acid) (PGA)


PLA


PGA

2.1. Synthesis [1] :

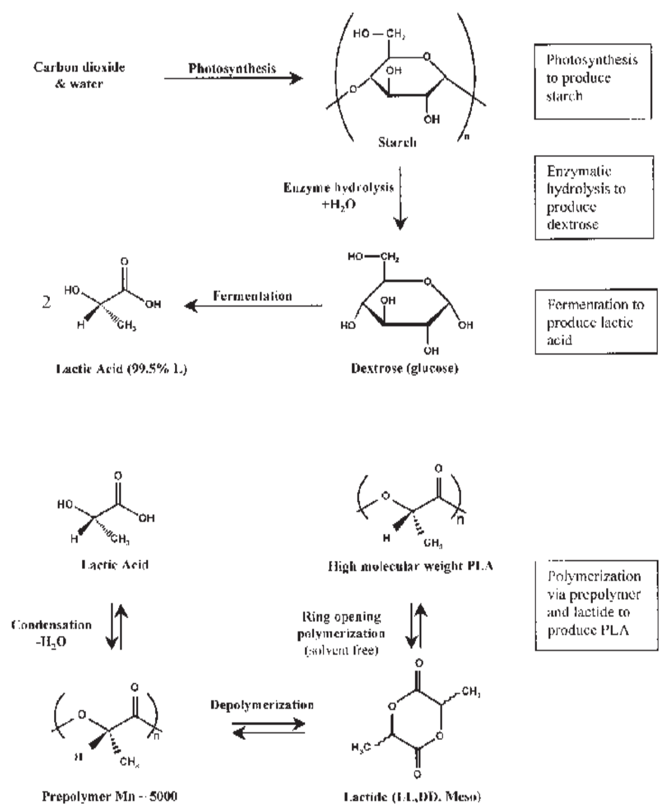


Fig. 2 : PLA Manufacturing Overview
Source: Ref. 3.

PLA belongs to the family of synthetic aliphatic polyesters. The basic building block for PLA is lactic acid. Figure 1 illustrates the various steps involved in the production of PLA starting with the growing of corn and ending with the production of PLA granules. The energy required for the biological processes of production of corn is obtained from solar energy, which is trapped by the process of photosynthesis. The basic product of photosynthesis is carbohydrate, primarily in the form of sucrose and starch. Hence, all the carbon, hydrogen, and oxygen present in the starch molecule as well as in the final polylactide molecule have their origin in water and carbon dioxide. Dextrose can be fermented into lactic acid at nearly neutral pH by acidulation and a series of purification steps the lactate salt fermentation broth if then purified to yield lactic acid. PLA can be produced from starch, or any other raw material as far as it rich in starch. Other alternatives are rice, sugar beet, sugarcane, wheat and sweat potato. There are two major routes to produce PLA from the lactic acid monomer:

- Direct condensation polymerisation of lactic acid monomer: This route involves the removal of water by condensation using solvents under high vacuum and temperature. The polymer produced by this route is of low/intermediate molecular weight, mainly because of the presence of water and impurities. The other disadvantage of this route is the requirement of a relatively large reactor required, the need for evaporation, recovery of the solvent and increased colour and racemisation.
- Ring opening polymerisation through the lactide intermediate: In this other route, through the lactide intermediate, first water is removed under mild conditions (and without the use of 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. The purified lactide is polymerised in a solvent free ring-opening polymerisation and processed into polylactide pellets. By controlling the purity of the lactide it is possible to produce a wide range of molecular weights.

Lactic acid can also be chemically synthesized resulting in a racemic mixture. Fermentatically derived lactic acid typically contains 99.5% of the L-isomer and 0.5% of the D-isomer. By controlling the amount of each isomer in the final polymer the overall crysatallanity can be controlled. Higher L-Lactide polymers are more crystalline as compared to D-Lactide polymers.

2.2. Energy Analysis [1] :

Cargill Dow Polymers (CDP) is a leading manufacturer of Nature Works TM PLA. In order to analyse the environment sustainability of PLA as compared to other synthetic polymers, CDP applied its life cycle assessment (LCA) tools to their Nature Works TM PLA. They first reviewed the contribution to the gross fossil energy requirement for PLA (54 MJ/Kg for PLA1, see FIG.3) compared to conventional plastics. Additionally, they proposed some ways and strategies for reducing the energy use by > 90%. The key improvements associated with the biomass feedstock technology stemmed from the use of the lignin fraction of the raw material to displace fossil fuel based requirements, and the resulting improved economic opportunity to rely on renewable energy (wind) for the balance of facility power need (7 MJ/Kg for PLA Bio/WP in Figure 2.

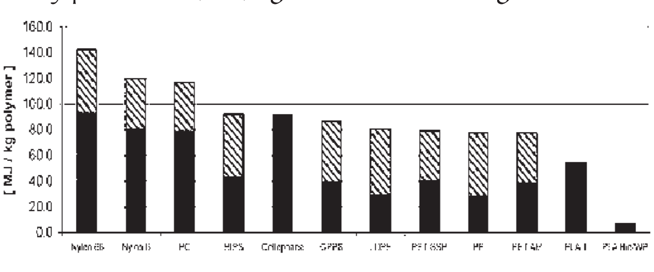
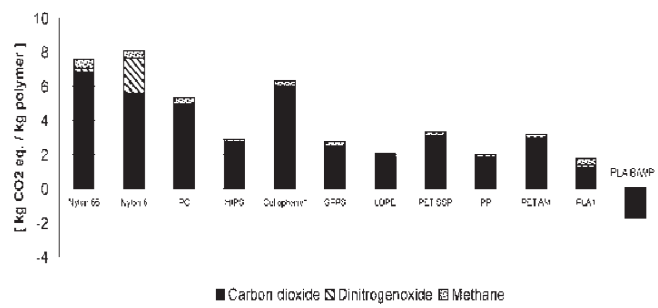
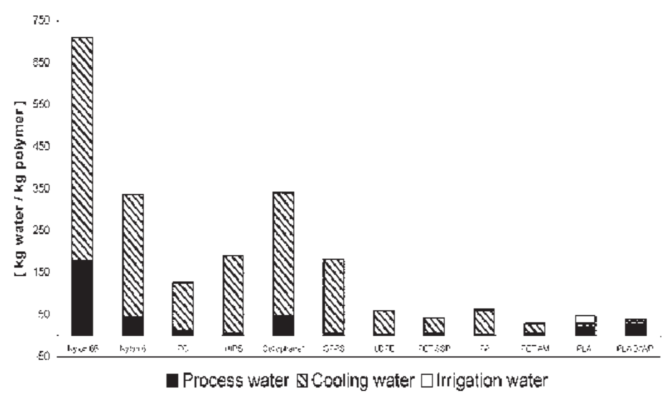


Fig. 2: Fossil energy requirement for some petroleum based polymers and polylactide. The cross hashed part of the bar represents the fossil energy used as chemical feedstock. The solid part of the bar represents the gross fossil energy use for the fuels and operations supplies to drive the production processes. PC = polycarbonate; HIPS = high impact polystyrene; GPPS = general purpose polystyrene; LDPE = low density polyethylene; PET SSP = poly(ethylene terepthalate), solid state polymerisation (bottle grade); PP = polypropylene; PET AM = poly(ethylene terepthalate), amorphous (fibres and film grade); PLA1 = polylactide (first generation); PLA B/WP polylactide, (biomass/wind power scenario).

PLA has also been compared with petrochemical based polymers taking into account the global warming and water use as impact indicators Figure 3 and 4. For example, CDP's objective is to decrease the emission of greenhouse gases from +1.8 down to -1.7 Kg CO2 equiv/Kg PLA, which can be compared to +6 Kg CO2 equiv/Kg nylon.





LCA demonstrates that PLA production can become both fossil energy free, as well as a source of carbon credits, paving way for many new and already existing fields of application.

2.3. Biodegradation of PLA [2] :

PLA can be mainly degraded by a non-enzymatically catalysed hydrolysis mechanism which is strongly temperature dependent. While, for instance, in compost (at temperature up to 70° C) PLA has been proved to be quite rapidly chemically depolymerised and then metabolised by microorganisms. This reaction mechanism is much slower at 25° C, where PLA is in the glassy state below its glass transition temperature T_g. Unlike the polymers made out of petrochemical feedstock, PLA does not contain any aromatic compounds, and therefore rots rapidly at the end of its useful life. All that remains is CO_2 and water.

3. Applications :

3.1. New Frontier Fibre [3-5] :

Cargill Dow commercially launched Ingeo™, a synthetic PLA fibre on January 21, 2003. Ingeo literally means ingredients from the earth. Subsequently partnerships with other companies were established all over the world to develop and market products developed from PLA. Kanebo Gohsen and Unitika imported PLA from CDP and produced PLA fibre under the brand name 'Lactron' and 'Terramac' respectively.

PLA has excellent properties and processability for materials (fibres) with melting point, strength, crystallinity suitable for practical use. Lactron is manufactured by melt spinning like nylon and polyester. It is processed in various shapes such as filament, staple, monofilament, spanbound, flat yarn spinning fibre, textile, knitting, non-weaved cloth and made into industrial material and general wearing materials.

3.1.1. Characteristics of PLA Fibre :

The properties of Lactron in comparison with nylon and polyester are summarised in Table 1.

Table 1: Characteristics of Lactron Fibre (Kanebo)

	Lactron	Polyester	Nylon
Physical Properties			
Density	1.27	1.38	1.14
Melting Point (°C)	175	260	215
Glass Transition Temperature (°C)	57	70	40
Absorption (%)	0.5	0.4	4.5
Combustion Heat (cal/g)	4500	5500	7400
Fibre Character			
Strength (cN/dtex)	4.5-5.5	4.5-5.5	4.5-6.0
Stretch (%)	30	30	40
Young's Modulus (Kg/mm^2)	400-600	12000	300
Stain			
Dye	dispersed	dispersed	acid
Staining Temperature (°C)	98	130	98

Source 1: Ref. 3

PLA fibres also have properties like:

- It resembles many other thermoplastic fibres in providing controlled crimp, smooth surface and a low moisture regain.
- Outstanding UV resistance.
- Lower refractive index which produces intense colour on dyeing.
- Improved wicking and faster moisture spread than polyester.
- Low odour retention as compared to polyester.
- Pure PLA fabric show excellent flame resistance properties.
- Superior fill power as compared to branded and unbranded polyester alternatives.

It should also be noted that PLA fibres have poor alkali resistance, which causes strength loss in conventional dye process, a low crystalline melt temperature which leads to low ironing temperature. However these problems can be overcome easily.

3.1.2. Uses of PLA Fibre :

Table 2 : Uses of PLA Fibre :

Classification	Use
Non Apparel	
Civil engineering & construction	Plant nets, non-weaved cloth, mat, plant soil, reinforcing material for weak soil
Agriculture	Easy covering material, anti weed net, net for vines
Fishery	Fishing nets, fishing lines
Life	Packaging, sanitation, convenience goods, suture threads, absorbance material
Apparel	Inner wear, outer wear, fashion goods

Source 2- Ref. 3

3.1.3. Biodegradability :

The steps followed in the biodegradation of Terrmac fibre are shown in FIG.6. These steps in general are applicable to the various PLA fibres under different brand names.

According to results obtained by the standard compost methods (ISO 148550), Lactron is completely degraded in about 70 days.

3.1.4. Future :

The main merit of 'corn fibre' is that it can solve the problem of dumping while keeping the advantage of conventional mixtures of synthetic and natural fibres. Moreover it can also be recycled and reused. Though initially the cost of production will be on the higher side, but as the market for PLA fibre develops, the costs are bound to come down. Factors like cheaply available raw material, environmentally sustainable processing and disposal will ensure that PLA fibre will be one of the most commercialised new frontier fibres.

3.2. Food Packaging [6,7] :

Avoidance of petrochemical derived package materials has been an objective of many environmentalists ever since their debut on the packaging space about 40 years ago. The overdrive today is biomass materials, because in theory they fulfil the sustainability objective. Many offerings have arisen from the basic notion of sustainable packaging, and PLA is the frontrunner amongst them. The special characteristics of PLA, such as GRAS status, biodegradability, and being a bio resource, put PLA in a unique position for food application.

As a plastic, PLA is high gloss and transparent; readily extruded to theroformable sheet or orientable films (analogous to polypropylene); and may be extrusion blow moulded or injection blow moulded into bottles. PLA is also reported to be an excellent flavour barrier. One of the drawbacks of PLA is that its temperature resistance is near 41° C, which limits its application to only cold-filled products and containment of products that are distributed under refrigeration; secondary packaging such as labels and shrink sleeves.

Demand for safe, minimally processed, "fresh" food products presents major challenges to the food packaging industry to develop packaging concepts for maintaining the safety and quality of packaged goods. Antimicrobial packaging can play an important role in reducing the risk of pathogen contamination as well as increasing the shelf life of minimally processed foods. Antimicrobial packaging systems incorporate antimicrobials into the packaging to prevent microbial growth on the surface of solid foods and to reduce the needs for larger quantities of antimicrobials in liquid foods.

In a recent study, PLA films were incorporated with nicin, a bacteriocin, to control food borne pathogens. The result of this study demonstrated the retention of nicin activity when incorporated into the PLA polymer and its effectiveness against foodborne pathogens. This study was just the tip of the iceberg. More research is required to test various other combinations of a biopolymer and natural bacteriocin, for their potential application in antimicrobial food packaging.

3.3. Pharmaceuticals [8-11] :

Various synthetic as well as natural materials have been examined in pharmaceutical application. Synthetic materials are preferred over natural material because greater control over uniformity any mechanical properties are obtainable. Synthetic material can be easily mass produced, and their properties can be easily tailored depending upon the application. For a synthetic material to be used in pharmaceutical application, it has to satisfy the following criteria:

- It has to be biocompatible and biodegradable (i.e. it should degrade in vivo to smaller fragments which can then be excreted from the body).
- The degradation product should be nontoxic and it should not have an inflammatory response.
- Degradation should occur within a reasonable period of time as required by the application.

PLA is one such material which satisfies all the above requirements. PLA can be hydrolytically degraded, and thus it can be degraded in human body systems which function in an aqueous environment. Biodegradation of PLA yields lactic acid, which is a normal intermediate of carbohydrate metabolism. Also, its rate of degradation can be suitably controlled by copolymerising it with polyglycolic acid (PGA) or any other suitable material depending upon the application. PLA has additional methyl groups with respect to PGA. As a result of its higher hydrophobicity PLA degrades at slower rate than PGA, even though PLA is less crystalline than PGA. The degradation rate of the amorphous copolymer can thus be easily controlled by altering the ratio of PLA and PGA in its composition.

3.3.1. Drug Delivery :

The use of PLGA copolymers, i.e. Poly (glycolic acid-co-lactic acid) copolymer, for controlled release of proteins and peptides has been widely studied. The first FDA approved PLGA product was the Lupron Depot drug delivery system (TAP Pharmaceutical Products, Inc.), which is a controlled release device for the treatment of advanced prostate cancer that used biodegradable microspheres of 75:25 lactide/glycolide to administer leoprolide acetate over period as long as 4 months (replacing daily injections).

According to a recent study, therapeutic compounds can be conventionally incorporated into the carrier polymer nanofibre (PLA) using elecrospinning. Electrospun polymer nanofibres containing drugs can be designed to provide rapid, immediate, delayed, or modified dissolution, such as sustained and pulsatile release characteristics. In general there are 3 modes of incorporating the drug in the nanofibre:

- Drugs as tiny particles are merely attached onto the surface of the nanofibre carrier.
- Both the drug and the nanofibre are electrospinnable, resulting in two kinds of nanofibres interlaced together.
- A blend of the drug and the carrier is integrated into one kind of composite nanofibre.

The first two modes give the problem of burst release in the initial stages, and therefore the last mode is preferred.

Alternatively, two or more components can be coaxially electrospun through different capillary channels and are integrated into a core shell structured composite fibre. With this, drugs can be released through the skin of the bicomponent nanofibre if the carrier polymer is permeable to the drugs wrapped, or can be released over a certain period of time while biological degradation of the carrier polymer is taking place. Another advantage of the coaxially electrospun nanofibres is that it provides temporal protection for certain bioactive substances such as growth factors which need to be protected for a certain period of time prior to playing their role in the early stage of wound healing.

3.3.2. Tissue Engineering :

Nowadays, one of the most stimulating areas of potential research is tissue engineering, a technique that consists of culturing cells on a biodegradable scaffold for the sake of implantation for tissue reconstruction. The advantages of tissue engineering are that a donor is not required and there is no problem of transplant reject. The purpose of the scaffold is to act as an extracellular matrix (ECM), where cells can adhere and grow, and thus to guide the development of new, fully functioned tissues. The initial requirement of the scaffold is to hold the cells together inspite of partial degradation.

Among the various degradable and biodegradable scaffolds presently under investigation, those made of PLGA three dimensional porous devices seem to be the most attractive. The main advantage of using PLGA is that it will be hydrolytically degrade leading to a completely biological implant. Dermograft™, a scaffold produced from multifilament yarn, a 90:10 copolymer of PGA and PLA is used for the treatment of diabetic foot ulcers.

To prepare these scaffolds, electrospinning has now been the most extensively used fabrication technique over dry-wet spinning method. Advantages of using electrospinning are:

- It provides a unique structure characterised by high surface area to volume ratio and three dimensional connected pore network both of which enhance cell attachment and proliferation.
- It is possible to use monopolymers, blends of polymers,

and composition of polymers with other materials or additives such as growth factors, other cell regulatory biomolecules, and even living cells to develop functionally active nanofibrous structures.

The above characteristics of a scaffold are conducive for tissue growth.

3.3.3. Medical Implants and Sutures :

The use of PLA as a suture has been known for decades. The biodegradable and biocompatible nature of PLA drew attention towards implants for bone fracture fixation. It is acknowledged by the researchers that the use of metallic implants for fixing bones may cause serious problems like osteoporosis, due to stress shielding caused by the mismatch of the metallic properties with that of bone, and necessary second operation for removal of the implant. Use of PLA alleviates these problems. Other advantages of using PLA are that it is light weight and its degradability can be set in accordance with the healing time required.

4. Conclusion :

Compared to most fossil resource based polymers which have reached maturity over the years, PLA clearly offers the best compromise for continued improvement against current performance characteristics. These improvements will be derived from a mix of material, process and volume improvements. As aforementioned, PLA is a versatile and an eco-friendly polymer. However some environmentalists are against diverting corn acreage for non food application when so many people suffer from hunger. Moreover corn cultivation uses more nitrogen fertilizer, herbicides and insecticides than any other crop. However these problems are too small when compared to the problem that arise out of using petrochemical based synthetic material. Over the long term, LCA demonstrates that PLA production can become both fossil energy free and a source of carbon credit. This bright future will come only with the investment of time, money and effort. No doubt, PLA is a 'next-gen' polymer.

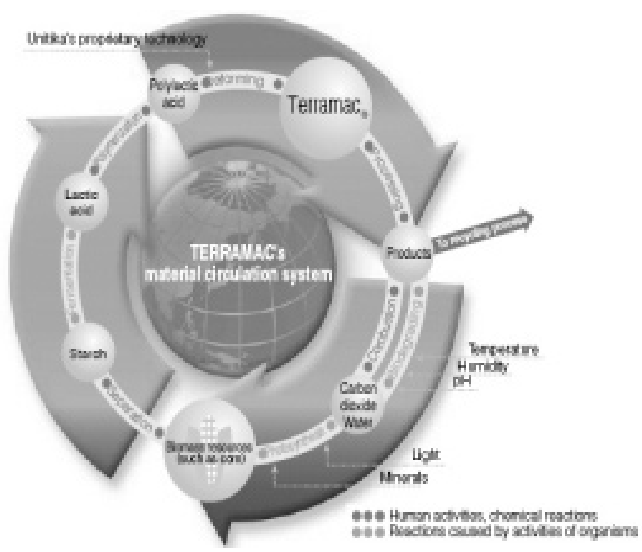


Fig.6 : Carbon Cycle of Terramac Fibre.

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