Case Study 3

An efficient, green synthesis of a compostable and widely applicable plastic (poly lactic acid) made from corn

Plastics have become an integral part of our lives due to their several advantages such as light weight, highly moldable, sturdy, and high durability. Plastic are generally obtained from non-renewable petrochemicals. These polymers can survive many centuries before nature is able to degrade it. This troublesome ability of plastic doesn't have great immediate impact on our environment, but its continuous dumping into seas and land will eventually create problems for future generations. However, the wide use of plastic product possess several disadvantages. therefore there is an urgent need of some biodegrable alterantive of conventional plastics.

The plastics derived from plant sources such as sweet potatoes, soya bean oil, sugarcane,hemp oil, and corn starch are called as bio-plastics. Less than 200,000 tons a year of bio plastics is produced worldwide as compared to 30 million tons of oil-based plastics. These bio-polymers are bio-degradable and are environmentally friendly as compared to traditional plastics. Bio-plastics can reduces the energy crisis. They posses unique properties due to which they can be employed for different applications.

Poly(lactic acid) PLA: Poly(lactic acid) (PLA), an aliphatic polyester, derived from renewable and degradable resources such as corn and rice. It is commonly made from hydroxyl acids, which also includes polyglycolic acid (PGA). It is one of the few polymers in which the stereo chemical structure can easily be modified by polymerizing a controlled mixture of l and d isomers to yield high molecular weight and amorphous or semi-crystalline polymers. Properties can be modified through the variation of isomers (l / d ratio). PLA and its degradation products, namely H_2O and CO_2, are neither toxic nor carcinogenic to the human body, hence making it an excellent material for biomedical applications including sutures, clips, and drug delivery systems PLA products have been approved by the US Food and Drug Administration (FDA) for direct contact with biological fluids. It possess several advantages over other polymers such as renewability, biocompatibilty, processability, and energy saving. PLA can be degraded by a biotic degradation i.e. simple hydrolysis of the ester bond without any catalysts. During the biodegradation process, and only in a second step, the enzymes degrade the residual oligomers till final mineralization (biotic degradation). It can help reduce the energy crisis as well as the dependence on fossil fuels of our society. Furthermore, PLA can be processed by film casting, extrusion, blow moulding, and fibre spinning due to its greater thermal processability as compared to other biomaterials such as poly(ethylene glycol) (PEG), poly(hydroxyalkanoates) (PHAs), and poly(caprolactone) (PCL).

Synthesis of PLA

The synthesis of PLA is a multistep process which starts from the production of lactic acid and ends with its polymerization. Lactic acid can be obtained from renewable sources like corn, potato, whey, sugarcane through fermentation. An intermediate step is often the formation of the lactide. Lactic acid is condensation polymerized to yield a low molecular weight, brittle polymer, which, for the most part, is unusable, unless external coupling agents are employed to increase its chains length (**Figure 1**).

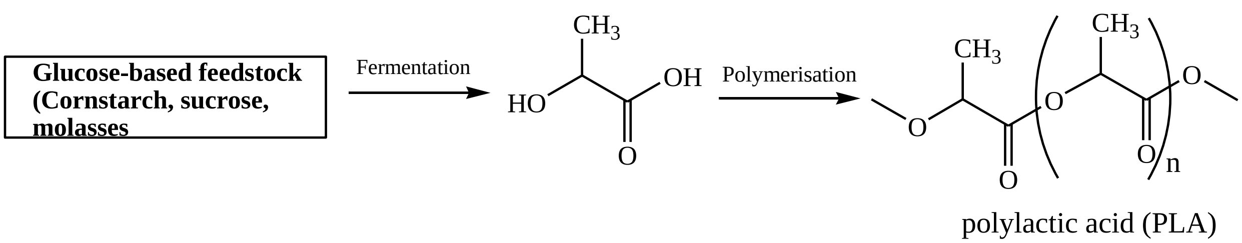
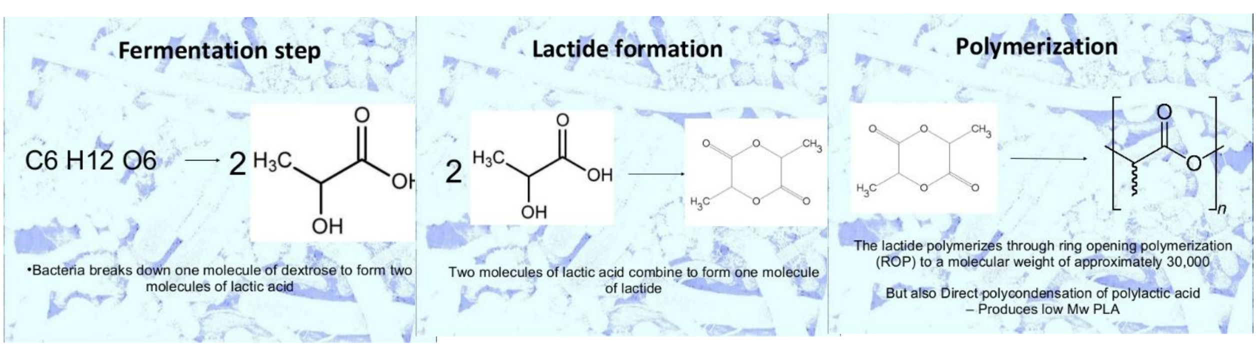


Figure 1: synthesis of PLA from natural feedstock



<u>Conversion of Corn to Dextrose</u>

It involves the following steps:

a) Conversion of corn to cornsugar (D-glucose) involving the process that begins with wet milling, (a mechanical process in water that separates starch, as well as other valuable components, from the corn kernel).

b) The starch is then heated with acid or enzymes, or both, to completely hydrolyze the starch to dextrose. The dextrose is isolated by crystallization or used as a liquid concentrate.

Conversion of Dextrose to L- Lactic Acid

Large amounts of D-glucose obtained from corn, potatoes, or molasses by acid hydrolysis enter industrial fermentation processes in the production of lactic acid. D-glucose is converted into two molecules of pyruvate, along with two molecules of ATP and two of NADH by plants, animals and many microorganisms by glycolysis. The process converts glucose into. Pyruvate is slightly more oxidized than glucose, and the hydrogen lost from glucose during the oxidation transforms NAD^+ to NADH (**Figure 2**).

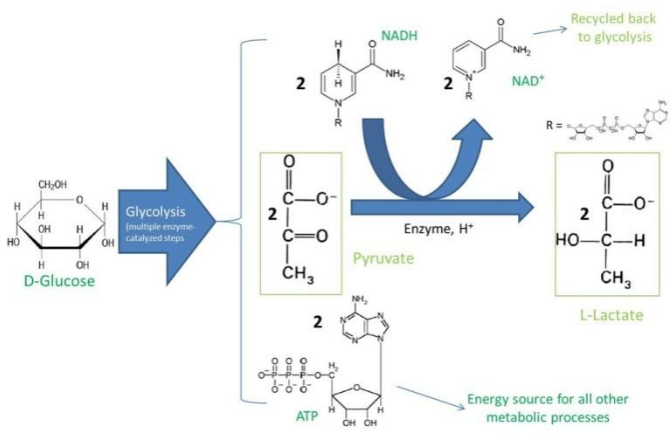


Figure 2. Conversion of D-Glucose to lactic acid

Polymerization

Poly-lactic acid with high molecular mass PLA of about 100 000 Daltons can be produced by using different routes.

a) **Direct condensation polymerization**

It usually leads to low molecular weight polymers which then can be converted to higher molecular weight polymers by addition of chain coupling agents. In this method lactic acid is polymerized in the presence of a catalyst at reduced pressure. It is the least expensive route but it is difficult to obtain high molecular weights polymers of above 100,000Da. The polymer obtained has a low molecular weight (1000-5000Da), because it is hard to remove water completely from the highly viscous reaction mixture. Thus through this route the polymer produced possesses inferior mechanical properties. However a high molecular weight polymer can be obtained by making use of coupling agents or adjuvant e.g. bis (tri-chloromethyl) carbonate and carbonyl diimidazole is required. These produce low PLA quality and reaction by-products (water & alcohols),that must be either neutralized or removed completely from high viscous reaction mixture, adding cost and complexity hence this route is not preferred in this research.

b) **Azeotropic dehydrative condensation**

In this method organic solvents are introduced into reaction mixture to ease up removal of water thus producing higher molecular weight product. In this polymerization, lactic acid is converted directly to high molecular weight PLA by an organic solvent-based (toluene, xylene or diphenyl ether) process with the azeotropic removal of water by distillation. This method yields high molecular weight polymers but with considerable catalyst impurities which can cause unwanted degradation, uncontrolled or unreproducible hydrolysis rates, catalyst toxicity and differing slow release properties. It also uses high activity catalyst (such as boric or sulphuric acid) and low boiling organic solvent; and water as a byproduct need to be removed azeotropically and catalyst dried and recycled to the reaction system. Uses of organic solvents which results in impurities, water removal and regeneration of catalyst increases process costs hence not feasible to this research.

c) **Ring opening polymerization (ROP)**

PLA is produced by formation of lactide monomer in the presence of catalyst which is then converted into final product. It allows producing PLA with controlled molecular weight and by controlling ratio of initial D- and L-lactic acid isomers concentration, properties of final product can be adjusted for specific needs (**Figure 3**). In this method the terminal end of a polymer chain acts as a reactive centre where further cyclic monomers can react by opening its ring system and form a longer polymer chain. In this route, lactic acid is first polymerized to low molecular weight oligomers, which is catalytically depolymerised through internal transesterification to lactide. The ring of lactide then opens to form high molecular weight PLA.

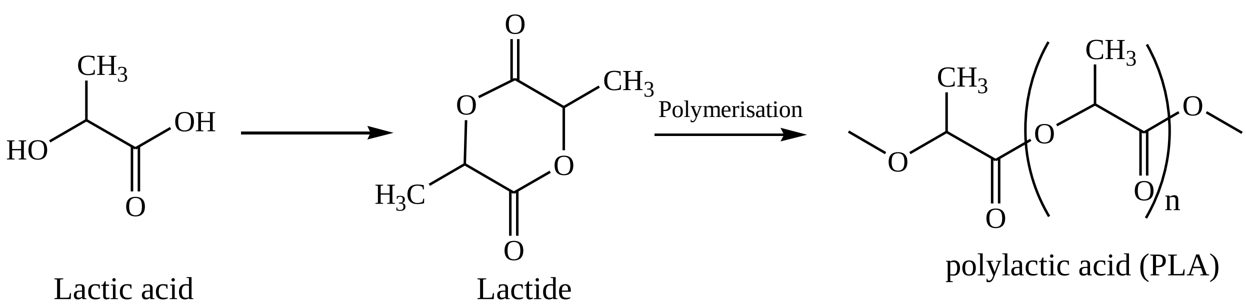


Figure 3. PLA synthesis using ring opening route.

Physical and Chemical Properties

Due to the chiral nature of lactic acid, several distinct forms of polylactide exist. Poly-L-lactide (PLLA) is the product resulting from polymerization of L, L-lactide (also known as L-lactide). PLLA is crystalline to around 37%, a glass transition temperature between 60-65 °C, a melting temperature between 173-178 °C and a tensile modulus between 2.7 16 GPa. However, heat resistant PLA can withstand temperatures of 110 °C. PLA is soluble in chlorinated solvents, hot benzene, tetrahydrofuran, and dioxane. PLA has similar mechanical properties to PETE polymer, but has a significantly lower maximum continuous use temperature. Polylactic acid can be processed like most thermoplastics into fibre (for example using conventional melt spinning processes) and film. The melting temperature of PLLA can be increased by about 40-50 °C and its heat deflection temperature can be increased approximately 60°C to up to 190 °C by physically blending the polymer with PDLA (poly-D-lactide). PDLA and PLLA form a highly regular stereocomplex with increased crystalline. The temperature stability is maximized when a 50:50 blend is used, but even at lower concentrations of 3-10% of PDLA, there is still a substantial improvement. In the latter case, PDLA acts as a nucleating agent, thereby increasing the crystallization rate.

Unique Characteristics

PLA (Poly Lactic Acid) is one of the most environment friendly bio-plastic available today. It is made from 100% bio based resources and has multiple end-of-life options (i.e., 100% recyclable and biodegradable). PLA is a highly efficient plastic. Emission of carbon dioxide is less when compared with other polymers. Bio-plastic gets decomposed in maximum 60 days and produces water and the greenhouse gas (CO2). Degradation of bio-plastic carried out in the digester by giving the appropriate condition such as temperature and this Carbon Dioxide can be recovered and store from the digester in this way, we can resolve the problem of evolution of CO_2 in the environment. The life span of the bio-plastic can be increased up to12 months by sizing and coating.

Properties of Bio-plastics

Biodegradability, Water resistance, Oxygen permeable, Solid polymer of high molecular weight, low decomposition temperature, Low melt strength, Slow crystallization rate.

Applications of Bio-plastics

There are various applications of green plastics are as follows: -

➢ It is mostly used in packaging for product such as shampoos and cosmetics.

➢ It is used for manufacturing disposable products used in the food industry.

➢ Plastic wrap for packaging.

➢ Used to produce bottles.

➢ Moisture barrier films for hygienic products.

➢ Coating for paper, cardboard, etc.

➢ It is used in agricultural applications.

➢ It is used for coating drugs.

Advantages of Bio-plastics

a) **Cheaper Alternative:** Bio-plastics are becoming more viable with volatility in oil prices
b) **Reduced Waste:** Bio-plastics reduce the amount of toxic run-off generated by the oil-based alternatives.
c) **Benefit to rural economy:** Prices of crops, such as maize, have risen sharply in the wake of global interest in the production of bio-fuels and bio-plastics, as countries across the world look for alternatives to oil to safe guard the environment and for attaining energy security.
d) **Reduced carbon footprint:** Oil based plastics require fossil fuel as a key raw material. In addition, oil-based plastics like PP and PS require more energy during the plastic development process when compared withbio-plastics. A Life Cycle Analysis for a typical PP or PS plastics shows a carbon footprint of approx. 2.0 kg CO_2 equivalents per kg of plastic (from cradle to factory gate). These CO_2 emissions are 4 times higher than the CO_2 emissions for Poly Lactic Acid (PLA) resin. One metric ton of bio-plastics generates between 0.8 and 3.2 fewer metric tons of carbon dioxide than one metric ton of petroleum-based plastics.
e) **Multiple end-of-life options:** Valuable raw materials can be reclaimed and recycled into new products, reducing the need for new material and negative environmental impact of 'used' plastic products can be greatly reduced, if not, eliminated.

Disadvantages of Bio-plastics

Few drawbacks of bioplastics have been discussed below:

(i) Biodegradable plastics can not be recycled.

(ii) If biodegradable plastic is not properly disposed of, it leads to an inefficient breakdown of the plastic, which can release toxins (CO_2, CH_4 etc.) into the environment.

Lactic acid is a compound that plays a key role in several biochemical processes. Lactic acid has been produced on an industrial scale since the end of the nineteenth century and is mainly used in the food industry to act as an acidity regulator, in cosmetics, pharmaceuticals and animal feed. In addition to this it is considered the monomer precursor of PLA. It can be obtained either by carbohydrate fermentation or by common chemicalsynthesis. Lactic acid is mainly prepared in large quantitiesby the bacterial fermentation of carbohydrates. These fermentation processes can be classified according to the type of bacteria used as:

(i) The hetero-fermentative method, which produces less than 1.8 mol of lactic acid per mole of hexose, with other metabolites in significant quantities, such as acetic acid,ethanol, glycerol, mannitol and carbon dioxide.

(ii) The homo-fermentative method, which leads to greater yields of lactic acid and lower levels of by-products, and is mainly used in industrial processes. The conversion yield from glucose to lactic acid is more than 90 per cent. The majority of the fermentation processes use species of Lactobacilli, which give high yields of lactic acid.