Green Plastics: Poly-lactic Acid Synthesis from Waste Tamarind Seed Powder & its Applications

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ABSTRACT

In the era of sustainable development there is a necessity to produce biodegradable polymers to minimize the soil pollution. With the need of the hour Green plastic is the polymeric material formulated for specific applications, which is derived from the Tamarind seed de-oiled cake starch. Through the series of unit operations, starch which is produced can be fermented by Lactobacillus delbrueckii, Lactobacillus amylophylus and Lactobacillus amylovirus. The polymerization reaction of Lactic Acid is carried out by using a catalyst. To cope up with the scarcity of valuable petroleum product & to minimize the environmental pollution, Green plastic materials play an important role for sustainable development.

Keywords: Poly lactic acid, Green Plastics, Biodegradable polymers, Waste Tamarind seed de-oiled cake starch

INTRODUCTION

The term green plastic is applied to any polymeric material derived from a source of natural origin or purely synthetic, process-able like conventional thermoplastics on existing equipments to finished product which are completely degradable either of the action of water or microbes. The term green plastic therefore applies strictly to the wholly degradable resins i.e. material with the degradable polymer as the matrix and not to the product containing 6% starch. They are 100% biodegradable for example starch, lignin, cellulose etc.

Green plastics are completely biodegradable by microorganisms or by water. Polymers which are mostly used today are not completely biodegradable, where the polymer may contain certain substituent which is biodegradable. For example in a polyethylene compound loading with 5% starch, only starch component is biodegradable while polyethylene is not, since the polymers are mainly petroleum base which are not completely biodegradable. So there is a chance of pollution problem and also a chance of oil depletion. To avoid such a problem, the development of green plastics is important. Though the advancements, developments and modifications were done with polymers, still they are the major cause of the environmental pollution even after disposal.

Need of Green Plastic

➢ To protect environment and human being from threats caused by accumulation of plastic waste.
➢ To serve the natural resource because generally the plastic is derived from the hydrocarbons.
➢ To reduce the release of toxic substances as compare to other polymer materials.
➢ To conserve the use of virgin polymers.

Need for reduction in use of fossil fuel feedstock & increase in use of renewable feedstock, thus reducing the pollution. This can be achieved by biodegradable plastic. Biodegradable plastic are those plastic when disposed into biologically active environment are converted into smaller molecules that are not harmful to the environment. Starch based biodegradable plastics are those which are easily attacked by soil micro-organisms which breaks the polymer chain & becomes the part of plastic\(^{10}\).

**Natural Polymers**

Almost all plastic today are made from synthetic polymers. There are however, polymers that occur in nature, biopolymers. Carbohydrates and proteins, for example are biopolymers. Many biopolymers are already being produce commercially on large scale. They are available to be used in the production of plastic.

Starch is found in waste Tamarind seed as well as in maize, potato, wheat and some other plants. Annual production of starch is well over 70 billion pound, with much of it being used for food and non-food purposes like making paper, cardboards, textile sizing and adhesives.

Collagen is the most abundant protein found in mammals. Gelatin is denature collagen and is used in sausage casing, capsules for drugs and vitamin preparation and other miscellaneous industrial applications including photography. Casein commercially produced mainly from cow’s skimmed milk. It is used in adhesives, binders, protective coatings and other products. Proteins (from waste Tamarind seed de-oiled cake) are abundant plant proteins basically tamarind seed de-oiled cake directly is use for making adhesives, coating for paper and cardboard\(^{10}\).

**Market Data of Waste Tamarind seed**

Tamarind has been described as one of the common and most important trees of India. India is the world's top producer, exporting several thousands of tones of seed, seed de-oiled cake and fruit pulp each year. Tamarind trees are often grown in gardens and along roadsides and are cultivated commercially in plantations. India is the only producer of tamarind on a commercial scale. A large part of India's production of tamarind is exported to West Asia, Europe and America, where it is used for food specialities like Worcestershire sauce. This spice also comes in the forms of pulp and juice concentrates which mainly go into the preparation of cool drinks, sea foods and a range of sophisticated cuisine. Tamarind is native to tropical America and this plant is widely seen throughout Asia and it has acquired the common name Aasam, meaning, simply, 'acid' as they are used as as acid flavors in the food Industry. Tamarind cultivars are divided into two basic categories: sweet and sour. India mainly grows sour cultivars in orchard-like plantations. Tamarind is widely used throughout the world. Tamarind pulp concentrate is widely used in Indian and Middle Eastern cooking.

Tamarind can be found in various forms like concentrated pulp with seeds, a canned paste, whole dried pods, or de-oiled cakeed. It is available in Indian and some other Asian markets. There is a wide variety of tamarind products available in the market for consumption. They include tamarind paste, seedless dried tamarind, tamarind pods, tamarind concentrate, tamarind syrup, tamarind drink concentrate, tamarind sauce, tamarind chutney, tamarind dipping sauce, tamarind gelatin, tamarind candy etc. Tamarind may also be used as a base for delicious raw or cooked chutneys, its fruity acidity combining well with sugar, chilli and other flavours. Moreover tamarind concentrates are extensively used as an ingredient and an effective substitute for vinegar, tomatoes and lemon juice.

Tamarind, an essential ingredient in the South Indian cuisine and a host of processed food items across the globe, can also offer livelihood security in rural and tribal areas, experts indicate. Its organized processing, supported by cold storage facilities, is found to be ideal for ensuring market price stability and rural employment. India is the largest producer and exporter of range of raw and processed spices. Processed spices demand is directly linked with its consumption in food processing industry and this is set to grow in India in coming period with growth of population and fast changing food habits as well as increase in spending power of the middle and upper class in India.

Why waste Tamarind seed de-oiled cake: The composition of waste Tamarind seed de-oiled cake
which is full of carbohydrates, protein, oil, minerals and others. The waste Tamarind seed de-oiled cake possesses starch of about 51.0% and after de-oiling of the tamarind seeds the starch contain becomes 55.0% which can be used for the production of green plastic. We need starch for production of PLA. Therefore we used waste Tamarind seed i.e. de-oiled tamarind de-oiled cake because it is enrich of starch.

| Composition       | Original | De-oiled |
|-------------------|----------|----------|
| Oil               | 7.6%     | 0.6%     |
| Protein           | 7.6%     | 19.0%    |
| Polysaccharide    | 51.0%    | 55.0%    |
| Crude Fibre       | 1.2%     | 1.1%     |
| Total Ash         | 3.9%     | 3.4%     |
| Acid Insoluble Ash| 0.4%     | 0.3%     |
| Moisture          | 7.1%     |          |

Natural Process in plants body by Photosynthesis

LA (Lactic Acid) to PLA
1. Carbon dioxide enters the pores.
2. Veins supply water to cell.
3. Solar energy entraps in chloroplast for photosynthesis.
4. Chloroplast produces sugar and oxygen. Sugar is used as fuel.
5. Unused sugar is send to kernel & stored as starch.
6. Carbon Dioxide when reacts with water in the presence of Sunlight gives Glucose with small amount of Oxygen released.
7. Micro-organisms convert starch to lactic acid.
8. Lactic acid molecules link together to form rings called lactide monomer.
9. These ring opens and polymerization of lactide monomer takes place resulting in formation of PLA.

Process for manufacturing Green Polymer
In the processing of green plastics, tamarind must be grown, harvest and transported to processors where seeds are removed and remaining part is used for pulp making and concentrate making. But we have to required only seeds for production of oil and then that de-oiled tamarind seeds de-oiled cake is used for glucose extracted and fermented into cell containing PHA Phytohaemagglutinin (lectin). The cell are washed, spun in a centrifuge and broken apart to release the PHA Phytohaemagglutinin (lectin), which is again washed and centrifuge.

Conversion of Waste Tamarind seed de-oiled cake to Plastic
There are various steps involved in the conversion of waste Tamarind seed de-oiled cake to starch.

Cleaning
The raw material is delivered in de-oiled tamarind seeds cleaning machine. The waste Tamarind seed is inspected and cob, dust, chaff and foreign material are removed. After cleaning the waste de-oiled Tamarind seed is transported to the sun drying.

Drying
A proper drying is essential for high yields and high starch quality. This is carried out to reduce the moisture content in seeds. It is necessary in order to avoid damage of seeds by micro organisms and for storing seeds for a long span of time. Drying is to be done to such a extent, so that it becomes very easy to grind.

Grinding and Screening
After germ separation the material of waste Tamarind seed de-oiled cake (germ) is transported to the grinding mill to release starch & glucose bond in the form of fiber. The ground tamarind seeds are then screened to obtain the desired size (.825, .412, .300mm).

Inoculation of micro organisms:
Inoculum is prepared by sterile water NaCl solution and pre-cultured microorganisms. The pH is maintained at 8.2 to 8.8 and initially nutrients (pectin de-oiled cake, Glucose-D) are provided to the inoculums for the initial growth of microorganism. Whole solid state fermentation is carried out in closed fermentor at 36 to 38°C.

Enzymes Used for Fermentation:
The desirable characteristics of industrial microorganisms are their ability to rapidly and completely ferment cheap raw materials, requiring minimal amount of nitrogenous substances, providing high yields of preferred stereo specific lactic acid under conditions of low pH and high temperature. The choice of an organism primarily depends on the carbohydrate to be fermented. Lactobacillus delbrueckii, Lactobacillus amylophylus and actobacillus amylovirus are able to ferment starch.

Starch Fermentation
To convert Waste Tamarind seed de-oiled cake Starch into Lactic Acid, Solid state Fermentation process is used. In this process, the Waste Tamarind seed de-
oiled cake starch is fermented with the help of *Lactobacillus delbrueckii*, *Lactobacillus amylophylus* and *actobacillus amylovirus* enzymes to produce Lactic Acid.

**Lactic acid Properties**  
Physical and Chemical properties of lactic acid

| Chemical formula | C₃H₆O₃ |
|------------------|--------|
| Chemical name    | (S)-2-hydroxy-propanoic acid |
| Molecular Weight | 90.08  |
| Physical appearance | aqueous solution |
| Taste            | mild acid taste |
| Melting point    | 53°C / 127°F |
| Boiling point    | > 200°C / 390°F |
| Solubility in water (g/100 g H₂O) | Miscible |
| Dissociation Constant, Ka | 1.38 * 10^-4 |
| pKa              | 3.86   |
| pH (0.1% solution, 25°C) | 2.9 |
| pH (0.1 N solution, 25°C) | 2.4 |

**Polymerization**¹  
Then the polymerization is carried out using conventional polymerization techniques.  
1) Bulk polymerization  
2) Suspension polymerization  
3) Emulsion polymerization  
4) Solution polymerization

**Polymerization of Lactide**  
Polylactides (PLAs) :-

- PLA can be easily produced through ring-opening polymerization of lactide using a (stannous octoate) catalyst.  
- Good moisture-barrier properties.  
- It is able to withstand the rigors of injection molding and blow or vacuum-forming processes.

**Degradation**  
Degradation is the process by which deteriorate ion in the properties occur due to reduction in molecular weight.

The above image shows the degradation of disposal glass made from green plastic and how it get decompose when it goes to the land filling. Life Span of the biodegradable plastic is up to 60 days and it can be increase by the sizing of the that polymer by means of shellac coating up to 1 year¹⁰.
Distinguish between synthetic plastic and green plastic:

| Sr. No. | Synthetic Plastics                                                                                                                                   | Green Plastics                                                                                   |
|---------|-------------------------------------------------------------------------------------------------------------------------------------------------------|--------------------------------------------------------------------------------------------------|
| 1.      | Plastic is a material that contain as an essential ingredient one or more polymer substance.                                                              | It is naturally occurring plastics made from plants.                                               |
| 2.      | The cost of synthetic plastic is lower than green plastic.                                                                                            | The cost of green plastic is much more than synthetic plastic.                                    |
| 3.      | It is non renewable.                                                                                                                               | It is renewable.                                                                                  |
| 4.      | It is non biodegradable.                                                                                                                              | It is biodegradable.                                                                             |
| 5.      | It is made from non renewable resources like petroleum, natural gas and coal which are exiting.                                                        | It is made from renewable sources like plant which are easily available.                          |
| 6.      | It is easily available                                                                                                                               | It is not easily available.                                                                       |

Processing Parameters of Green Plastic
There are two main types to bear in mind when processing green plastics:-

- The limited thermal stability of the polymer, the polymer degrading rapidly above 195°C.
- The need to optimize conditions to allow a maximum rate of crystallization and thus reduce cycle time. The maximum rate of crystallization is reported to be at about 55-60°C.
- Processing temperature should not exceed 180°C.
- Duration of time the material is in the melt state should be kept to a minimum when blow molding the blow pin and mould should be at about 60°C to optimize crystallization state. Similarly injection moulds are recommended to be held at 60 or 65 degree Celsius.

Properties of Green Plastics
- Biodegradability
- Water resistance
- Oxygen permeable
- Solid polymer of high molecular weight
- Low decomposition temperature
- Low melt strength
- Slow crystallization rate.

Applications of Green 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 Green Plastics:
- High resistance to the effect of atmosphere.
- Easily possible to being processed into complex shape.
- It is light in weight for easy transportation.
- Because of low thermal and electrical conductance it is used as thermal and electrical insulators.
- It is not attacked by fungi, insects, etc.
- Green plastics are biodegradable.
- It is environmental.
- Green plastics are transparent as well as translucent.
- It has low maintenance cost.

Disadvantages of Green Plastics
- Cost of green plastic is very high as compare to synthetic plastic.
- Energy required for green plastic is more than synthetic plastic.
- After disposal of green plastic it produces green house gases.
CONCLUSION

The abundant availability of naturally occurring polymers is of great technical importance in industrial basis on environment point of view as far as biodegradability is concerned. Green plastic materials play vital role in deciding the cost factor of the compound. Taking a sustainability factor into account, disposal and environmental problems can be greatly reduced by the use of green plastic end products for specific applications. Apart from that use of green plastic will provide a solution on the deficiency of the petro-product or the rock oil is concerned. Bioplastics gets decomposed in maximum 60 days and produces water and the greenhouse gas (CO₂). Degradation of bioplastic carried out in the digester by giving the appropriate condition such as temperature and this Carbon Dioxide can be recovered and stored from the digester in this way we can resolve the problem of evolution of CO₂ in the environment. The life span of the bio-plastic can be increases up to 12 months by sizing and coating.

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