

# Bioplastics from Starch

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**Abstract-** Once the most beloved commodity plastics have now become a liability. With Environmental degradation ,improper waste disposal it is high time we search for alternatives which can also alleviate stress from conventional sources of energy from producing it. Bio-plastics are environment-friendly and biodegradable hence provide an effective way to replace the conventional plastics. In this paper we review starch as a source for producing bioplastics. We discuss how to generate bioplastic films from different starches, Role of plasticizers (especially glycerol and sorbitol) in producing them, discuss their properties and conclude with its importance and find ways to bring this technology to India.

**Keywords-** Starch, Biodegradable, Bioplastics, Plasticizers, Non-conventional sources.

## I. INTRODUCTION

About 4% of the world's total petroleum reserves are used for plastic preparation, which are getting exhausted precipitously. The volatile oil prices in past few years, due to the political tensions in the Middle East and Africa, the major crude oil producing regions have actuated research in the area of bioplastics. They are derived from biological resources like starch from corn, tapioca, cassava, wheat, rice, etc. which are easily available in bulk quantities.

## II. STARCH

The starch granules consist of amylose and branching points of amylopectin molecules. Amylose constitutes linear chains of the starch, with glucose residues linked by  $\alpha$ -D-(1-4) bonds. Depending on the species, it constitutes 20- 30% of starch. Amylopectin has a branched structure and is composed of 300-6000 D-glucose units which are joined by  $\alpha$ -glycosidic linkages between C-1of one D-glucose unit to C-6 of other D-glucose unit. The amylopectin content in starch is about 70% by weight that varies on the source.

## III. EXTRACTION OF STARCH

Extraction of starch from potato, maize, corn etc. involves crushing of potato or maize or corn into a paste and then soaking in a bowl filled with water. The mixture is squeezed properly and the paste has to be crushed after an interval of 30 minutes for three to four times. Then paste is sieved and cloudy water collected in separate bowl. Water is vaporised and starch is obtained.

## IV. PREPARATION OF BIOPLASTIC FILM

Starch is casted with glycerol and flexibiliser sorbitol and mixed directly with distilled water to make batches with a total weight of 25 g along with acid like HCl. The mixture is then heated from 30 to 95°C and maintained at 95°C for 10 min, with regular shaking (75 rpm) and constant heating rate

to obtain a thick gelatinized suspension neutralized by adding base like NaOH. The final product spread out evenly on acrylic plate and dried to get plastic film.

## V. PLASTICIZERS

### A. Requirement

The glass transition temperature ( $T_g$ ) of dried starch is about 240°C [40,41] more than thermal degradation point (220°C) [27]. This high glass transition temperature is due to the presence of strong inter-molecular and intra-molecular hydrogen bonding between the starch macromolecules [40,41]. Thermoplastic starch (TPS) polymers derived solely from starch are very water sensitive and can undergo significant molecular weight change during processing [28]. Therefore, modifications are made in starch by incorporating plasticizers, for the breakdown of the crystalline granules and decrease the  $T_g$  and melting temperature ( $T_m$ ) [30]. Decrease in  $T_g$  with increase of glycerol concentration can be related to hydrophilicity of this plasticizer. By exposing the hydrophilic hydroxyl groups, water molecules adsorption in starch films on its more active sites is facilitated on addition of glycerol. Due to water's low molecular weight and its plasticizing effect, its addition to starch films, acts as a mobility enhancer and an increase in molecular mobility of amorphous and partially crystalline polymers due to an increase in free volume thus, decreasing glass transition of films.

### B. Function

A semi-crystalline granule of starch is converted into a homogeneous material with hydrogen bond broken between the starch molecules. This process is called gelatinization and it leads to loss of both crystallinity and double helices [30]. Starch-starch interactions are replaced by starch-plasticizer interactions. This plasticized mouldable thermoplastic material called TPS which is similar to the other synthetic thermoplastic [18, 18, 20, 21].

### C. Selection

Polyols like Glycerol, Glycol, Sorbitol, Xylitol, Maltitol, Ethylene glycol, Propylene glycol, Butane diol [6,7,8,31,40,41], Sucrose, Fructose, Mannose [43,44], Fatty acids (such as myristate or palmitate) etc. are used. Though water is good plasticizer it is not used alone as it gives a brittle product when equilibrated with ambient humidity [6, 7, and 8] and due to evaporation of water. Glycerol due to its low cost, non-toxicity, high boiling point (292 °C) and some economic benefits like during the hydrolysis and/or transesterification of lipids (triglycerides) into fatty acids for the biodiesel industry is used widely. But it leaches out due to aging and humidity exposure

#### D. Recent Studies

Multi-functional ionic liquid plasticizers such as 1-allyl-3-methylimidazolium chloride [34] and 1-butyl-3-methylimidazolium chloride as a plasticizer [29] and a compatibilizing agent of starch have been reported. Because of their unique properties which includes non-volatility, non-flammability, low viscosity, chemical stability, electrochemical stability [12]. They have a tendency to form strong hydrogen bonds with starch due to high concentration of chloride ions like in 1-butyl-3-methylimidazolium chloride that showed a much higher elongation at break in the rubbery state than the glycerol-plasticized TPS samples [29].

#### E. Improvisations

Chemical modification is an effective method for improving the performance of starch based bioplastics. For example Hydroxylation [3,4], Acylation [2], Oxidation, Acetylation[42] of starch by substituting the ester or ether groups for the hydroxyl group.

The starch acetates have higher thermal stability and hydrophobicity due to the reduction of the hydroxyl group due to acetylation. Other changes that have been recently reported in the literature include blending of TPS with protein, PVA, poly-caprolactone, poly-hydroxybutyrate, poly-methacrylate, polystyrene mostly in the presence of urea and polyol plasticizers.

### VI. PROPERTIES OF TPS AND FACTORS AFFECTING THEM

#### A. Storage

Samples containing high concentration of starch are stored below its  $T_g$  so as to increase its process to reach thermodynamic equilibrium and the chain mobility becomes more uniform as the glassy starch reaches a thermodynamic equilibrium.

#### B. Water Vapour Permeability(WVP)

Water vapour permeability (WVP) decreases with increase of glycerol content as unplasticized starches form brittle films with pore or cracks, which facilitates the water vapour permeation,[9,10] then, formation of pores or cracks are avoided on adding glycerol at a concentration of 20 g glycerol/100 g starch, forming a compact structure, resulting in a probable decrease in WVP values.

#### C. Effect of Temperature

As temperature increases, starch molecules vibrate more vigorously, thus breaking the intermolecular hydrogen bond and allowing penetration of water. As a result, there is more free water available to facilitate the movement of particles in suspension yielding low shear stress values. Activation energies and frequency factors varied at different shear rates.

#### D. Solubility in Water

Potential applications require water insolubility to enhance product integrity and water resistance. It has been found that film solubility decreases with the increase in alkaline treatment time before gelatinization. The amylose polymer is more flexible in alkaline solution than in neutral water. As

pH increases, a progressive increase in negative charge on the polymer molecule (due to enhanced ionization degree) is expected which results in an expansion of the amylose coil from charge repulsion [35].

#### E. Plasticizer effect on Moisture Control

As glycerol concentration is increased, a small drop on water sorption is first observed and a further increase produces water sorption to increase. At lower glycerol content, there is a competition between glycerol and water for hydrophilic sites on film surface. Glycerol present in film formulation reduces the amount of active sites available for water fixing and film moisture content declines. When glycerol content reaches 10–12% of starch, film moisture content increases. These results could be related to structural modifications of starch network produced by the plasticizer.

#### F. Plasticizer Effect on Film Thickness

Starch based films when plasticized with 40 %- 50% of the plasticizer were thicker than those plasticized with 30%. Moreover starches plasticized with glycerol were thicker than those with sorbitol. This can be explained as these plasticizers can penetrate the starch network at a faster rate as compared to others forming a thicker and stronger film than un-plasticized films as said by Galdeano et al. (2009).

#### G. Mechanical Properties

With the decrease in Young's modulus and tensile strength there is an increase of glycerol in the starch film. Direct interactions and proximity between starch chains reduce on the incorporation of plasticizer such glycerol in a starch network. According to Lourdin et al[15,16,17], the ratio of amylose to amylopectin determine the mechanical properties of starch films. On heating of starch granules in water, swelling takes place resulting in collapse and rupturing of the amylose and amylopectin. The ruptured amylopectin has low affinity towards interaction and gives weak, cohesive and flexible amylopectin films. While amylose being present in high solution have a higher tendency to interact with the hydrogen bonds forming stiffer and stronger gels [25,26,36].

#### H. Biodegradability

These materials are degraded into the environment over comparatively short periods of time. In addition, studies are undertaken using biodegradation enzymes which rapidly degrade the TPS by using  $\alpha$ -amylase. Amylose is partially resistant to attack by  $\alpha$ -amylase because of the residual starch in the material. The use of other types of enzymes that can accelerate the process of biodegradation requires further investigations.

### VII. INDIAN SCENARIO

The emergence of bioplastics in India is inchoate due to lower awareness levels in comparison to the European market, where bioplastic production is done commercially at large scale. Despite an increasing interest in the bioplastic industry of India, lack of environmental concern, price, and regulation are the key factors that are affecting its growth. A well regulated body responsible for carrying out research in this is needed since we cannot deny that this technology is the future.

## VIII. CONCLUSIONS

Bioplastics are obtained from Renewable plant resources hence give variety of options for deriving plastics. One metric ton of bio-plastics generates between 0.8 and 3.2 fewer metric tons of carbon dioxide and uses less energy than their conventional counter-parts [16]. Also it doesn't contain any harmful chemicals like bisphenol A, that some of the normal plastics do. So, we safely conclude that to a financial executive they are a means at cost savings and for savvy industrialists and mankind bioplastics is the future that should not be ignored.

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