

Preparation and Characterization of Dioscorea-Bulbifera Starch Based Bio Films as Edible Food Wraps with Natural pH Indicator

Dr.Litty Joseph¹, Teenamol Joseph²

^{1, 2} Kuriakose Elias College, Mannanam ,Kottayam, Kerala

Abstract- Plastic reverberates as a perfect packaging in this new age of moderation but often regarded as the pollutant because of its absolute lack of degradability. The use of a bio-degradable material based on natural polysaccharides, especially starch, helps minimise the use of non-degradables materials, and is an environmentally sustainable alternative to conventional petro-plastic polymers. An eco-friendly alternative to conventional petro-plastic polymer with a futuristic application as edible food wraps was investigated in our present work. In this study, the use of *Dioscorea-bulbifera* (air potato) for the production of biogel and bioplastic is explored. An eco-friendly alternative to conventional petro-plastic polymer with a futuristic application as edible food wraps was intended as the outcome. Bio films were prepared by conventional solution-casting technique. In this process, film forming solution is cast on a non-adhesive surface, and water or solvent is evaporated. Glycerol was used as plasticizers to investigate the effect of plasticizer on the developed films. TGA measurements were used to determine the thermal and oxidative stabilities of bioplastics as well as their compositional properties. The physical and thermal properties of the bio films were found to vary with the composition of starch, and glycerol in the sample. Addition of glycerol reduced the melting and glass transition temperatures of samples. Bio films from air potato starch were found to be high density plastic, with density greater than that of water. The results showed that air potato based biofilms have potential applications in the food packaging, medical and pharmaceutical industries.

Keywords- Air potato, plasticizer, bio films

I. INTRODUCTION

Plastics have become the key drivers of innovations and application development. In the packaging industry, wrapping goods, retail and garbage bags, fluid tubes, household clothing, toys, and consumer items, and building material, plastics have wide variety of applications. As a consequence, we see plastic nearly anywhere today. These

plastics make their way through the oceans and in the form of micro-plastics, they often contaminate our drinking water. We all know how plastic poses a serious environmental danger, causing damage to humans and the planet's wildlife. But somehow, we're using it. Green chemistry has been obsessed with the quest for sustainable and environmentally friendly energy for greater sustainability and eco-efficiency. As an alternative to conventional plastics, there has been a rising interest in the production of biodegradable plastics. The main distinction between regular plastic and biodegradable plastic is that, relative to conventional plastic, biodegradable plastic is environmentally friendly.

Bioplastics are classified as all plastics that are either biodegradable or biobased, or both, according to 'European Bioplastics'[1]. Bioplastics are plastics that are manufactured from natural materials (plants such as rice, tapioca, tomatoes, sugar and algae) and are entirely or partly bio-based and/or biodegradable or compostable. Starch is the most common among bio-based materials; it is available in bulk at a low cost in all parts of the world. Starch is one of the most promising of all the possible biopolymer materials[2], on the grounds of biodegradability, availability, renewability, non-toxicity and affordability. The use of starch allows a portion of a synthetic polymer to be substituted by a natural resource.

In cold water, the starch granules are insoluble. Starch granules swell when heated in excess water and the ordered arrangement is interrupted at the temperature level of gelatinization, resulting in an increase in viscosity. Biopolymer-prepared films are also too brittle to survive treatment, such as bending or stretching. They must then be plasticized using substances of low molecular weight that reduce the interactions between the biopolymer chains. By reducing strong intermolecular interactions between starch molecules, the ultimate function of plasticizers is to increase the stability and processability of starch[3]. As a consequence, the mobility of polymeric chains is increasing, enhancing the flexibility, elongation and ductility of the plastic films.

Packaging is a crucial entity in today's economy with a wide niche covering agricultural commodities. In this new age of modernization, plastic reverberates as the perfect packaging; the same also accounts for its absolute lack of degradability as the most feared environmental pollutant. The need for this hour is an alternative to this synthetic polymer that combines both durability and full degradation. This has led the research to investigate natural polymers; their abundance, affordability, non-toxic impact and simple degradation lead to the attractiveness and preference of the same as substitute packaging material. Active and intelligent packaging[4] is the next thing and improvement in the field of packaging, with the former providing an underlying function to provide the packaged goods with extra security, while the latter is interested in educating customers about the content of the packaged items. Among the advancements in smart packaging, color-changing packets are one of the most fascinating and one that makes consumers quick to determine the freshness of the same visually. Changes in temperature (thermo chromic materials), light irradiation (photochromic materials), the application of electrical potential (electro chromic materials) or changes in pH[5] may be the reason for this successful packaging while adjusting colour. With red cabbage extracts, an effort to create color-changing bio-plastic to provide a proof of concept that could lead to futuristic production of color-changing bio-wraps or bio-dips for edible products as a means of detecting spoilage was attempted here. The result was intended as an eco-friendly alternative to traditional petro-plastic polymers with a futuristic use as edible food wraps.

As the technology advances and population increases, plastic materials are widely used in daily life and in industries. Polymers outline the backbones of plastic materials and are repeatedly being employed in a mounting range of areas. It is a challenge before us to develop bio-degradable environment friendly materials essentially a polymer based on the natural resources and replaces the conventionally used polymers. As a result many researchers are investing time into modifying conventional materials to make them more user-friendly, and into designing original polymer composites out of physically occurring materials. A number of biological materials may be integrated into biodegradable polymer materials.

These industrial plastic products, such as polyethylene, poly-butylene, polystyrene, poly-vinyl chloride and polyethylene terephthalate, are very hazardous to the environment because they are non-bio-degradable. Biodegradable plastics have arisen as an alternative to conventional plastics in order to solve the issue of non-biodegradability. Biodegradable plastics are plastics synthesised using renewable materials that by means of

microbes, allow straight forward decomposition in the environment. Because of its suitability to be processed into thermoplastic materials and then to be used in various applications due to its proven biodegradability, availability and economic viability, the chemical and physical properties of starch have been extensively investigated[6]. The fundamental network structure of the film is created by biopolymers including starches and proteins. Films made from biopolymers, though, are often too delicate to survive treatment, such as bending or stretching. It is hydrophilic (water soluble) and cannot be processed by wet-based routes without being degraded [7]. It does not possess thermoplastic properties, despite the many benefits of starch, and should not be used specifically as a packaging material[8]. Furthermore, it has low dimensional stability and mechanical properties in its end products[9]. In several tests, native starch based materials are stated to be very brittle with many surface cracks and are hard to treat. These disadvantages can however be overcome by applying plasticizers to pure starch to maximise its functionality and eliminate film fragility[10]. It must then be combined with high-performance synthetic polymers such as polyvinyl alcohol. Several scholars have proposed the mixing or grafting of starch with synthetic polymers as an effective route for enhancing properties[11],[12],[13].

By reducing strong intermolecular interactions between starch molecules, the ultimate function of plasticizers is to increase the stability and processability of starch[14]. As a result, the mobility of polymeric chains is increasing and the flexibility, elongation and ductility of plasticized films are improving. In the contrary, film mechanical resistance is reduced by the addition of plasticizers. The form and concentration of plasticizer used has a considerable influence on the physical, thermal, mechanical and barrier properties of films[15]. Therefore, they have to be plasticized using low molecular weight compounds, such as polyols, which minimise interactions with the biopolymer chains. The bioplastic sheets without plasticizer are weak and fragile. Better handling properties may be obtained due to plasticization, whereas other properties may degrade, such as water sorption, gas permeability, and mechanical properties. Plasticizer decreases interactions between biopolymer chains, such as amylose and amylopectin, thus preventing their close packing which results in lower degree of crystallinity in the film. Pores and cracks in the film could be also prevented by using plasticizers [16].

The next thing and innovation in the field of packaging is active and smart packaging[5], with the former providing an intrinsic function to provide the packaged goods with additional security, while the latter is involved in informing customers about the quality of the packaged items.

Of the developments in smart packaging, color-changing packets are one of the most fascinating and one that makes consumers easy to determine the freshness of the same visually.

II. MATERIALS AND METHODS

Preparation of Bio plastic using air potato and Red cabbage extract

The basic ingredients for starch-based bioplastics are starch, plasticizer and water. Fresh *Dioscorea-bulbifera* were grated finely, soaked in distilled water, washed extensively and sieved and left for 2 hours for the starch molecules to settle. The supernatant was then decanted, leaving behind sediments which was dried in a laboratory oven at 50 °C for 5 hours. 250 gm of the red cabbage was sliced into small pieces and boiled in low heat for 15 min in 500ml distilled water. The extract was filtered. 15 g starch was mixed with 300 ml of red cabbage extract instead of distilled water in a glass vessel. The mixture was heated in a hot plate till the mixture started gelatinizing or melting. After achieving the gelatinization of starch about 5 ml glycerin as plasticizer was added and placed for 10 min in hot water bath following by layering the mixture. The layering was executed with thin layer plating. A control was also prepared using air potato starch and plasticizer.



Fig: 1 Starch powder

Fig: 2 Gelatinized starch

Fig: 3 Film castings

Film Preparation

The starch based films were prepared by conventional solution-casting technique. In this process, a film forming solution is cast on a non-adhesive surface. Water or solvent is evaporated from the solution in order to form the film. As a result of solvent evaporation, biopolymer increases with the result that hydrogen bonds are formed and basic film structure is created. The film forming solutions were left to cool down, prior to their casting in glass petri-dishes. The glass petri-dishes served as casting surfaces, enabling the film to have a smooth and flat surface. The fresh casted films were

placed in an oven (40°C) to allow evaporation. After 24 h of drying, films were peeled from the casting surfaces and stored in desiccators. The bioplastic thus prepared were cut into equal square slices and stored in desiccator for further analysis.

Measurement of Density

The densities of the samples were measured using the orifice can. A portion of sample A was cut and weighed using a digital weighing balance, the mass was recorded. The orifice can was filled with distilled water until the water starts flowing through the orifice. When the water stopped flowing, the weighed sample was dropped into the water in the orifice can and the water displaced was collected in a beaker whose mass has been measured. The mass of the beaker and the water displaced was also measured using a weighing balance. The mass of water displaced (upthrust) and the volume of water displaced was determined. The density of the sample was then determined by

$$\text{Density of sample} = \frac{\text{mass of sample in air}}{\text{volume of water displaced}}$$

Tests for Solubility in Solvents

10ml each of cold water, hot water, benzene solution and ethanol solution were added to 1g of sample in different test tubes, and allowed to stay for 24 hours. The degree of solubility of the sample in the solvents was recorded.

Determination of Melting Temperature

The melting temperatures of the samples were measured by using melting point apparatus. The apparatus has a melting point measuring range of 40 – 280 °C, and accuracy of + 0.5°C. A portion of sample A was crushed and filled in three thin-walled capillary melting point tubes. The capillary tubes were 120 mm long with about 1 mm inside diameter and sealed at one end. The capillary tubes with the densely packed sample were placed in the apparatus.

Effect of pH on bio-plastic with Red cabbage extract

Red cabbage extract comprise of anthocyanin, natural water soluble pH indicators that give reddish pink to violet colour in acidic conditions (pH 1-6) whereas in basic or alkaline condition (pH 8-14) colour change from blue to green and finally and to yellow at extreme alkaline condition[18]. In the current study the change in colour was observed in extreme acidic condition using con, HCl and alkaline conditions using 2M NaOH solution.

Thermo gravimetric analysis (TGA)

TGA was carried out on a TGA Q50 TA Instrument. An approximate 10–20 mg of the specimen was loaded in the open platinum pan. The samples were heated from 25 to 500°C under nitrogen atmosphere at constant heating rates of 10°C/min.

III. RESULT AND DISCUSSION

Solubility

Both were slightly soluble in cold water and highly soluble in hot water. This is due to the highly hydrophilic nature of starch. Hence, the samples will readily disintegrate when they come in contact with water. Samples were resistant to the organic solvents, and hence they can be used in handling such solvents.

Density

1.17 g/cm³, and, 1.248 g/cm³ are the measured densities of plasticized bio films with cabbage extract and without cabbage extract. Based on the fact that these plastics have densities greater than that of water (1.0 g/cm³). We can conclude that they are high density plastics.

Melting points

The melting temperature of plasticized samples is 86.9°C which is much lower than that of pure of sample 129°C hence, starch based sample will withstand higher service temperature than sample with glycerol.

Variation of colour at different Ph

The colour change observed here proved that the bioplastics coupled with these natural pH indicator has applicability. Normal colour of the synthesised biofilm with natural pH indicator was pale yellow, In acidic condition this biofilm becomes pink in colour where as in alkaline solution it becomes blue. This proves as a simple and smart method of signaling consumers the quality of the food that is dependent of pH change.

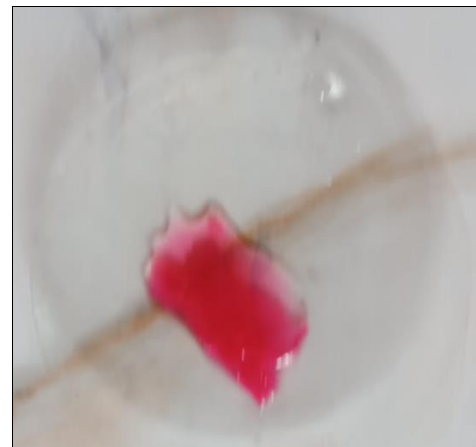


Fig:4 Bio films with indicator Fig:5 Colour of biofilm in acidic medium Fig: 6 Colour of biofilm in alkaline medium

TGA Analysis

Thermal-gravimetric analysis technique was utilized to determine the thermal decomposition and stability of plasticized films with indicator and without indicator. The results of the TGA curves were presented in Figure:6 in which the mass (mg) losses of film samples were plotted as a function of temperature (°C). As seen in the TGA curves, the

thermal decomposition of films occurred in three main steps.

The degradation of the film occurs in three stages of mass loss, the first between approximately 51.82 and 149.8 °C. The mass loss at this stage can be associated with the evaporation or dehydration of loosely bound water and low molecular weight compounds in the films [17]. The second mass loss, about 50%, occurs between 200.58 and 352.71 °C, while the third step occurs between 372.0 and 604.7 °C. TG curve of film with indicator shows an 11% mass loss in the range of 50.8–154.0 °C (water), while the second loss of mass happens between 250 °C and 322.°C and third between 400.5 and 697.0 °C. Comparing both TG curves, there is similarity in the mass loss of films. However, film with indicator has a higher mass loss at a lower temperature than film without indicator.

This behaviour can be explained due to the composition of film, which has incorporated red cabbage extract, indicating that the extract has a low thermal stability. Furthermore, the results indicate that both films have thermal stability until the temperature of 50 °C, thus having thermal stability to be safely applied in the food industry.

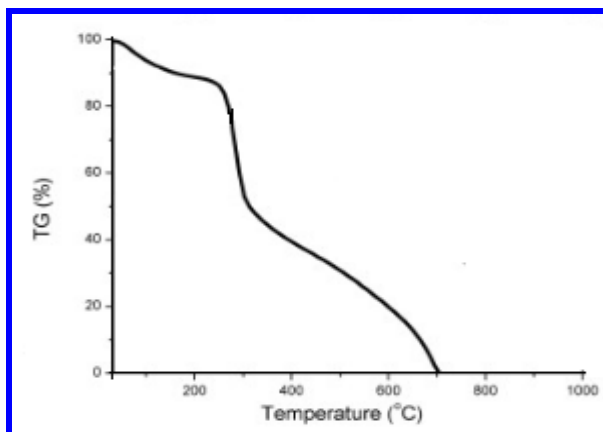
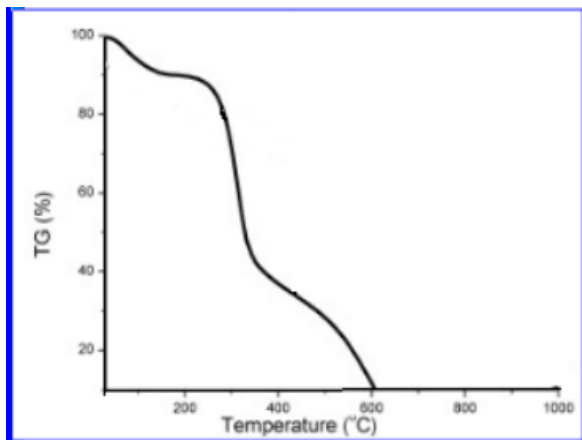


Fig: 7.a TGA curve of plasticized starch films Fig: 7.b TGA curve plasticized starch films with pH indicator

IV. CONCLUSION

It is a challenge before us to develop bio-degradable environment friendly materials essentially a polymer based on the natural resources and replaces the conventionally used polymers. Therefore the primary goal of this work was to synthesis a starch based film and to improve the film properties. Our work showed that bio films can be produced from natural air potato starch. The film was prepared by blending starch with, glycerol and water and then gelatinizing it. The physical and thermal properties of the bio films were found to vary with the composition of starch, and glycerol in the sample. The results show that a very sensitive visual pH indicator film based on renewable sources has been developed. The e film components do not react with each other and that the blend has good thermal stability. The indicator has good response to pH variations. Thus, it has potential to be used as a visual indicator of food deterioration. Future developments include the study of the film response in various temperatures, the study of extract stability in the film, as well as the study of the mechanical properties of the film. These should provide a clear picture on the real potential use of this system as part of a smart food packaging.

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