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BIOPLASTICS PRODUCTION & CHARACTERIZATION

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Abstract

Accumulation of plastics is an important problem faced by world today. 80-90% of plastics are made of petroleum fractions, which are non -degradable. In Dubai alone, 1 million tons of plastic waste was produced in 2017. Not only that the plastic pollution is invading our planet earth, but the supply of petroleum is diminishing with 30-40 years at most. Ergo, alternatives of Petro-based plastics are becoming a necessity. Another issue arising is the increase in food waste. It is estimated that waste food generated globally is equivalent to 1.3 billion tons per year. Bioplastics are plastics made from biomass and organic raw materials. Instead of using processed and refined starches, utilization of waste organic food to form PLA and biodegradable bioplastics. The project aims at producing biodegradable plastics from food waste. The agricultural and food waste from corn, rice and wheat are pulverized and fed along with water and various synthesis parameters to a batch reactor with stirrer and with provision of minimal heat, the resultant mixture is then molded and dried. The obtained product is a bioplastic ready to undergo characterization tests such as yield, heat resistivity, solubility, and most importantly the degradability test. The feasibility and validity of these bio-based plastics over the Petro-based plastics is achieved with the help of process optimization carried out in ASPEN PLUS. Furthermore, the derived bioplastics are biodegradable, renewable and sustainable.

Keywords: biodegradable; bioplastics; food waste; PLA; starch

1. INTRODUCTION

The plastic waste not only ends up in landfills, but also in rivers, lakes and ocean, creating health and environmental problems to the whole ecosystem. Its production also leads to increase in energy consumption and higher greenhouse gases emission with the release of hazardous chemicals [1]. Plastics made from bio-origins doesn't necessarily means they are degradable such as *Polycaprolactone*, however biodegradable bioplastics can be 100% biodegradable if they don't contain polyolefins as their main constituent. The bio-based plastics have two main advantages over their conventional versions; they save fossil fuels and use biomass that regenerate annually and provides the unique potential of carbon neutrality. Furthermore, they are biodegradable. the resources for bioplastics production are ecofriendly, sustainable and renewable and can reduce carbon dioxide emissions.

The chemistry behind this is that starches are polysaccharides means it is large branched polymers that consists of sugar molecules that when heated with an acid it gets hydrolyzed and the bonds between branches break, using certain plasticizers can make the stiff long linear chains of

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polysaccharides flexible and not brittle. Maintaining an optimum heating time and different synthesis parameters will yield strong, tear resistant, ecofriendly and biodegradable plastics.

In this study, edible starch-based bioplastics were developed from food and agricultural wastes that can be used as materials in food packaging as well as kids' toys. Castor oil was added to increase the moisture barrier property of the plastics. The research aims to examine and determine the effect of the various synthesis parameters and their variation on the different characteristics as well as the physiochemical and mechanical properties of bioplastics. The research also focuses on the biodegradability of the plastics in plantation soil. The degradation under aerobic conditions releases carbon dioxide. The carbon dioxide was measured by first trapping it in a sodium hydroxide solution and then performing titration methods.

2. MATERIALS & METHODOLOGY

2.1. Materials

The rice, corn and wheat starches were prepared from the agricultural and food waste. The collected rice, corn and wheat wastes were then washed, dried and pulverized until a fine starch was obtained. The various starch obtained was kept at room temperature. The plasticizer used is propan-1,2,3-triol also known as glycerin labelled as a food grade. The acids used for hydrolysis are acetic acid and hydrochloric acid. Distilled water was used to maintain a safe, toxins-free bioplastics. Sodium hydroxide was used as a neutralizer and the hydrophobic fluid used is castor oil.

2.2. Preparation of the Bioplastics

The corn, rice and wheat bioplastics were prepared by the same method, casting. 9.5g of starch was mixed with propan-1,2,3-triol (glycerol) and distilled water to obtain a gelatinous starch solution of 16% (w/w) of starch dispersion with glycerol solution concentration of 10%. Hydrochloric acid with a PH of 3 was used for hydrolysis of the gelatinous starch solution. However, acetic acid was also used in some as an option to produce edible bioplastics. Castor oil was then added to obtain 3% (w/w) into the solution as a hydrophobic fluid. Subsequently, the starch solution was then stirred continuously with provision of heat. The temperature was set between 60-70°C, and the hydrolysis process time was kept between 15-20 minutes. The obtained gelatinous mixture was neutralized by addition of sodium hydroxide. The neutralized mixture was then molded as 5mm wet thickness film in a petri dish and kept in an incubator at 40°C for 24 hours to dry completely. The film then was removed from the mold and cut into 3g pieces of uniform shape. The process was repeated further with all the different starches, and combinations of the three different starches was made by making 1:1 ratio of each; corn:rice, corn:wheat and rice:wheat starch mixtures were also prepared following the same procedure.

2.3. Variation of synthesis parameters

In some of the samples, sodium hydroxide was not added in the final step and the mixture was molded immediately. The plasticizer amount was also varied in some trials to obtain more flexible or harder bioplastics. The hydrophobic fluid was added to corn starch samples only to increase the moisture barrier; since corn starch is hydrophilic and has a low moisture barrier.

2.4. Characterization

2.4.1. Tensile test

Tensile strength was tested using force tester. The sample's weight taken before the test was 0.0294N. The sample was attached to the hook on one side and pulled slowly from the other side. The elongation of each sample was different based on the starch type as well as the combinations used. The breakpoint was noted, and the tensile force was obtained for various samples.

2.4.2. Heat resistance test

One of the major drawbacks in bioplastics is its brittleness and low heat resistivity. To test the thermal resistivity and its profile of the bioplastics produced, the samples were kept in a closed water bath and heated from 10 to 110°C. Simultaneously, it was incubated to check the thermal profile of the bioplastics made under standard conditions and room temperature (50°C). The melting temperature, Tm was observed.

2.4.3. Solubility test

The water absorption was determined following ASTM D 570-98 and ISO 62 plastics standards [2]. The bioplastics made weights were taking as 0.3g each. Each sample was then immersed water. The immersion time set was 2 hours. The samples were then withdrawn, wiped off the excess solution and weighed. The percentage increase in weight during immersion was calculated as:

$$\text{increase in weight}(\%) = \frac{\text{wet weight} - \text{conditioned weight}}{\text{conditioned weight}} \times 100$$

Where, conditioned weight is the weight is the weight taken prior to immersion.

2.5. Biodegradability test

Degradation and biodegradation are two different terms. As defined by ASTM and ISO terminology, degradable plastic is a plastic designed to undergo a significant change in its chemical structure under specific environmental conditions resulting in a loss of some properties that may vary as measured by standard test methods appropriate to the plastic and the application in a period of time that determines its classification, whereas biodegradable plastic is a degradable plastic in which the degradation results from the action of naturally-occurring microorganisms such as bacteria, fungi, and algae [3].

The biodegradation test was determined according to ASTM D 5988-03 [4]. The inoculum used is plantation soil. The inoculum was collected from the topsoil 4-7 cm deep. 1g of compost was added to the soil. 50g of the prepped soil was kept in a 200ml incubated glass jar, with 0.3g of the bioplastics made buried deep in the soil, each sample in a different experiment setup. Subsequently, it was connected by a tube to another 200ml incubated glass jar containing 20ml of 0.1N sodium hydroxide.

The test was carried out for 30 days and maintained at room temperature (40-50°C). A sample of HDPE plastic was used as a reference.

2.5.1 Carbon dioxide analysis

A blank test was performed to calculate the evolved carbon dioxide, further trapped in the sodium hydroxide solution. The sodium hydroxide mixture was titrated every 3 days against 0.1N hydrochloric acid. Phenolphthalein indicator was used. The amount of carbon dioxide evolved during the biodegradation process, is equivalent to the amount of hydrochloric acid needed to neutralize the solution into pink color.

The reaction of carbon dioxide with sodium hydroxide:

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O$$

Titration reaction:

$$Na_2CO_3 + 2HCL \rightarrow 2NaCl + H_2CO_3 \rightarrow 2NaCl + H_2O + CO_2$$

The carbon dioxide evolved was calculated using theoretical carbon dioxide formula:

$$ThCO_2 = C_t \times \frac{12}{44}$$

Where, C_t is the total carbon content of the sample.

The biodegradation rate was calculated, by derived formula of the mineralization of the test samples:

$$D_t(\%) = \frac{CO_{2(T)} - CO_{2(B)}}{ThCO_2} \times 100$$

Where, D_t is the biodegradation rate expressed in percentage, $CO_{2(T)}$ is the total carbon dioxide released from the soil with bioplastics present and $CO_{2(B)}$ is the carbon dioxide released from blank test without presence of bioplastics.

2.6. Process optimization

To obtain maximum yield of the bioplastic product, the process was simulated in Aspen Plus polymers. The reactor used for the process was a batch reactor with a stirring mechanism. A mixer was used in the beginning to ensure uniform distribution of the materials. The obtained product was passed through an air dryer to remove excess water. The final product was a starch-based plastic (PLA). Excess water was released in the form of water vapor.

3. RESULT & DISCUSSION

3.1. Mechanical properties

The tensile strength for the produced bioplastics films is shown in Table.1. The bioplastics made from rice, corn and wheat looked almost similar, they were transparent, however, wheat starch showed a high flexibility and maintained a uniform shape and thickness throughout the drying process. Whereas, the rice starch showed some rigidity and brittleness comparatively. When mixing the rice starch with either corn starch or wheat starch, it increased the strength of the bioplastics, and reduced its flexibility. It also caused the bioplastics to break faster during the tensile test. The wheat and corn starch combination didn't yield a very flexible bioplastic either. The corn starch bioplastic was the most flexible of all, which showed a tensile strength of 3920 KPa.

Table.1. Tensile strength of the produced bioplastics films

	Corn bioplastic	Rice bioplastic	Wheat bioplastic	Corn-rice bioplastic	Corn-wheat bioplastic	Rice-wheat bioplastic
Tensile strength (KPa)	3920	3100	3240	3401	3530	3153

3.2. Thermal properties

The thermal profile of bioplastics obtained is shown in Table.2. All the bioplastics showed high temperature profiles. The bioplastics showed no change in properties or appearance at room temperature (50°C), even after an incubation period of 5 days. The addition of rice starch to corn starch or wheat starch, increased the heat resistivity of the bioplastic. The rice starch bioplastic had the highest melting point of 110°C.

Table.2. Melting points of the produced bioplastics films

	Corn bioplastic	Rice bioplastic	Wheat bioplastic	Corn-rice bioplastic	Corn-wheat bioplastic	Rice-wheat bioplastic
Melting point, Tm (ºC)	97	110	100	103	97.3	106.7

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3.3. Waster absorption capacity

The starch-based bioplastics main drawback is its low moisture barrier. To overcome this problem, a hydrophobic fluid, castor oil, was added to the mixture to increase the moisture barrier. The samples prepared without any addition of hydrophobic fluid (corn-bioplastic A), resulted in an increase in water absorption, and swelled faster than the ones containing hydrophobic fluid (corn-bioplastic B). The addition of hydrophobic fluid to the bioplastic increased the water barrier significantly, which depreciated the water absorption percentage from 26.7% for bioplastic without addition of hydrophobic fluid to 10.4% only with the addition of hydrophobic fluid. The water absorption and percentage increase in weight during immersion are illustrated in Table.3. The rice-based bioplastic had the highest water absorption percentage of 39.2%.

Table.3. Water absorption of the produced bioplastics films

	Corn bioplastic A	Corn bioplastic B	Rice bioplastic	Wheat bioplastic	Corn-rice bioplastic	Corn-wheat bioplastic	Rice-wheat bioplastic
Water absorption (%)	26.7	10.4	39.2	27.6	30	39	28.9

3.4. Biodegradation rate

The biodegradation in plantation soil by microorganism was done aerobically by maintaining a degree of moisture in the soil [4]. The bio-degradation of starch-based bioplastics releases carbon dioxide, water and heat. The evolved carbon dioxide levels shown in Figure.1. varying from time to time for the various bioplastics produced. The blank test was done with no bio-mass involved. The carbon dioxide released off in the blank test was very low, with highest amount of 0.13mg. The carbon dioxide released from HDPE plastics was similar to the blank test. After the addition of the bioplastics to the soil, the carbon dioxide released from the bioplastics was increasing in the first week, with highest levels of 4.87mg for wheat and corn-based bioplastics. All the bioplastics including the corn-based bioplastic with hydrophobic fluid (corn-bioplastic B), had similar levels of carbon evolution. After 14 days, the released carbon dioxide levels started decreasing below 3g, and continued to decline below 2g. Furthermore, the evolved carbon dioxide showed stable levels by the end of the test.

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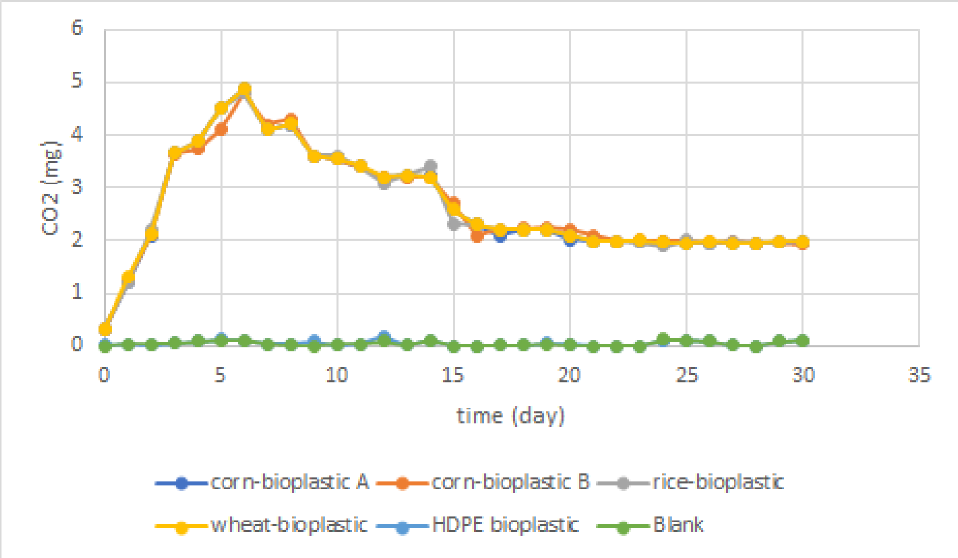

Fig. 1. Carbon dioxide released during biodegradation test.
[Corn-bioplastics A is corn starch-based bioplastics without addition of hydrophobic fluid. Corn-bioplastic B is corn starch-based bioplastics with the addition of hydrophobic fluid]

While performing the biodegradation test, almost same levels of carbon dioxide were evolved for all the starch-based bioplastics. And the biodegradation curves for rice, wheat and corn bioplastics showed a negligible difference. Therefore, for a neat illustration, the biodegradation curve for corn starch-based bioplastic was taken as a representation for the other bioplastics. To test the influence of the hydrophobic fluid addition on bioplastics, biodegradation percentage of corn starch-based bioplastics samples is illustrated in the Figure.2. Biodegradation pattern for corn bioplastic A and corn bioplastic B were similar in the first 10 days of the evaluation test, with only 3.6% and 3.7% for corn bioplastic A and corn bioplastic B respectively. The biodegradation rate was meager, with slight increase every day. Only 12.6% of the bioplastic sample without the addition of hydrophobic fluid was biodegraded after 30 days. The addition of hydrophobic fluid to the starch-based bioplastic, increased its moisture barrier, which resulted in lower biodegradation rate of 9.3% in 30 days.

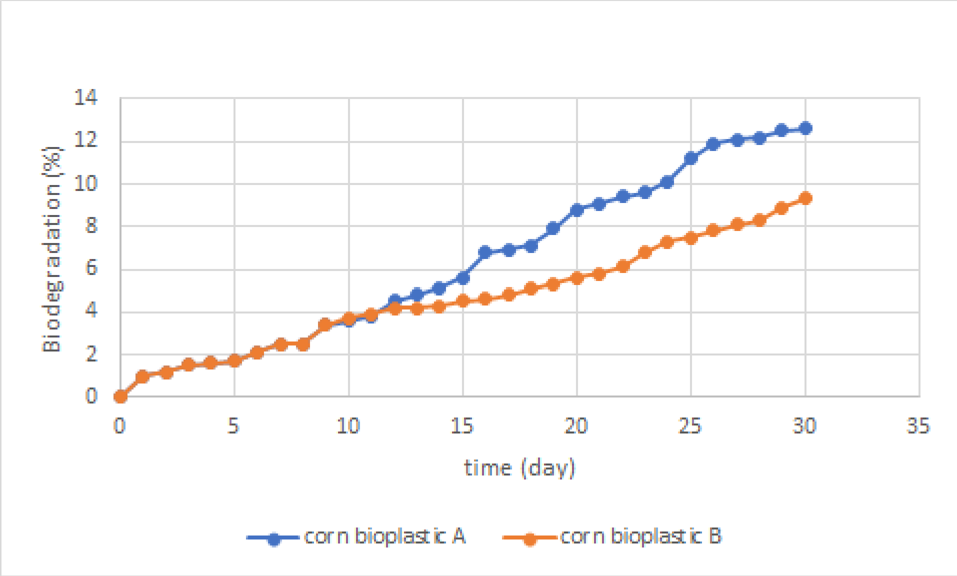

Fig. 2. Biodegradation curves of bioplastics.
[Corn bioplastic A, a corn starch-based bioplastic without addition of hydrophobic fluid. Corn bioplastic B, a corn starch-based bioplastic with the addition of hydrophobic fluid]

3.5. Process optimization parameters

The production process of starch-based bioplastics, which also commonly known as polylactic acid (PLA) plastics, was simulated in Aspen Plus in a batch reactor. The reactants were introduced first in the mixer at a flowrate of 100g/min, to obtain a homogenous mixture. The homogenous mixture was then poured into a batch reactor with a stirring mechanism (Hydrolyzer) for hydrolysis of the starch for 1 hour at 70°C. The hydrolyzed solution was transferred to another batch reactor where sodium hydroxide was introduced to neutralizer the solution. The neutralized solution is then kept in an air drier at 50°C to remove excess water. The final product obtained is a PLA film. The yield of the product was found to be 70%. To increase the product yield to 90%, the input water flowrate was minimized, and the hydrolysis time was set to 50 minutes only.

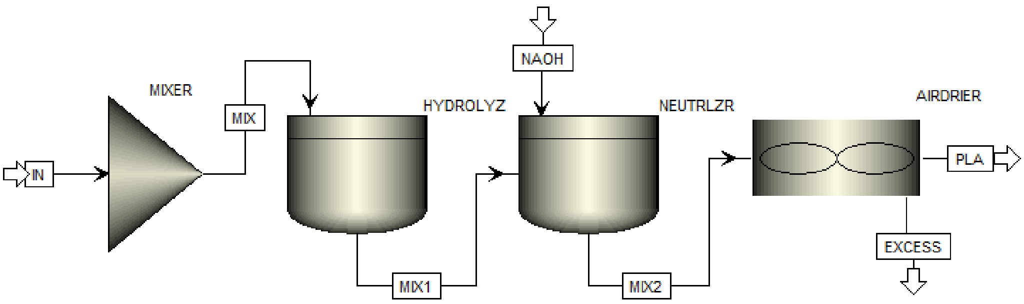

Fig.3. Flowsheet of Aspen Plus simulation for starch-based bioplastics (PLA) batch process

CONCLUSION

Throughout various characteristics tests performed, the starch-based bioplastics are a feasible alternative material to conventional plastics in food packaging and kids' toys. It projects no harm on the environment or the people and is a safer alternative to the conventional plastics. With the addition of any other bio-materials, its properties can be enhanced and remain its biodegradability. The starch-based bioplastics are biodegradable at room temperatures and by indigenous microorganisms. However, the biodegradation rate of the bioplastics may be increased by supplying other microorganisms. Utilizing bio-waste, such as food waste and agricultural waste to produce bioplastics, doesn't only result in reduction of waste, but also reduces production costs.

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