

PRODUCTION AND CHARACTERIZATION OF RICE STARCH AND CORN STARCH BASED BIODEGRADABLE BIOPLASTIC USING VARIOUS PLASTICIZERS AND NATURAL REINFORCING FILLERS

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The present study focuses on testing the potential of starch from two different sources: corn and rice, to produce bioplastics, and the impact of natural agricultural waste materials (eggshells and rice hulls) as fillers. Bioplastic samples with different starches, plasticizers and amounts of fillers, in varying combinations, were prepared to determine the feasibility of the produced bioplastics. The physico-chemical properties of the bioplastics, such as moisture content, water absorption, water and alcohol solubility, biodegradability, tensile strength and Young's modulus, were investigated. FT-IR analysis was also performed. The RTV silicone coating of the samples was tested to induce hydrophobic properties to water-soluble bioplastics. This study demonstrated that the utilization of starches from different sources, various types of plasticizers, as well as filler types and amounts, can have a significant impact on the physico-chemical properties of the bioplastics. Moreover, the bioplastics produced are safe for the environment and biodegradable, so starch-based bioplastics can be a promising environmentally friendly alternative to harmful petroleum-based plastics.

Keywords: corn, rice, starch, bioplastic, biodegradable, polymer, environment

INTRODUCTION

Plastics undoubtedly play a very important role in the daily life of us humans, and we have become dependent on them. Plastics have strength, light weight and long life, and these positive aspects allow them to find a plethora of applications in almost every industry. Plastics have even left paper and glass behind in packaging applications.¹ Plastics, such as PVC, PET and polyester *etc.*, are synthetic macromolecular substances that are usually made from petroleum.^{2,3} Plastics have many advantages, but being unable to biodegrade in nature, they jeopardise our environment, as the accumulation of highly persistent plastic waste is polluting our water and land resources.⁴ Petroleum-based plastics are not only non-biodegradable, but are also sometimes toxic because of the existence of some toxic chemicals in them.⁵ Annually, around 150 million tons of plastic waste is generated around the globe.⁶ Thus, what our world needs now is an efficient and environment-friendly alternative to conventional plastics, such as bioplastics.

Bioplastics are substances that are produced mostly from biomass materials, such as proteins, lipids and polysaccharides.⁷⁻⁹ These materials that are synthesized using renewable organic resources have been proven as good substitutes for petroleum-based plastics and will likely reduce our reliance on fossil fuels, as well as the quantity of plastic waste being produced.¹⁰ Bioplastics have the potential to solve the issue of ever-increasing plastic waste in our world, as they are biodegradable¹¹ and can find applications in various fields, such as agriculture, pharmaceuticals, packaging, and opto-electronic technology *etc.*¹² Renewable bioplastics are overall an efficient answer to the multiple problems associated with petroleum-based plastics.¹³

Polysaccharides are one of the most commonly used materials to synthesize biodegradable plastic films and they have found applications in many industries, including the food industry, medicine *etc.*¹⁴ Bioplastics produced from polysaccharides are environmentally friendly and boast qualities like good mechanical properties and resistivity and stoppage of O₂ and CO₂ gases at average or low humidity.^{15,16} Starch is the most plentiful polysaccharide in flora. Starch is a major component of

various plants, such as corn and wheat, containing 82% and 8%, starch, respectively.¹⁷ Starch is also abundant in rice.¹⁸ Starch is considered one of the best natural polymers due to its abundance, renewability, cost-effectiveness and biodegradability.¹⁹⁻²¹ However, starch biopolymers are dissolvable in water and have low mechanical strength, which has proved to be a major negative aspect. Researchers have attempted various methods to enhance the properties of starch biopolymers, such as using reinforcing fillers.^{21,22}

Many different types of materials, natural, synthetic, organic and inorganic, can be used as reinforcing fillers, such as talc, glass fibers,²³ corn waste lignocellulosic fibre,²⁴ cocoa pod husk,²⁵ eggshells,²⁶ rice husk²⁷ etc. Agricultural waste is a common type of waste produced in huge quantities, such as sugarcane bagasse and rice husk etc. Rice husk is an agricultural waste²⁸ that is produced in huge amounts in countries where rice is grown. These agricultural waste materials can be powdered into fine or coarse particles²⁹ and used as fillers, reducing the problems associated with the disposal of agricultural residues. The food manufacturing industry is another great source of waste products that can be utilised as fillers. Chicken eggshells are produced in huge amounts around the globe,³⁰ the food manufacturing industry being a common source.³¹ Disposing eggshell waste is a complicated task, as it can attract vermin.³² Thus, finding a use for waste eggshells can decrease the problem of their disposal and can help achieve sustainable development.^{33,31} Local restaurants and bakeries, as well as the food manufacturing industry, such as biscuit and bakery factories produce waste eggshells in huge quantities and are thus a good source to obtain this residue.

Starch is a carbohydrate with the chemical formula $(C_6H_{10}O_5)_n$. Pure starch is a tasteless and odourless white coloured powder, which is not soluble in cold water.³⁴ It is composed of two polysaccharides: (i) amylose, which is a linear polymer, and (ii) amylopectin, which is a highly branched polymer.³⁵ Plants store their food in the form of starch. Starch can be commercially extracted from different grains and tubers.³⁶ The characteristics of starch-based bioplastics strongly depend on starch microstructure, such as amylose/amylopectin ratio. The percentage of amylose and amylopectin present in regular corn starch is around 26% and 74%, respectively,³⁷ while the percentage of amylose and amylopectin present in basmati rice is around 20-25% and 75-80% respectively.³⁸

Glycerol is a simple polyol with the chemical formula $C_3H_8O_3$. Its IUPAC ID is propane-1,2,3-triol. It is a commonly available, inexpensive, environmentally friendly, non-toxic, colourless and odourless viscous liquid. Sorbitol is a sugar alcohol with the chemical formula $C_6H_{14}O_6$. Acetic acid is an organic compound with the chemical formula CH_3COOH . Acetic acid was used in this process due to the fact that its combination with glycerol results in the production of cellulose acetate, which ameliorates the produced bioplastics' compressive strength.³⁹ Acetic acid can be used as a starch esterification reagent, thus starch reacts with acetic acid to produce starch acetates. When starch and acetic acid react, the acetyl groups replace some of the hydroxyl groups on the anhydro-glucose units, resulting in the formation of starch acetates (esters). The extent of these acetyl groups replacements depends upon many factors, including the concentration of acetic acid.⁴⁰ Chemical modification through acetylation also enhances matrix reinforcement and adhesion of the bioplastic composites.⁴¹ According to Nandiyanto *et al.*,⁴² acetic acid also acts as a catalyst during starch-glycerol bonding, as it helps release OH groups during this bioplastics formation process.

Fillers are added into bioplastics to improve some of their mechanical properties.⁴³ Rice hull is composed of 28-30% inorganic and 70-72% organic compounds.⁴⁴ The major inorganic component is silica (SiO_2), while the major organic components are carbon (C), hydrogen (H), oxygen (O) and nitrogen (N), in amounts of 39.8-41.1, 5.7-6.1, 0.5-0.6 and 36.6-37.4 percent by weight, respectively.⁴⁵ Eggshells are composed of 96% calcium carbonate ($CaCO_3$) by weight, which is an amorphous crystal.⁴⁶ Other than $CaCO_3$, eggshells also contain small amounts of magnesium carbonate ($MgCO_3$), calcium phosphate ($Ca_3(PO_4)_2$), organic components and water.⁴⁷

The past few years have seen advancements in the development of biodegradable materials based on agricultural resources.⁴⁸ Starch, a natural carbohydrate polymer, has noticeably been the most researched upon and promising raw material for producing bioplastics.⁴⁹ One downside of plastics made from starch is that they are brittle, thus the addition of plasticizers while producing them is a common practice. It ensures the plastic produced will not be brittle, but quite strong and flexible, and not easily breakable.^{50,51} Glycerol and sorbitol are two commonly used plasticisers when it comes to producing bioplastics.^{52,53} To further improve the physical and mechanical properties of the biodegradable plastics made from starch, many scientists have experimented with the use of fillers as

reinforcement. Adding a filler to a biodegradable plastic has been observed to ameliorate its tensile strength and Young's modulus.^{54,55}

The present study was focused on the production of biodegradable bioplastics based on starch from two different natural sources, corn starch and rice starch, and improving their mechanical and physical properties by using waste materials as reinforcement fillers, as well as glycerol and sorbitol separately and in combination (1:1) as plasticizers, followed by their characterization and comparison. RTV silicone coating of bioplastic sample was also experimented, in order to test its effect on the water solubility and biodegradability of the sample. According to the best of the authors' knowledge, this is the first report in Pakistan on the use of different proportions of rice and corn starch, separately, along with glycerol and sorbitol plasticizers, as well as rice hulls and eggshells as natural fillers, for manufacturing bioplastics. It is also the first study in Pakistan that explores the use of RTV silicone as a hydrophobic coating for bioplastics. In addition, rice starch and corn starch sources are cheap and abundantly available options to produce bioplastics in Pakistan.

EXPERIMENTAL

Starch from two different natural sources – rice and corn – was used, and was obtained locally. Natural waste materials to be used as reinforcing fillers, such as rice hulls and eggshells, were also obtained from local sources. Corn starch and rice starch were used to prepare twelve different samples of bioplastics (CS-1–CS-12 for corn starch and RS-1–RS-12 for rice starch), each with a variety of combinations of plasticizers and eggshell powder or rice husk as a filler, respectively. The samples (CS-1 and RS-1) without plasticizers or filler were used as control (Table 1).

Chemicals

All the chemical reagents used in the present study, such as glacial acetic acid (Merck), glycerol (Merck), sorbitol (Merck), ethanol (Merck) and RTV silicone (GMSA), were of analytical grade.

Preparation of 5% acetic acid solution

Glacial acetic acid was used to prepare a 5% acetic acid solution. Precisely measured 5 mL of glacial acetic acid was slowly added into 95 mL of distilled water and mixed thoroughly to get a 5% dilute solution of acetic acid.

Table 1
Composition of bioplastics based on starch, glycerol, sorbitol and filler

Bioplastic sample No.	Starch (mL)	Acetic acid (5%) (mL)	Glycerol (mL)	Sorbitol (g)	Filler (g)
1	40	5	-	-	-
2	40	5	5	-	-
3	40	5	-	5	-
4	40	5	2.5	2.5	-
5	38	5	-	-	2
6	38	5	5	-	2
7	38	5	-	5	2
8	38	5	2.5	2.5	2
9	36	5	-	-	4
10	36	5	5	-	4
11	36	5	-	5	4
12	36	5	2.5	2.5	4

Pretreatment of reinforcing fillers

Following the modified methods of Darni *et al.*⁵⁶ and Yaacab *et al.*,⁵⁷ reinforcing fillers were prepared to be used in starch-based bioplastic production.

Eggshells: Waste eggshells of chicken eggs were obtained from a local bakery in Lahore. The thin shell membrane of the eggshells was removed from the inside and they were thoroughly rinsed. The eggshells were then broken down into smaller pieces and left to dry in an oven at 85 °C for 5 hours. The dried eggshells were then converted into a fine powder using a blender. The powder was then sieved using a sieve of size 63 µm.

Rice hulls: Rice hulls were obtained from a local rice mill in Lahore. They were then dried in an oven at 85 °C for 5 hours. The dried rice hulls were then converted into a fine powder using a blender. The powder was then sieved using a sieve of size 63 µm.

Production of bioplastics

Corn starch bioplastic

Corn starch bioplastic was produced by combining and modifying the procedures of Sujuthi and Liew,⁵⁸ and Patel *et al.*⁵⁹

A 20% w/v corn starch solution was prepared by dissolving 8.0 g of powder corn starch (without any pretreatment) in a suitable amount of distilled water and diluted with solvent to a total solution volume of exactly 40 mL in order to get the desired concentration of 20% w/v.

The main ingredients for starch based bioplastics are the starch solution, 5% acetic acid, and a plasticizer. Four variants of bioplastics were produced from the starch solution, three using various plasticizers (glycerol, sorbitol and their combination in 1:1 ratio) and one without any plasticizer – which was used as control, to explore the effects of each on the bioplastics produced. Each of these variants was then prepared with the addition eggshell powder as reinforcement filler in the ratio of 0:100, 5:95 or 10:90 (% w/v) of the starch solution, to further investigate the effects of eggshell powder as a reinforcement filler in corn starch bioplastic. A total of 12 variants of corn starch bioplastics (CS20-1–CS20-12) were produced from the starch solution. For the preparation of each of these, 5 mL of 5% acetic acid and 5 mL/5 g of plasticizer were kept constant, while the amount of starch solution and reinforcement filler was varied: 40:0, 38:2 and 36:4 mL to grams, based on their respective w/v percentages as established before.

The general procedure for the production of corn starch bioplastic was the following: the corn starch solution was measured and transferred into a 100 mL beaker, followed by the addition of 5% acetic acid, plasticizer and reinforcement filler. The mixture was then stirred properly using a glass stirring rod and heated on a hot plate at 220 °C for 15 minutes with continuous stirring till the corn starch solution became a thick paste. The bioplastic mixture was spread onto a glass Petri dish, which was priorly lined with aluminum foil to aid easy removal of the bioplastic after drying. The mixture was allowed to dry at room temperature for 24 hours until it no longer stuck to the surface and was then placed in the oven at 85 °C for 2 hours. The bioplastic sheet produced was then allowed to cool at room temperature, after which it was removed and placed into a zip lock bag for further characterization.

Rice starch bioplastic

Rice starch bioplastic was produced by combining and modifying the procedures of El-Naggar and Farag⁶⁰ and Sultan and Johari.⁶¹

Rice was boiled for 30 minutes in water. The rice was strained and the starchy supernatant was separated. The starchy supernatant was then heated on a hot plate at 220 °C with frequent stirring till its volume reduced by 50%.

The main ingredients for the starch based bioplastics are starch solution, 5% acetic acid, and plasticizer. Four variants of bioplastics were produced, three using varying plasticizers (glycerol, sorbitol and their combination in a 1:1 ratio) and one without any plasticizer, which was used as control, to explore the effects of each on the bioplastics produced. Each of these variants were then prepared with the addition of rice hulls powder as a reinforcement filler in ratios of 0:100, 5:95 and 10:90 (% w/v) of the starch solution, to further investigate the effects of the rice hulls powder as a reinforcement filler in corn starch bioplastic. A total of 12 variants of rice starch bioplastic were produced (RS1–RS12), following exactly the same procedure as described above for corn starch bioplastic production.

Analysis and characterization

Moisture content

The moisture content was determined by using the method adopted from Sanyang *et al.*⁶² with modifications. Bioplastic samples were cut into 1.5 x 1.5 cm² pieces, followed by determining their initial weight (W_i) and then drying them in the oven at 90 °C for 24 hours. The dried samples were again weighed to find their final weight (W_f) and the moisture content was calculated using the following equation:

$$\text{Moisture Content (\%)} = \frac{W_i - W_f}{W_i} \times 100 \quad (1)$$

Water absorption

The water absorption of the bioplastics was determined using the ASTM D570-98 method with modifications. Bioplastic samples with a dimension of 1.5 x 1.5 cm² were dried in an oven at 90 °C for 24 hours and then gravimetrically determined using an electronic weighing balance to find their initial dry weight (W_i). The samples were then placed in 40 mL of distilled water and kept at the temperature of 26 ± 2 °C for 24 hours. After 24 hours, the residual bioplastic was harvested by filtration using a filter paper and was again gravimetrically determined to find the final weight (W_f). Water absorption was determined using the equation given below:

$$\text{Water Absorption (\%)} = \frac{W_f - W_i}{W_i} \times 100 \quad (2)$$

Water solubility

The water solubility behaviour of the bioplastic samples was determined by employing the method reported by Sanyang *et al.*⁶² Samples with a dimension of 1.5 x 1.5 cm² were dried in an oven at 90 °C for 24 hours and then gravimetrically determined using an electronic weighing balance to find their initial weight (W_i). The samples were then placed in 40 mL of distilled water in beakers, which were sealed and kept at the temperature of 26 ± 2 °C for 24 hours. After 24 hours, the residual bioplastics were harvested by filtration using a filter paper and allowed to dry in an oven at 90 °C for 24 hours, followed by gravimetric determination to find their final weight (W_f). The solubility of the bioplastic samples was calculated using the following equation:

$$\text{Water Solubility (\%)} = \frac{(W_i - W_f)}{W_i} \times 100 \quad (3)$$

Alcohol solubility

Alcohol solubility was determined using exactly the same method as water solubility,⁶² the only difference being that the samples were placed in 2 mL of ethanol in capped test tubes, instead of water. The solubility of the bioplastic samples was calculated using the following equation:

$$\text{Alcohol Solubility (\%)} = \frac{(W_i - W_f)}{W_i} \times 100 \quad (4)$$

Soil burial biodegradability test

The biodegradability of the samples was determined using the method reported by Tan *et al.*⁶³ with modifications. Soil was obtained from the garden and 50 g of soil was weighed and placed into a Styrofoam cup. All bioplastic samples were cut into 1.5 x 1.5 cm² pieces and gravimetrically determined to find their initial weight (W_i). These samples were then buried under 10 cm of moist soil sealed and kept at 25 ± 2 °C for 5 days. After 5 days, the residual samples were recovered from the soil, washed with distilled water and then allowed to dry in an oven at 90 °C for 24 hours, followed by another gravimetric determination to find their final weight (W_f). The percentage weight loss, that is, the biodegradability of the bioplastics, was determined using the equation given below:

$$\text{Weight loss (\%)} = \frac{W_i - W_f}{W_i} \times 100 \quad (5)$$

Fourier transform infrared spectroscopy (FT-IR)

A Fourier Transform Infrared Spectrophotometer (FT-IR) (IRTracer-100, Shimadzu) was employed to determine the chemical structure, *i.e.* the functional groups of the bioplastic samples. The wavenumber range was from 4000 to 650 cm⁻¹ and the resolution 2 cm⁻¹.

Mechanical properties

Tensile strength and Young's modulus were determined by using a Universal testing machine (Lloyd Instruments LF Plus) according to a modified ASTM D882-91 method. The specimens were cut into 80 mm long and 15 mm wide rectangular strips using a pair of scissors. The crosshead speed was set at 10 mm/min, while the gauge was kept 40 mm in length and 15 mm in width. The tensile strength value and Young's modulus of the samples were obtained from the instrumental data.

Hydrophobic coating

To impart hydrophobic properties to the water soluble bioplastics, 100% RTV silicone sealant was used. A thin layer of silicone (approximately 1 mm thick) was coated onto the entire bioplastic sample using a brush and allowed to dry completely for 24 hours. The biodegradability, water solubility and alcohol solubility of these coated bioplastics were determined using the aforementioned methods.

RESULTS AND DISCUSSION

Optimization of production conditions

Effect of plasticizer on bioplastic production

A varied range of plasticizer amounts was used to find the optimum one (3 mL, 5 mL, 7 mL, 10 mL, and 12 mL). It was found that the optimum plasticizer amount was 5 mL, as bioplastics produced from corn and rice starch with 3 mL plasticizer were brittle and inflexible, while those produced with 7 mL, 10 mL, 12 mL were moist and sticky. Thus, the plasticizer amount of 5 mL proved best for bioplastics synthesis (Figs. 2 and 4).

Similar tests with different plasticizer amounts were also carried out by Seixas *et al.*,⁶⁴ who experimented with glycerol 5, 7 and 10% v/v, as well as by Chinnan and Park,⁶⁵ who experimented with plasticizer levels of 0, 0.11, 0.22 and 0.33 mL PEG/g cellulose. Similar results were reported by Sanyang *et al.*,⁶² namely that with an increasing amount of plasticizer, the flexibility and stickiness of the bioplastic also increases, due to the smaller molecular size of the plasticizer, which allows them to easily move between the intermolecular voids of polymer chains, making the intermolecular hydrogen bonds less strong and thus as a resulting in better molecular mobility.

Effect of filler on bioplastic production

A varied range of filler amount (% w/v) was used to optimize it (5%, 10%, 15%, 20%, and 25%). During the present study, it was found that the optimum filler amounts were between 5% and 10%, as the bioplastics produced with higher amounts of filler (15%, 20% and 25%) were rough in texture, with cracks and easily breakable, which crumbled upon handling (Figs. 1 and 3). The filler amount in the range of 5% and 10% has provided better results in the production of bioplastics from corn and rice starch.

High filler amounts cause deterioration in the intermolecular interaction of the starch bioplastic. This may result in the formation of a heterogeneous bioplastic structure and disruptions.⁶⁶ The results of a study by Saurabh *et al.*⁶⁷ also showed that adding filler up to 10% enhances the characteristics of nano-composites, however any further increase in the amount of the filler resulted in deterioration in strength and the appearance of cracks in the films.

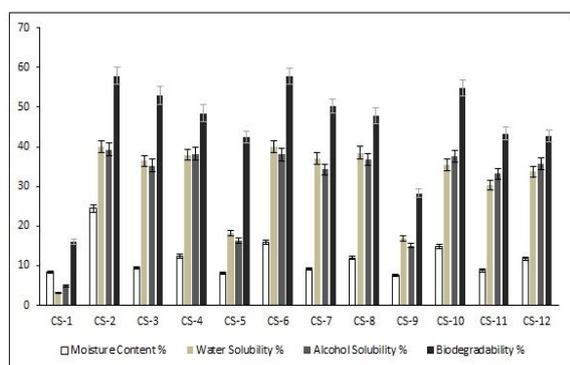


Figure 1: Effect of filler amount on the physical properties of corn starch bioplastics

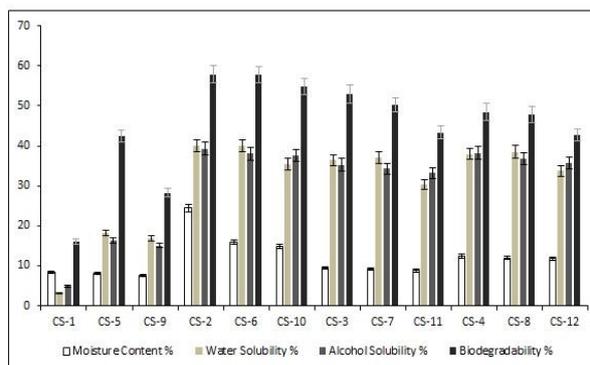


Figure 2: Effect of plasticizers on the physical properties of corn starch bioplastics

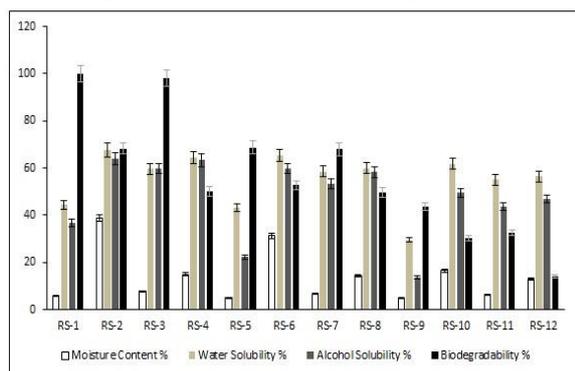


Figure 3: Effect of filler amount on the physical properties of rice starch bioplastics

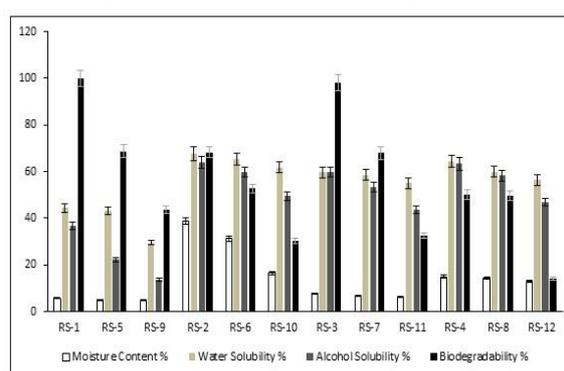


Figure 4: Effect of plasticizers on the physical properties of rice starch bioplastics

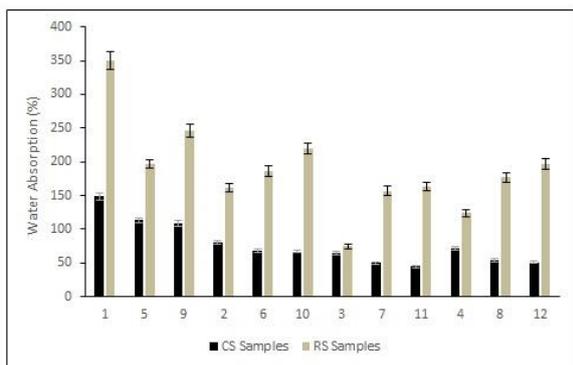


Figure 5: Effect of plasticizers on the water absorption (%) of corn starch (CS) and rice starch (RS) bioplastics

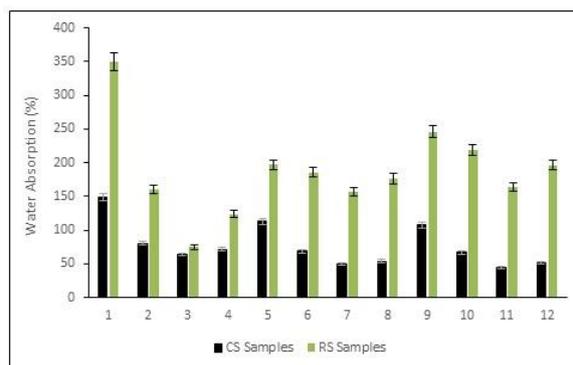


Figure 6: Effect of filler amount on the water absorption (%) of corn starch (CS) and rice starch (RS) bioplastics

Physico-chemical properties of prepared bioplastic samples

Moisture content

The moisture content for both corn starch (Fig. 2) and rice starch samples (Fig. 4) was observed to increase with the addition of plasticizer, as unplasticized samples had the lowest moisture content. Of the plasticized samples, the moisture content was the highest for glycerol plasticized bioplastics, followed by glycerol-sorbitol plasticized, while the lowest – for sorbitol plasticized bioplastic. The addition of filler was seen to be inversely proportional to the moisture content for both types of bioplastics, as increasing the amount of filler decreased the moisture content (Fig. 1 and Fig. 3).

The moisture content value is an important parameter for bioplastics. As explained by Cerqueira *et al.*,⁶⁸ the probable reason for the obtained trend in moisture content can be the fact that glycerol contains hydroxyl groups that have strong attraction for water molecules, which allows them to form hydrogen bonds and hold water in their matrix. On the other hand, sorbitol molecules have stronger hydrogen bonding with starch molecules, hence the attraction between sorbitol and water molecules is lesser, as compared to that between glycerol and water.⁶² The trend obtained for the addition of fillers can be explained by considering similar results reported by Mohan *et al.*,⁶⁹ where moisture content decreased by 40% with the addition of filler in corn starch-based films.

Water absorption

The water absorption values were seen to be the highest for the control samples of both types of bioplastics. Higher values of water absorption were observed for unplasticized bioplastic samples, compared to the plasticized samples of both types of bioplastics (corn starch and rice starch). In plasticized bioplastic samples, glycerol plasticized samples were the most water absorbent, while sorbitol plasticized samples were the least (Fig. 5). The water absorption capacity of corn starch based bioplastics with eggshell powder as a filler demonstrated to be decreasing with an increase in the filler content (Fig. 6). However, in the case of the rice starch based bioplastics with rice husk powder as filler, the samples without filler (except the control) had the lowest water absorption capacity, while the addition of filler showed a constant increase in the water absorbance capacity (Fig. 6).

Water absorption values were noted to be the highest for the control samples of both types of bioplastics, because starch is hydrophilic and the hydroxyl groups in starch are attracted towards water. Added to this is the fact that the process of gelatinization also ruptures starch granules, which allows water to diffuse easily into it.²¹ This was also previously reported in various studies observing that the water absorption capacity increases at a high amount of starch.^{21,58} Higher values of water absorption obtained for unplasticized bioplastic samples than for the plasticized samples of both types of bioplastics (corn starch and rice starch) verify that the addition of plasticizer reduces the water absorption and water retaining capacity of starch-based bioplastic samples. The fact that in plasticized bioplastic samples, glycerol plasticized samples were the most water absorbent, while sorbitol plasticized samples were the least, may be attributed to the strong hydrogen bonds present between sorbitol and starch intermolecules, which cause reduction in interaction between the hydrophilic functional groups of starch molecules and water molecules.⁶² The water absorption capacity of glycerol-sorbitol plasticized samples was seen to be in between those two extremes of glycerol

plasticized samples and sorbitol plasticized samples, which shows that the presence of glycerol impacted the water resistant property of sorbitol bioplastics.

The inverse relation between the filler content and the water absorption capacity in corn starch based bioplastics can also be explained by considering the type of filler used. In corn starch based bioplastics, eggshell powder was used as a filler, which is composed of 95% calcium carbonate by weight.⁷⁰ This result is in agreement with that presented by Dawale and Bhagat⁷¹ in a similar study on potato starch based film blended with calcium carbonate nanoparticles, in which water absorption was observed to significantly decrease with an increase in calcium carbonate nanoparticles. In another similar study by Sujuthi and Liew⁵⁸ on the properties of bioplastic sheets made from different types of starch, with the addition of recycled newspaper pulp as a filler, it was observed that the addition of filler to the bioplastics decreased the water absorption capacity. The direct relation between the filler content and the water absorption capacity in rice starch based bioplastics can be similarly explained by considering the type of filler used, which, in this case, was rice husk powder. This result is in agreement with that of a previous study by Darni *et al.*,⁵⁶ where the addition of a sorghum stalk filler into sorghum starch bioplastic increased the water absorption due to the fact that sorghum stalks consist of cellulose, which is hydrophilic in nature. On dry basis, the rice husk that was used as a filler in the rice starch based bioplastic contains 44.32% cellulose by weight.⁷² An excess amount of cellulose can increase the amount of water absorbed because of intramolecular hydrogen bonding.⁶⁶

Water solubility and alcohol solubility

The water solubility of both bioplastic types (corn starch and rice starch based) was found to increase with the addition of plasticizer (Fig. 2 and Fig. 4). Of the plasticized samples, glycerol plasticized samples had the highest water solubility, followed by glycerol-sorbitol plasticized samples and sorbitol plasticized samples, respectively. The addition of fillers was, however, in an inverse relation to water solubility for both types of bioplastics (Fig. 1 and Fig. 3). Alcohol solubility for both types of bioplastics (corn starch based and rice starch based) showed exactly the same trends as those for water solubility, however, the percentage values for alcohol solubility were observed to be generally lower than those for water solubility for the same samples (Figs. 1, 2, 3, 4).

The results exhibited that an increasing water solubility with the addition of plasticizer is consistent with the common knowledge that starch granules show cold water insolubility because of the presence of hydrogen bonding and crystalline structure of the molecule.⁷³ The plasticizer type affecting water solubility was also reported previously.⁷⁴ The results are consistent with the previous findings of Sanyang *et al.*,⁶² who observed that plasticizers are hydrophilic in nature (especially, polyols) and play a substantial role in causing the interactions between polymer molecule chains to become weaker, resulting in an increase in the free space between chains. This helps water diffuse into the polymer matrix and therefore, enhancing the solubility of the plasticized bioplastic samples, as compared to the unplasticized samples. The greater solubility of glycerol plasticized bioplastics over that of sorbitol plasticized bioplastics can be attributed to glycerol, which shows greater affinity to water than sorbitol, as well as to its lower molecular weight, which allows easy penetration into polymer chains.⁷⁵ An inverse relation between the addition of filler and water solubility may be due to the fact both fillers used in the current study, eggshell powder and rice husk powder, are very slightly soluble or insoluble in water, as eggshell is mainly composed of calcium carbonate,⁷⁰ while rice husk is mainly composed of cellulose.⁷² It has been widely reported that calcium carbonate is only slightly soluble in water,⁷⁶ starch granules show water insolubility at room temperature,⁷⁷ while cellulose also exhibits water insolubility.⁷⁸ These results are similar to the findings of Dawale and Bhagat,⁷¹ where an increase in the amount of CaCO₃ nanoparticles as a filler resulted in a decrease in the water solubility of the potato starch based bioplastic.

In our study, alcohol solubility being generally less than water solubility for the same samples may be due to the fact that starch is insoluble in ethanol at room temperature, while sorbitol is only slightly soluble in ethanol, as compared to its solubility in water.⁷⁹ As regards the fillers, the insolubility of calcium carbonate in ethanol has been reported by Gomaa,⁸⁰ while that of cellulose in inorganic solvents has been reported by Pinkert *et al.*⁷⁸ This may be attributed to the fact that ethanol is much less polar than water.⁸⁰

Biodegradability

The bioplastic samples produced were determined to be biodegradable with rapid degradation occurring in the five day soil burial test. Corn starch based bioplastics were observed to have the lowest biodegradation in the control samples, and the biodegradation rate increased with the addition of plasticizer (Fig. 2). Of the plasticized samples, glycerol plasticized samples had the highest biodegradation, followed by sorbitol plasticized samples and then glycerol-sorbitol plasticized samples, respectively. The addition of filler was found to be inversely proportional to the biodegradation value, with an increase in the filler content resulting in a decrease in degradation (Fig. 1). On the other hand, the rice starch based samples presented a control boasting the highest biodegradation, while the addition of plasticizer decreased the biodegradability. Sorbitol plasticized samples had the highest biodegradability value out of the plasticized samples, followed by glycerol plasticized and glycerol-sorbitol plasticized samples, respectively (Fig. 4). The addition of filler was observed to reduce the biodegrading ability of the samples, as increasing the amount of filler reduced the biodegradation capabilities of the samples (Fig. 3), similarly to the corn starch based bioplastics.

The biodegradability of a bioplastic depends upon its physical and chemical properties, such as its surface area, hydrophilicity or hydrophobicity, chemical structure and molecular weight *etc.*⁸¹ According to Gautum and Kaur,⁸² the percentage weight loss during soil burial biodegradation studies is caused by two factors: microorganisms invading the substrate and water absorption. The act of microorganisms feeding upon the substrate aids in the percentage weight loss. The addition of plasticizer increasing the biodegradability of the samples can be ascribed to greater water uptake and solubility of the samples, which is due to the hydrophilicity of plasticizers. The filler reduced the biodegradation ability of both corn starch and rice starch based bioplastics. The current results regarding biodegradation for both corn starch and rice starch based bioplastics are in agreement with Mohan *et al.*⁶⁹ In this previous study, similar results to ours were presented, where the biodegradation of corn starch-based biopolymer films exhibited a delay upon the addition of nanoclay as a filler. It was concluded that the reduction in biodegradability was a function of filler content in the film.⁶⁹ However, the bulk of fillers used in this study should also be considered while analysing the results of the soil burial biodegradability test.

Tensile strength and Young's modulus

Plasticizers were observed to have a common trend in both types of bioplastics produced (corn starch based bioplastics and rice starch based bioplastics), with glycerol plasticized bioplastic samples having the lowest tensile strength and Young's modulus values, while sorbitol plasticized bioplastic samples had the highest tensile strength (Fig. 7) and Young's modulus values (Fig. 8). The type of filler and its amount were also observed to have an impact on the tensile strength and Young's modulus of the bioplastic samples of both types. For corn starch based bioplastics, both tensile strength and Young's modulus were seen to increase upon the addition of filler and were found to be directly proportional to the amount of filler added. However, for rice starch based bioplastics, both tensile strength (Fig. 7) and Young's modulus (Fig. 8) decreased with the addition of filler and the relation between them was found to be inversely proportional.

Polymeric materials undergo a variety of stresses when being used, thus inspecting the mechanical properties of bioplastic sheets is extremely important for both research and practical application purposes.²¹ Results similar to ours with sorbitol plasticized bioplastics having more tensile strength than glycerol plasticized bioplastics have been previously demonstrated by Sanyang *et al.*⁶² Meanwhile, the fact that glycerol plasticized bioplastic films had a lower Young's modulus than sorbitol plasticized films has been reported by Ooi *et al.*⁸³ The results found in the current study were also consistent with those of Ballesteros-Mártinez *et al.*,⁸⁴ who similarly concluded that glycerol has better plasticization ability than sorbitol in sweet potato starch films. In comparison, Aguirre *et al.*,⁸⁵ in a study on the effects of glycerol and sorbitol on the properties of triticale protein films also showed that glycerol boasts a plasticizing efficiency greater than that of sorbitol. This behavior can be explained by taking into account the smaller molar mass of glycerol (92.09 g/mol) than that of sorbitol (182.17 g/mol). The smaller molar mass makes the interaction between glycerol and the starch molecular chains easier.⁶² Glycerol-sorbitol plasticized bioplastic samples had values ranging in between those of glycerol and sorbitol. Glycerol-sorbitol plasticized bioplastic samples contained both glycerol and sorbitol in equal amounts, which resulted in an interesting interaction between the two

plasticizers, with sorbitol improving the overall tensile strength and glycerol deteriorating the overall tensile strength of the bioplastic samples.⁶²

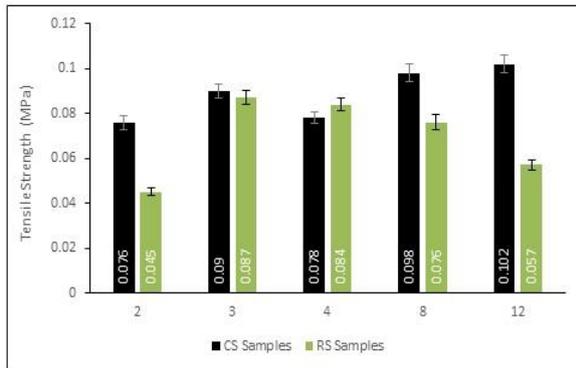


Figure 7: Effect of plasticizer and filler on the tensile strength of corn starch (CS) and rice starch (RS) bioplastics

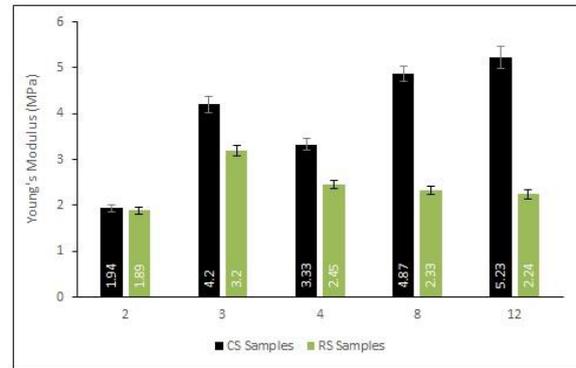


Figure 8: Effect of plasticizer and filler on Young's modulus of corn starch (CS) and rice starch (RS) bioplastics

As shown in the results, for corn starch based bioplastics both tensile strength and Young's modulus were seen to increase upon the addition of filler and were found to be directly proportional to the amount of filler added. In a similar study by Maulida *et al.*⁶⁶ on cassava peel starch bioplastic, tensile strength also increased with the increasing content of Avicel PH101 microcrystalline cellulose as a filler. The amelioration of these characteristics can be ascribed to good interfacial adhesiveness that can create strong hydrogen bonds in between the starch matrix and the filler.²¹ Young's modulus was reported to be in a direct relation to the amount of filler by Ikejima *et al.*,⁸⁶ and Dawale and Bhagat.⁷¹

However, as also shown in the results, for rice starch based bioplastics, both tensile strength and Young's modulus decreased with the addition of filler and the relation between them was found to be inversely proportional. Similar results have also been reported by Syafri *et al.*,⁸⁷ who found an inverse relation between the mechanical properties of cassava starch bioplastics and the amount of precipitated calcium carbonate filler added. Similar findings were also obtained for PLA based bioplastics, as Yaacab *et al.*⁵⁷ also reported that the addition of paddy straw powder as a filler to a polylactic acid/paddy straw powder composite resulted in a decrease in the tensile strength. This may be caused by inadequate dispersion of the filler in the polymer matrix and by poor adhesion amongst the polymer and the filler.⁸⁸ A decrease in the tensile strength and Young's modulus of sorghum starch-cellulose bioplastics upon addition of sorghum stalk filler was also reported by Darni *et al.*⁵⁶ The tensile strength and elastic modulus values for commercial bioplastics, such as polylactic acid (PLA), are 59 Mpa and 3500 MPa, respectively,⁸⁹ while those for polyhydroxybutyrate (PHB) and polyhydroxyalkanoate (PHA) are 11-40 MPa and 3500-4000 MPa, respectively.^{90,91}

Fourier transform infrared spectroscopy

Fourier transform infrared spectroscopy (FTIR) analysis was carried out to investigate the functional groups present in the bioplastic samples and to observe if the addition of plasticizers and fillers resulted in the addition of any new functional groups. All the batches of bioplastics analyzed were observed to have characteristic peaks ranging between 2929-3011 cm^{-1} in all the samples tested. (Figs. 9 and 10). The addition of plasticizer was seen to cause new peaks to arise at 3288-3316 cm^{-1} . Three to four characteristic peaks in the ranges of approximately 990-1036 cm^{-1} and 1075-1155 cm^{-1} were observed in all unplasticized and plasticized samples of all types. The fillers were not seen to have any significant impact on the presence of the functional groups in the bioplastics, nor were they seen to add any additional functional groups.

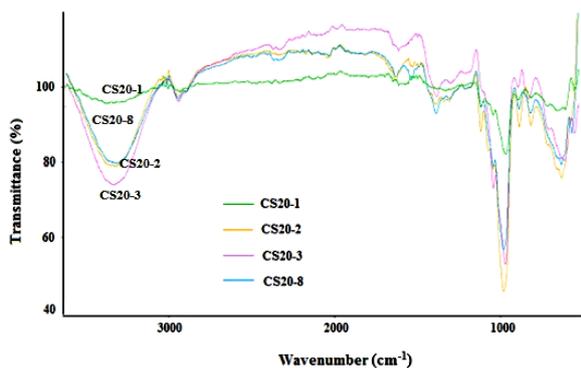


Figure 9: FTIR spectra of corn starch based bioplastic sheets with different plasticizers and fillers compared to the control

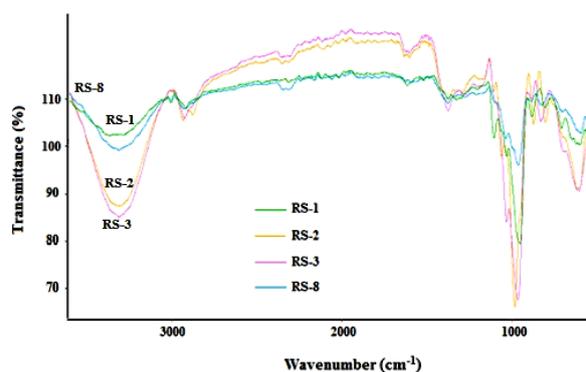


Figure 10: FTIR spectra of rice starch based bioplastic sheets with different plasticizers and fillers compared to the control

FTIR is a widely employed analytical technique that allows the investigation of molecular structures⁹² and the interaction of components,⁶⁶ as well as the determination of functional groups present in a substance.⁵⁶ The characteristic peaks ranging from 2929-3011 cm^{-1} ($=\text{C-H}$ stretching) in all the samples tested were due to the presence of starch. Characteristic peaks within this range were also reported in a previous study by Yin *et al.*⁹³ As reported, the addition of plasticizer was seen to cause new peaks to arise at 3288-3316 cm^{-1} , which are characteristic of the O-H functional group. The presence of these peaks can be attributed to the fact that both glycerol and sorbitol are sugar alcohols or polyols,⁹⁴ and polyols consist of a large number of hydroxyl groups, which results in a broad peak ranging between 3600 and 3200 cm^{-1} .⁹⁵ This indicates that the addition of plasticizer can add new functional groups to the bioplastics. Three to four characteristic peaks in the range of approximately 990-1036 cm^{-1} , showing the C-O-C functional group, and of 1075-1155 cm^{-1} , showing C-O-H, were observed in all unplasticized and plasticized samples of all types. Many earlier studies have reported the presence of characteristic peaks between 990 and 1200 cm^{-1} corresponding to the C-O bond stretching.⁹⁶ In a similar study on silica-filled sago starch/PVA films, peaks at 1145 cm^{-1} and 1081 cm^{-1} , representing C-O stretching in C-O-H functional group, were observed, while at 1000 cm^{-1} , C-O stretching in C-O-C functional group was observed.⁹⁷

As mentioned above, the fillers were not seen to have any significant impact on the presence of functional groups in the bioplastics, nor were they noted to add any new functional groups. No formation of new functional groups upon the addition of filler was also reported in a previous similar study on starch based bioplastics with sorghum stalks as filler.⁵⁶ This may also be attributed to the fact that the peaks that would have been seen for the fillers used in this study, rice hulls and eggshells, lie within the values of the broad peaks that have already been seen for the bioplastics. Rice hulls are mainly composed of cellulose and eggshells are mainly composed of CaCO_3 . The peaks that can be seen around 3440-3500 cm^{-1} indicate the O-H group of cellulose, while the peaks seen around 1080-1094 cm^{-1} indicate the C-O group of the glycosidic bond that exists between the cellulose monomers.^{98,99} The peak at 3400 cm^{-1} may be attributed to the slight adsorption of water on carbonate particles,¹⁰⁰ while the peak at 946 cm^{-1} corresponds to C-O bending vibration in carbonates.¹⁰¹

Interactions between the components of the bioplastics can be observed through the FTIR spectra. No alterations can be seen in the spectra if the bioplastic components do not blend properly, while if the components blend properly, some changes can be noted.¹⁰² The addition of filler alters the starch matrix. These filler-matrix interactions can also be observed using the FTIR spectra. The addition of eggshell powder filler results in lowering of the transmittance percentage, showing higher levels of absorption. Similar results were also reported by Pratomo *et al.*¹⁰³ and Syafri *et al.*⁸⁷ The peak at about 3296 cm^{-1} shows hydrogen bonded O-H stretching.¹⁰⁴ Its transmittance percentage is seen to get lower with the addition of eggshell powder filler. This can be attributed to the disruption of hydrogen bonds with the starch matrix.¹⁰⁵ The peaks around 1010-1070 cm^{-1} show bending vibration of C-O, and O-H,⁸⁷ which also witness lowering of transmittance percentage upon the addition of filler. As compared to eggshell powder, the rice hulls filler was not seen to lower the transmittance percentage to a great extent, so it can be concluded that the eggshell powder filler causes more disruption in the matrix than rice hulls.

Induced hydrophobicity to corn starch bioplastic using RTV silicone

In the current study, RTV silicone coating was used to impart hydrophobic properties to sample CS-1 and this effort was successful as the water solubility of this coated sample was recorded as 0% (Table 2). It was also observed that the coated sample exhibited 0% biodegradability when buried whole, while the one coated whole and then broken into two pieces before burying it in soil exhibited 4.66% biodegradability, as compared to 16.08% for the uncoated sample in the 5 day soil burial test (Table 3). The result remained constant at 0% biodegradability for the sample coated whole upon extension of the test to 10 days and then further to 20 days.

Table 2
Water solubility of the bioplastic sample coated with RTV silicone

Bioplastic sample	Initial weight (g)	Final weight (g)	Water solubility (%)
Coated	0.421±0.0126	0.421±0.0124	0±0
Uncoated	0.401±0.011	0.388±0.0095	3.24±0.13

Table 3
Biodegradability of the bioplastic sample coated with RTV silicone

Bioplastic sample	Initial weight (g)	Final weight (g)	Biodegradability (%)
Coated; whole	0.691±0.021	0.691±0.022	0±0
Coated; broken	0.408±0.015	0.389±0.013	4.66±0.16
Uncoated	0.311±0.012	0.261±0.011	16.08±0.52

Starch based bioplastics are hydrophilic in nature and not water-resistant,¹⁰⁶ and this characteristic can severely limit their practical applicability and usability.¹⁰⁷ Hence, it is imperative to explore methods to induce hydrophobicity to bioplastics. The experiment of using RTV silicone coating for imparting hydrophobic properties to a bioplastic sample was successful, as the water solubility of this coated sample was observed to be 0%. This is due to the fact that silicones have the ability of repelling water and forming watertight seals.¹⁰⁸ Thus, coating bioplastic samples with RTV silicone to induce water resistance to bioplastics was proven to be a viable option. It has also been reported by Denstedt and Atala¹⁰⁹ that RTV silicone is hydrophobic and insoluble in water, and that it has a safe history of use as it is not toxic or irritant. The results of the biodegradability test of the RTV silicone coated CS-1 sample were also very promising, as the sample coated whole exhibited 0% biodegradability, the one coated whole and then broken into two pieces exhibited 4.66% biodegradability, as compared to 16.08% for the uncoated sample in the 5 day soil burial test. The result remained constant for the sample coated whole, even when the soil burial time period was extended to 10 days and then further to 20 days. The sample remained non-biodegradable. This can be attributed to the fact that silicone does not support microbial growth and shows resistance to water and oxygen,¹⁰⁸ thus making the biodegradability of the coated sample impossible, without breaking it into pieces and exposing the inner biodegradable polymer. This property can greatly enhance the practical usability of the starch based bioplastics.

CONCLUSION

It is concluded from the present research work that the utilization of starches from corn and rice sources, various types of plasticizers, as well as the amount and nature of the filler used, can have a significant impact on the physical and chemical properties of produced bioplastics, namely, on moisture content, water absorption, water solubility, alcohol solubility, biodegradability, tensile strength and Young's modulus. RTV silicone coating of the bioplastic samples was found to be efficient in inducing hydrophobic properties to water soluble bioplastics, to enhance their resistance to water solubility and biodegradability, thus different types of environmentally friendly coating materials need to be further investigated. On the whole, the study has demonstrated that starch-based

bioplastics can be a promising environment-friendly alternative for conventional plastics. Moreover, all the bioplastic samples produced may be a sustainable option to reduce plastic pollution.

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