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Production of Starch-Based Bioplastic from the Mixture of Potato and Cassava Peel Wastes Starch Using Glycerol as Plasticizers: A Comparison on the Effect of $CaCO_3$ and HCl as Fillers

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Abstract

This study investigates the production of starch-based bioplastics from the mixture of potato and cassava peel waste starch using glycerol as plasticizer (20% wt/v) and comparing reinforcement with calcium carbonate and hydrochloric acid (4% wt/wt of filler to starch). The potato and cassava peel starch used in the production of the bioplastics were at a ratio of 3:1, 1 1, and 1:3 (wt/wt)), whereas the pure starches of the potato and cassava peel were studied as control. The physical appearance, density, water uptake, and tensile strength of the bioplastics produced were determined. The findings suggest that amongst all the bioplastics produced, hydrochloric acid as a filler exhibited the lowest water uptake compared to $CaCO_3$, while $CaCO_3$ enhances density and tensile strength. This study, for the first time, established that the properties of bioplastics produced from pure potato and cassava peel starches could be enhanced by mixing the potato and cassava peel starch at the ratio of 3:1 (wt/wt). The bioplastic produced from the mixture of potato and cassava peel starchs at the ratio of 3:1 (wt/wt) exhibited the highest density (1.4 g/cm^3) and tensile strength (38 Mpa) with $CaCO_3$ reinforcement as compared to HCl, which has a density of 1 g/cm^3 and tensile strength of 18 Mpa. On the contrary, HCl favors the reduction of water uptake (18.4 %) than $CaCO_3$ (34%).

Keywords: Bioplastic; Calcium Carbonate; Cassava Peel; Potato Peel; Starch

Nomenclature

ASTM: American Society for Testing and Materials, CPS: Cassava Peel Starch, PPS: Potato Peel Starch, HCl: Hydrochloric Acid, WDS: Electronic Universal Testing Machine

Introduction

Over the past 50 years, researchers have studied the global production of carbon-based polymers extensively. There is a high demand for plastics and it is expected to double in the next 20 years. In 2018, 360 million tons of plastic were produced [1].

The increase in environmental problems caused by petroleum-based plastics in recent years is worrying. In terms of using alternative materials, researchers have begun to investigate new sources of biomass, such as agricultural waste and microorganisms, as potential substitutes for petroleum-derived plastics. Biofuels don't compete with food crops, so there's no need to worry about running out of food to fuel our cars. Researchers are instead focusing on developing new biofuels to replace traditional fuels. For this reason, researchers have been focusing on the deployment of wastes as potential feedstock for the production of bioplastics [2].

Bioplastics can break down into carbon dioxide, water, and inorganic compounds. This is predominantly due to the enzymatic activity of microbes. The market for environmentally friendly materials is growing rapidly, with a growth rate of 10-20% per year. The global market for biodegradable polymers is projected to grow to 206 million pounds at a compound annual growth rate of 12.6% by 2020. Biodegradable polymers are divided into agropolymers (starch, protein, chitin) and biopolyesters (polyhydroxyalkanoates, polylactic acid, etc.) [5].

Polysaccharides are the most plentiful macromolecules in plants and animals, making them a good source of starch for bioplastics. This renewable, sustainable material is also abundant and cheap. Starch also has good thermoplasticity and is biodegradable. Starch is mainly composed amylose and amylopectin glucose macromolecules (Pérez and Bertoft, 2010), but there are functional and structural differences between the different types, so the effectiveness of starch as a bioplastic raw material depends on its specificity. Structure and composition (Shafqat et al., 2021).

According to Food and Agriculture Organization Corporate Statistical Database (FAOStat), Africa accounts for about 64% (192 million tons) of global cassava production, with Nigeria taking the lead with a production of over 59 million tons in 2019 (Adeoye, 2021). Also, Nigeria is the seventh largest producer of potato in Africa with production of 1.2 million tons (Egbedi, 2019), with concomitant generation of millions of tons of solid and liquid wastes. These wastes are disposed indiscriminately into the environment, causing degradation with attendant serious health hazards to both flora and fauna. Therefore, proper management of these wastes is required for a sustainable environment (Oghenejoboh et al., 2021), potato and cassava peel starches were used in our study as we reflect the sustainable use of these peels, which are often degraded into waste and readily available at every grocery store.

Water plays a vital role in bioplastic production. First, by acting as a solvent in dissolving the starch. Secondly, it assists the heated starch molecules to remain disrupted. The filler $CaCO_3$ was chosen because of its many advantages over other fillers, including its non-toxicity and odorless qualities, its softness and dryness, and its lower cost.

This study is the first to investigate the production of a bioplastic from the mixture of potato and cassava waste peel starch using glycerol as a plasticizer and water as a solvent. The study considered how two different types of fillers (calcium carbonate and hydrochloric acid) affect the appearance, density, water uptake and strength of starch-based bioplastic products.

Materials and Methods

Sample collection and preparation

Cassava peel was obtained at Samaru Market, Zaria, whereas potato peel was obtained at Frizzlers restaurant in Ahmadu Bello University, Zaria. Both peels were washed before further analysis.

Isolation of starch

In this study, starches were extracted from potato peel (Solanum Tuberosum) and cassava (Jatropha Manihot) peel wastes. Figure 1(a) displays a schematic depiction of the starch preparation.

150 g of potato peel starch was produced from 3 kg of potato peel waste with a yield of 5%, and 250 g of cassava peel starch was obtained from 2 kilograms of cassava peel waste with a yield of 8.3%

Using scissors, the peel wastes were divided into little pieces (about 3 inches) after being thoroughly cleaned with clean water. Later, the peels were soaked in water for about 100 ml and blended using a kitchen blender (Kenwood BLP15). After blending for about a minute, the liquid was decanted using a sieve cloth, and the starch was allowed to settle to the bottom of the beaker for 30 minutes. A fine powder was produced by removing the starch from the slurry, washing it with distilled water, and then drying it in an oven for 40 minutes at 70°C.

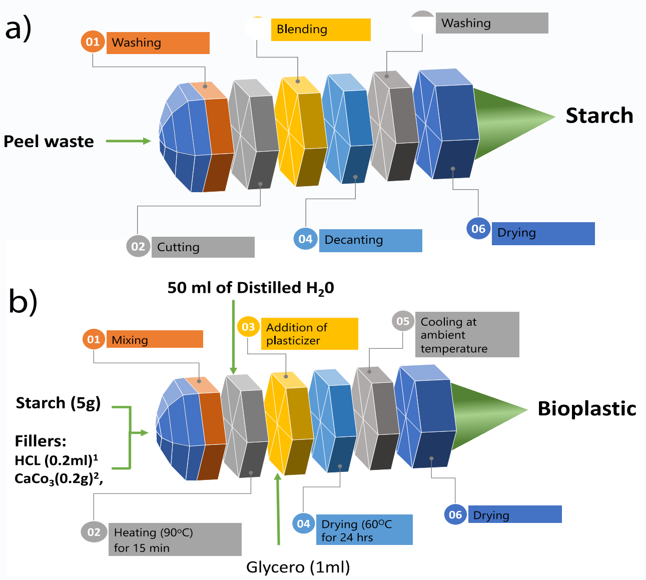

Figure 1: The schematic diagrams of the preparation of (a) starch from cassava and potato peel wastes and (b) preparation of bioplastic from starch.

Production of bioplastic film

As shown in Figure 1(b), filler was added to 5g of the sample (0.2 g using $CaCO_3$ or 0.2 ml using HCl). Before adding 50 ml of distilled water, the mixture was mixed and heated on a heating mantle at 90°C for 15 minutes. The mixture was then given a 1 ml glycerol addition before being put into a petri dish and dried for 24 hours in a 60°C oven. When the bioplastic had dried, it was chilled to room temperature before being peeled off the flat [3].

Sample labeling

A total of five samples were prepared in duplicate varying the ratio (g/g) of potato (PPS) to cassava peel (CPS) starches were prepared and labeled as; (i) 100% PPS, (ii) 75% PPS+25% CPS, (iii) 50% PPS+50% CPS, (iv) 25% PPS+75% CPS, and (v) 100% CPS. (see Figure 1 (a & b)).

Bioplastic Characterization

Density: The ASTM D792-91 standard was used to test the density of the bioplastic film with dimensions of roughly 2x2 cm and a thickness of 0.1 cm. The mass of the film was calculated using an analytical balance. Equation 1 was utilized to calculate density.

$$Density = \frac{mass\ (g)}{volume\ (cm^3)}\ x\ 100, \qquad \text{Eq....1}$$

$$Volume\ cuboid\ =\ L\ x\ B\ x\ T, \qquad \text{Eq....2}$$

L - Length, B-Breadth, and T – Thickness

Water absorption test: By cutting a piece of film that was roughly 2x2 cm in size and then weighing the mass, water uptake was measured in accordance with ASTM D570-81. A 250 ml beaker containing distilled water was used to hold the film for 24 hours. After immersion in water, the film was removed from the water and weighed to measure the wet weight. This is how water uptake was calculated:

$$Water\ uptake = \frac{wet\ weight - dry\ weight}{wet\ weight}\ x\ 100, \qquad \text{Eq....3}$$

Tensile strength: The WDS-3KN Electronic Universal Testing Machine was used to measure the tensile strength using the ASTM D882-91 standard at an extension rate of 10 mm/min at room

Table 1: A description of bioplastic films' visual appearance.

Sample	PPS & CPS starch ratio (%)	Appearance of film with filler 1 (HCl)	Appearance of film with filler 2 ($CaCO_3$)
A	100 PPS + 0 CPS	Transparent, brittle, fragile, rigid	Transparent, brittle, not sticky
B	75 PPS + 25 CPS	Mustard brown, more flexible than A1	Mustard brown, not brittle, not sticky, easy to peel and handle
C	50 PPS + 50 CPS	Russel brown, not brittle, not fragile, easy to peel and handle	Almond brown, darker than B2, not sticky, easy to peel
D	25 PPS + 75 CPS	Caramel brown, darker than C1, easy to peel and handle	Russet brown, darker than C2, not easy to peel, sticky
E	0 PPS + 100 CPS	Syrup/ dark brown, darker than D2, very sticky and flexible, not easy to peel	Cinnamon brown, darker than D2, very sticky and flexible, not easy to peel

temperature. The tensile strength value was determined using the observed data. After that, the maximum tensile strength was measured and noted. The materials were cut into 10 x 1 cm rectangular pieces before being analyzed.

Results

Amount of isolated starch from potato and cassava peel waste

The yield of starch isolated from cassava peel waste was 5%, which was white-brownish in color, whereas the potato peel waste yielded a starch of 8.3%, which was white.

Physical appearance of bioplastic films Produced

The photographic images of the films with varying ratios of potato peel starch to cassava peel starch using HCl as filler are presented in Figure 2(a) and Figure 2(b) for the samples prepared using $CaCO_3$ as filler. Moreover, detailed descriptions of their visual appearances are given in Table 1.

Density Measurement

The density of the bioplastic film was affected by the potato-to-cassava peel starch ratio and filler ($CaCO_3$ and HCl), as shown in Figure 3a. Lower-density plastics tend to have open structures that are permeable to fluids such as H_2O, O_2 or CO_2 (Bierley et al., 1988). Density is higher for calcium carbonate-filled bioplastics than HCl-filled bioplastics due to the higher density of $CaCO_3$ (2.71 g/cm^3) compared to HCl (1.18 g/cm^3). The highest density can be seen in a blend of 75% PPS + 25% CPS due to the higher ratio of potato peel starch in the sample.

Water absorption measurement

To confirm the impact of filler type and the ratio of potato to cassava peel starch on the hydrophilic character of starch-based films, the biofilms created in this study were submerged in water. Water seeps through the film's network chains, causing the film to inflate. All of the films swelled quickly during the first 6 hours, then more slowly until they reached equilibrium after 20 hours. This phenomenon might be brought on by the films' numerous active hydroxyl groups, which were unoccupied at the start of the absorption process. However, the active sites progressively became overloaded until they were unable to hold any more water molecules.

This point is known as the equilibrium state [9]. The water uptake of bioplastic films obtained is shown in Figure 3b. It can be seen that as the amount of cassava starch in the bioplastic increased, so did the rate of water absorption. This is because both glycerol and Cassava starch has hydrophilic characteristics. These characteristics boosted the glycerol and water's affinity, increasing the absorption of water (Suryanto, 2017). The presence of hydroxyl (OH), carbonyl (CO), and ester (COOH) groups in cassava starch demonstrates that films with a higher ratio of cassava peel starch than potato peel starch have a concentration of hydrophilic characteristics. Therefore, hydrophilic starch and glycerol with high concentrations produce a faster breakdown in the soil. Additionally, the hydrophobic qualities of $CaCO_3$ cause the sample to repel water, which is why biofilms generated using $CaCO_3$ as a filler absorbed less water than films made with HCl. A similar pattern was also seen by Maulida et al., with an improved outcome. As a result, the presence of $CaCO_3$ tends to make the bioplastic film stronger.

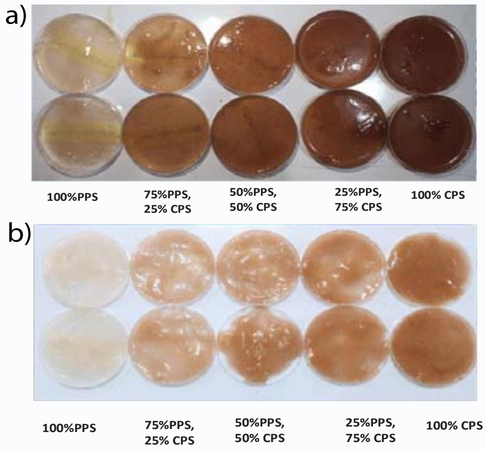

Figure 2: Biofilms produced using glycerol as plasticizers with (a) HCl and (b) $CaCO_3$ as filler.

Tensile strength

To use films in prospective future applications, such as the food packaging business, one must be aware of their mechanical qualities. Figure 3c displays the results obtained for the films' maximum tensile strength.

Tensile strength ranged from 10 to 18 Mpa for bioplastic films produced using HCl as filler and 15 to 38 Mpa for films produced using $CaCO_3$ as filler. According to other research, the amylose content has an impact on how the films behave mechanically. According to the results, starches with a higher amylose content (75% PPS+25% CPS) produce films with higher tensile strength and greater resistance (Montalbán, 2019). The film's crystallinity and mechanical behaviour are connected. In this study, films using a filler of $CaCO_3$, 75% PPS, and 25% CPS produced more durable films with a tensile strength of 38 Mpa, which is an improvement over films described in the literature. The enhancement of the mechanical characteristics may be due to these crystalline domains contained in the amorphous matrix. The mechanical properties achieved outperformed those reported by Azieyanti et al. and Maulida et al., who used comparable filler and plasticizer concentrations. The amylose/amylopectin ratio has a significant impact on the characteristics of starch bioplastic.

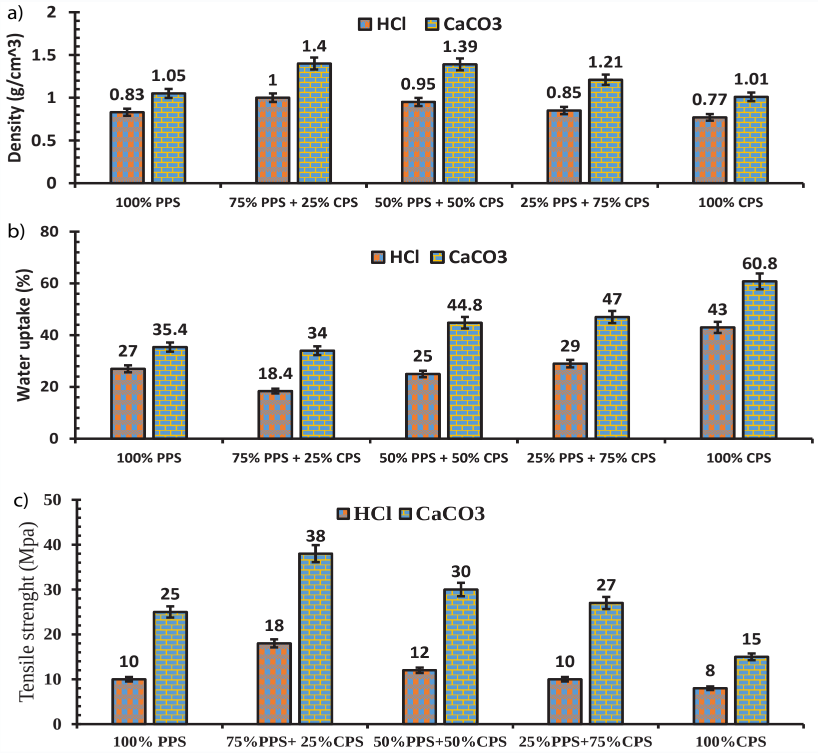

Figure 3: (a) Density (b) water uptake (c) Tensile strength.

Table 2: Results of related research work.

Starch source	Bioplastic type	Plasticizer	Filler	Mechanical and Physical Properties	Reference
Potato peel	Starch-based film	Glycerol (20% wt/wt)	HCL and $CaCO_3$ (4% wt/wt)	Density: 0.83g/cm^3 (HCl), and 1.05 g/cm^3 ($CaCO_3$) Water uptake: 27% (HCl), and 35.4% ($CaCO_3$) Tensile strength: 10 Mpa (HCl), and 25 Mpa ($CaCO_3$)	This work
Cassava peel	Starch-based film	Glycerol (20% wt/wt)	HCL and $CaCO_3$ (4% wt/wt)	Density: 0.77g/cm^3 (HCl), and 1.01 g/cm^3 ($CaCO_3$) Water uptake: 43% (HCl), and 60.8% ($CaCO_3$) Tensile strength: 8 Mpa (HCl), and 15 Mpa ($CaCO_3$)	This work
Mixture of potato and cassava peel starch (3:1) (wt/wt)	Starch-based film	Glycerol (20% wt/wt)	HCL and $CaCO_3$ (4% wt/wt)	Density: 1 g/cm^3 (HCl), and 1.4 g/cm^3 ($CaCO_3$) Water uptake: 18.4% (HCl), and 34% ($CaCO_3$) Tensile strength: 18 Mpa (HCl), and 38 Mpa ($CaCO_3$)	This work
Potato peel	Starch-based films	Glycerin	Vinegar	Water absorption: 83.57%	Arikan & Bilgen, (2019)
Cassava peel	Starch-based film	Sorbitol	Microcrystalline Celllulose (Mcc) Avicel Ph101	Density: 1.5g/cm^3 Water uptake: 72% Tensile strength: 6.8 MPa	[6]

In general, high-amylose starches have better mechanical qualities; for example, the starch from potato peels has a higher amylose-to-amylopectin ratio (20:80) than that from cassava peels (19:81). In contrast to films with a higher ratio of cassava peel starch, films with a higher ratio of potato peel starch often have better tensile strength.

As the amount of cassava peel starch gradually increased, the tensile strength decreased, weakening the link between the matrix and the reinforcement and, ultimately, the resistance of the resultant films [4].

Comparison of this study and other related research works

Results of related research works reported for various bioplastic films produced from potato and cassava waste peel are compared with the findings in (Table 2). As can be seen in Table 2, there is a major improvement in barrier properties (density and water uptake) as well as tensile strength (38 Mpa) in the bioplastic film produced with a 3:1 potato-to-cassava peel ratio. This implies that the mixture of these raw materials at 3:1 would enhance the variable applications of bioplastic in the packaging industries to replace the unwanted fossil-based plastics.

Conclusion

In conclusion, a bioplastic made from a combination of potato and cassava peel starch makes excellent packaging material. The packaging materials are a good contender to replace petroleum-based plastic because of its barrier qualities and renewable sources when made from a suitable blend of filler, glycerol, and starch. This biodegradable bioplastic will aid in raising awareness of the value and necessity of using biodegradable materials in our daily lives to create a greener ecosystem.

Conflict of Interest

The authors declare that there are no conflicts of interest regarding this article.

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