Journal of Digital Food, Energy & Water Systems [JD-FEWS]

JDFEWS 5 (1): 34 - 44, 2024
ISSN 2709-4529

# Thermal Stability, Transparency, and Water Sensitivity Properties of Bleached, Cross-Linked Cassava Starch Film

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**Received**: 04 June 2024
**Review**: 11 June 2024
**Accepted**: 26 June 2024
**Published**: 30 June 2024

**Abstract—**This work investigates a novel study of the effect of bleaching and cross-linking cassava starch film. Native cassava starch was bleached with hydrogen peroxide ($H_2O_2$), cross-linking was carried out with oxidized sucrose, while glycerol was added to enhance the plasticity of the film. Operating temperature and time of 90 ˚C and 10 Minutes, respectively, adding 0.5 ml of glycerol gave the best bleached, cross-linked cassava starch film. UV-visible spectrophotometer analysis revealed that the cassava starch film produced at the above reaction conditions retained 88.2 % of its transparency at 96 hours of water immersion. The water solubility test shows that the film experienced 52.02 % weight loss after 96 hours of immersion in water. The thermo-gravimetric analysis (TGA) shows a significant improvement in the thermal stability with a Temperature peak ($T_p$) of 420.75 ˚C, compared to 374.13°C $T_p$ of the control sample (unbleached, uncross-linked) of the cassava starch film.

**Keywords—** *bleached, cross-linked, transparency, water solubility, thermal stability*

## 1 Introduction

Native starches possess numerous characteristics and advantages that present them as excellent materials for non-food applications in industries. They exhibit biological and chemical properties such as poly-functionality, non-toxicity, and high reactivity to chemicals (Wang et al., 2018). However, their hydrophilic nature limits the development of industrial starch-based materials.

Chemical modification, including etherification, esterification, oxidation, hydrolysis, and crosslinking, is commonly employed to enhance the film-forming capacity of starch. This method introduces new functional groups into the starch molecule, altering its physicochemical properties. Cross-linking, a prevalent approach in polysaccharide chemistry due to its cost-effectiveness, involves bi-functional or multifunctional reagents that create intermolecular bridges between polysaccharide molecules, thereby improving mechanical and thermal properties, water stability, and resistance to high temperatures and pH variations (Ali & Syed, 2009; Canisag, 2015; Monteiro et al., 2017).

Despite its advantages, traditional cross-linking agents like glutaraldehyde and formaldehyde are highly reactive and toxic, posing environmental and health risks (Sapula et al., 2023; Soliman, 2020; Jeong et al., 2021). Recent studies emphasize the demand for non-toxic alternatives that enhance tensile strength and elongation. For instance, citric acid has been explored as a natural and non-toxic cross-linker, significantly improving the stability and strength of starch films (Sharmin et al., 2022; Wang et al., 2018).

Recently, oxidized sucrose derived from periodate cleavage has been investigated as a cross-linker for starch films. Wang et al. (2018) demonstrated that modifying the crystal structure through cross-linking enhances thermo-plasticity and water binding capacity, resulting in films with excellent hydrophilic properties at various temperatures.

This study proposes a novel approach involving bleaching starch with $H_2O_2$ and cross-linking the starch films with oxidized sucrose to introduce aldehyde groups, thereby enhancing the stability and strength of the films. The effects of process variables such as time, glycerol concentration, and temperature on film transparency, thermal properties, and water stability were systematically studied.

In conclusion, while starch remains a cost-effective and abundant resource for biodegradable materials, advancements in cross-linking technologies, particularly those utilizing non-toxic agents like oxidized sucrose, are crucial for overcoming the mechanical limitations of starch films in industrial applications. The knowledge gap in this study is therefore, the need for non-toxic and effective crosslinking agents to enhance the properties of starch-based materials for industrial applications to investigate the use of oxidized sucrose, derived by periodate cleavage to introduce aldehyde groups as crosslinkers for starch film by assessing the effect of this chemical modification to improve the thermal and mechanical properties while examining the influence of process variables such as time, glycerol concentration and temperature on these characteristics. This research addresses the current limitations of starch films, particularly their poor mechanical properties, by exploring a potentially safer and more efficient crosslinking method using oxidized sucrose.

## 2 Materials and Methods

The research methodology adopted in this work follows standard procedures obtained from previous research and reviewed literatures.

### 2.1 Experimental materials

Cassava starch was obtained from local farmers in Bida, Niger State, Nigeria. Other materials used were distilled water, Sodium periodate (>98%), glycerol (99.8 %), sucrose, barium dichloride, and hydrogen peroxide (%) sourced from existing standard laboratories.

### 2.2 Experimental methods

The methods adopted in this work are as follows;

#### 2.2.1 Preparation of oxidized sucrose

The oxidized sucrose was prepared according to the method reported by Wang *et al.* (2018). Periodate cleavage was adopted for the preparation of oxidized sucrose. 6.6g of sucrose was weighed into 250 ml reactor beaker followed by the addition of 12.9 g of sodium periodate. 200 ml of distilled water was added to the reactor content and stirred for about 26 hours at room temperature. Complete precipitation was achieved by adding 7 g barium dichloride to the reaction mixture at 5 oC with constant stirring for 60 minutes. The reactor content was then poured into a filter paper, thereafter, the filtrate containing polyaldehyde was stored at 5 $^{o}$C.

#### 2.2.2 Bleaching of cassava starch with $H_2O_2$ and Cross-linking with oxidized sucrose.

The starch film was prepared by measuring 50 ml of distilled water into a 250 ml beaker and heated on a hotplate magnetic stirrer until the temperature reaches 50 $^{o}$C. 3g of cassava starch was measured into the beaker, and the temperature was allowed to attain 70 $^{o}$C before 0.5 ml of Hydrogen peroxide, $H_2O_2$ (30% V/V) was added for bleaching to improve the transparency, 0. 5 ml of the oxidized sucrose was added for cross-linking and further oxidation. 1.2 ml of glycerol was added to improve the plasticity. Five other experimental runs were repeated at varying time, temperature and amount of glycerol to obtain the cassava starch film (see Table 1).

#### 2.2.3 Thermo-gravimetric Analysis (TGA)

The thermal stability of materials was analyzed with the help of TGA, since TGA helps to understand the trend of thermal degradation of a material on continuous exposure to heat (temperature) (Brown, 2007). 10 mg of each cassava starch film was weighed into the crucible and placed in a TGA analyzer (PerkinElmer TGA 4000) with a 40 cc/min nitrogen purge. The heating rate was fixed at 10 $^{\circ}$C/min to imitate a slow pyrolysis condition, while the cooling water/algaecide mixture temperature was fixed at 15 $^{\circ}$C. Percentage weight retained was plotted against temperature. The data recorded was also subjected to derivative thermo-gravimetric (DTG) analysis to determine the rate of weight retained as a function of differential temperature gradient.

#### 2.2.4 Water Absorption Analysis

In determining the water resistivity of the films, the weight and percentage transmittance of the films were kept in-check as the films were soaked in water for several hours. Each film (of 2.2 cm height and 1 cm breadth) was weighed, and its percentage transmittance was measured before immersing in water for several hours at intervals of 24 hours, until the film totally dissolved in water. Each film's weight and percentage transmittance after immersion in water was measured by removing it from the water and allowing it to dry (Moritiwon et al, 2020).

#### 2.2.5 Transparency Analysis

The transparency of the starch films was determined by measuring the amount of light that was able to pass through each film in the form of percentage transmittance. Before the percentage transmittance measurement, all films were scanned using spectrum mode of Shimadzu UV-Visible spectrophotometer, and peaks were observed within the 200 - 214 nm range. Each film was cut to make a height of 2.2 cm and breadth of 1 cm, and placed in a cuvette (of 2.5 cm height and 1 cm breadth), which was then placed inside spectrophotometer and the percentage transmittance was measured at 214 nm. The higher the percentage transmittance, the more the transparency of the film (Moritiwon et al, 2020).

## 3. Results and Discussions

### 3.1 Mechanism of oxidized starch film

The presence of hydroxyl group (OH) in starch could be linked to its low thermal stability at high temperatures, low water resistivity over a prolonged period, and low transparency. In order to improve on the properties of starch film and make it fit for industrial applications, an alternative approach of starch film modification was carried out in this study. The mechanism of modification (Figure 1) involves the opening of the cyclic ring in sucrose in the presence of sodium periodate; this makes the oxidized sucrose available for bonding with starch molecule. The starch was first bleached with $H_2O_2$, the oxidized sucrose acting as a cross-linker between the starches molecules to create a cleavage that improves its mechanical properties. The introduction of glycerol helps to create a stronger covalent bond between the oxygen atom from starch and the oxygen atom from glycerol which then replace the weak covalent bond in the hydroxyl group of starch. This overall bonding could be linked to the improved plasticity of modified starch film.

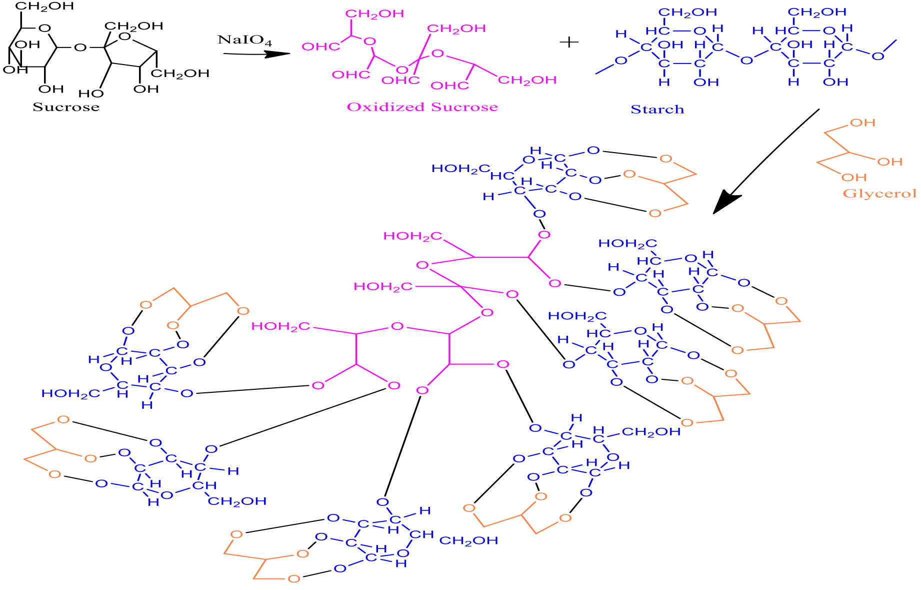

**Figure 1.** Mechanism of modified starch film with oxidized sucrose, glycerol and hydrogen peroxide

**Table 1**. Changes in Transparency of the Films at various hours and intervals of 24 hours

| | | | | Exposure Time (Hours) | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Process parameters | | | | 0 | 24 | 48 | 72 | 96 | 120 |
| Samples | Temperature | Time | Amount of Glycerol (ml) | Degree of Transparency (%) | | | | | |
| 1 | 70 | 5 | 0 | 95.544 | 76.826 | 0 | 0 | 0 | 0 |
| 2 | 83 | 12 | 0.8 | 98.558 | 86.998 | 0 | 0 | 0 | 0 |
| 3 | 90 | 10 | 0.5 | 96.917 | 91.759 | 90.205 | 88.412 | 88.197 | 0 |
| 4 | 80 | 5 | 0.5 | 98.558 | 91.23 | 54.291 | 0 | 0 | 0 |
| 5 | 80 | 15 | 0.5 | 97.169 | 91.23 | 81.677 | 0 | 0 | 0 |

### 3.2 Transparency

As shown in Table 1 above, five samples of oxidized starch films were produced at different temperatures, times, and amounts of glycerol. The oxidized sucrose and hydrogen peroxide were kept constant due to almost fixed-point effects during this study's preliminary experiment on the starch modification, as seen in Table 1 above. Figure 2 shows the result of the transparency after the immersion in water and measurement were taken at intervals of 24 hours. From the preliminary study, starch film formation begins at a temperature of 70 $^{o}$C. No glycerol was added to sample one (control sample), which has the least transparency of 95.54 %, after 24 hours immersion in water it transparency dropped to 76.82 %, and at 48-hour water immersion, the starch film experienced disintegrations (figure 3); hence it was no longer considered fit for transparency. Sample two and four both have the highest transparency of 98.56 % at 0-hour water immersion, after 24 hours in water the transparency of sample two dropped to 87 % while that of sample four dropped slightly to 91.23 %. On further immersion in water, sample two began to disintegrate (figure 4) while the transparency of sample four dropped sharply to 54.29 %, sample four recorded disintegrations (figure 5) at 72 hours of water immersion. Sample three had a transparency of 96.72 % at 0 hour of water immersion, a slight drop in transparency (91.76 %) was observed at 24 hours of immersion in water, another slight drop in transparency (90.2 %) was also observed at 48 hours water immersion. Transparency of 88.41 % was recorded at 72 hours in water while there was no significant change in the transparency (88.2 %) at 96 hours of water immersion, sample three experienced disintegration (figure 7) at 120 hours. For the industrial application of cassava starch film where transparency is important, sample three is considered to be the best due to its ability to retain a high percentage of its transparency up to 96 hours in water, however, previous studies failed to examine this important property of starch film.

### 3.3 Water Absorption Analysis

The water absorption analysis was carried out in order to determine the extent to which the film material can retain its properties before it completely dissolves in water. This can also be used to determine its area of application. The result in Table 2 and Figure 2 shows that sample one has the least percentage weight loss of 4.38 % at 24 hours of immersion in water, on further immersion in water material completely dissolved in less than 48 hours. The result of sample three is of utmost interest as it experiences only 14.38 % at 24 hours of immersion in water, 23.28 % weight loss at 48 hours, 31.5 % weight loss at 72 hours in water, and 52.05 % weight loss in water at 96 hours. The ability of sample three to retain a high proportion of its weight in water over a long period could be attributed to the overall contributory effect of oxidized sucrose, hydrogen peroxide, glycerol, as well as the high reaction temperature (90 °C), which enhanced the proper bonding of the starch film. Pawinee and Natchanan (2019) reported that the water solubility of cassava starch film modified with glycerol ranges from 10 to 36 % in 24 hours of water immersion. This shows that there is a significant improvement in the water solubility of the oxidized cassava starch film produced in this study and that it can be recommended for use where water solubility is less desired in starch film.

**Table 2**. Weight variation of the films at various hours at intervals of 24 hours

| Process parameters | | | | Exposure Time (Hours) | | | | |
|---|---|---|---|---|---|---|---|---|
| | | | | 24 | 48 | 72 | 96 | 120 |
| Samples | Temperature ($^{o}$C) | Time (Min) | Amount of Glycerol (ml) | Degree of weight lost (%) | | | | |
| 1 | 70 | 5 | 0 | 4.375 | - | - | - | - |
| 2 | 83 | 12 | 0.8 | 50 | - | - | - | - |
| 3 | 90 | 10 | 0.5 | 14.38 | 23.28 | 31.5 | 52.05 | 0 |
| 4 | 80 | 5 | 0.5 | 42.85 | 61.9 | - | - | - |
| 5 | 80 | 15 | 0.5 | 18.18 | 30 | - | - | - |

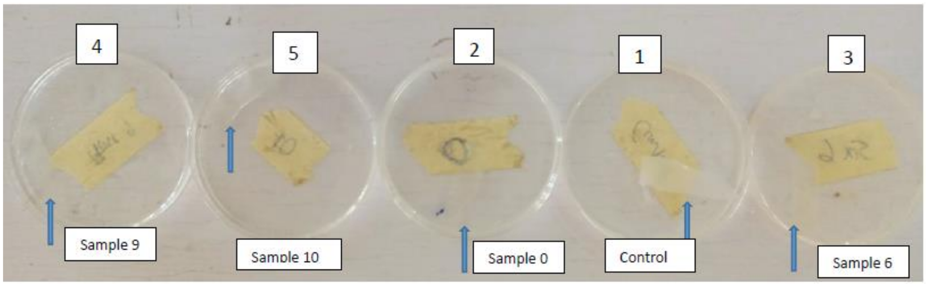

**Figure 2**. Nature of the films at 0 hour of water immersion

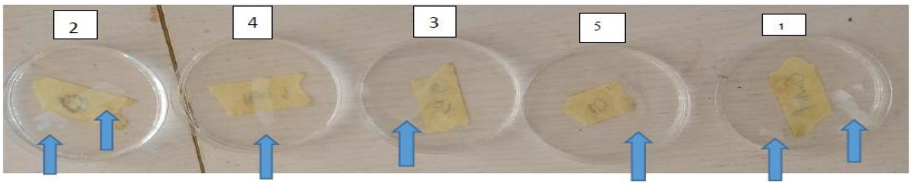

**Figure 3**. Nature of the films after 24 hours of water immersion

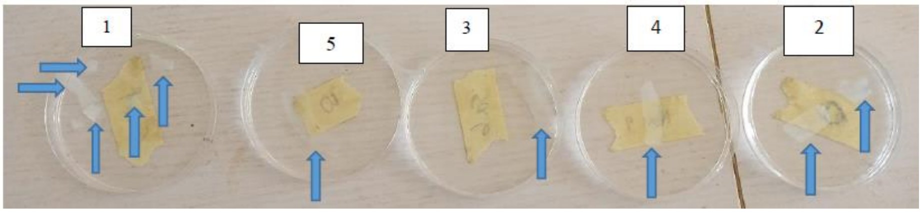

**Figure 4.** Nature of the films after 48 hours of water immersion

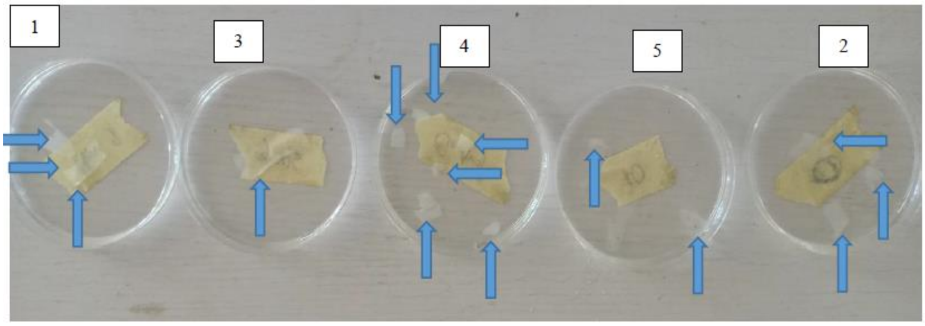

**Figure 5.** Nature of the films after 72 hours of water immersion

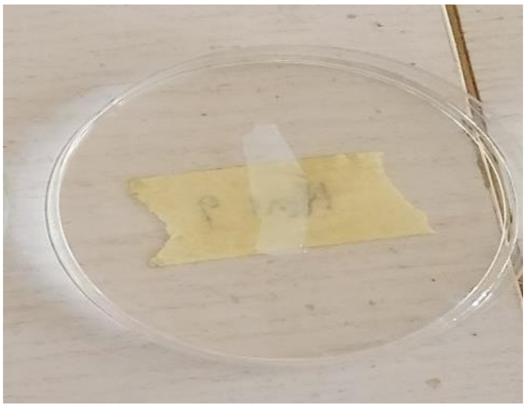

**Figure 6**. Nature of film (Sample 3) after 96 hours

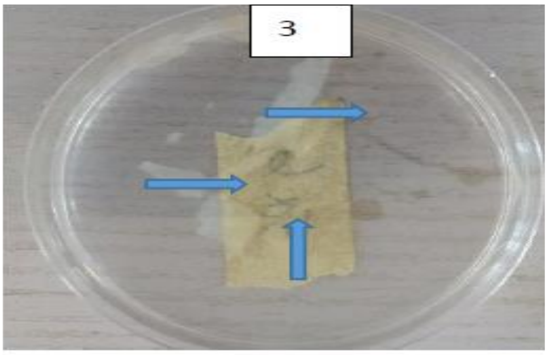

**Figure 7**. Nature of film (Sample 3) after 120 hours of water immersion

### 3.4 TGA of Starch film

Thermal gravimetric analysis helps to understand the behavior of a material on exposure to heat (Brown, 2007). Table 3 below shows the percentage weight of starch film samples that are retained at different temperature exposures. Sample 5 has the highest capacity to retain 99 % of its weight at temperature of 150 °C while both samples 3 and 4 have 98 % weight retention at the same temperature. On further exposure of the samples to temperatures up to 300 ˚C, sample 5 has the highest weight retention of 98 % while sample 3 has the least weight retention of 82 %. Significant weight loss started on all the samples when the temperature was raised to 360 ˚C and above.

**Table 3:** Weight variation of oxidized starch film on thermo-Gravimetric analysis

| | ` Weight Retained (%) | | | | |
|---|---|---|---|---|---|
| Temperature (ºC) | Sample 1 | Sample 2 | Sample 3 | Sample 4 | Sample 5 |
| 30 | 100 | 100 | 100 | 100 | 100 |
| 150 | 98.4 | 97 | 98 | 98 | 99 |
| 300 | 95 | 91 | 82 | 92 | 98 |
| 360 | 70 | 67 | 60 | 26 | 70 |
| 390 | 51 | 57 | 50 | 15 | 55 |

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Figure 8 shows the graphical representation of the percentage weight retained at various exposure temperature of all the oxidized starch film samples. Earlier studies did not report the thermal stability of starch film. The loss of moisture content of both uncross-linked and cross-linked starch film was first recorded at 150 $^0$C due to evaporation, this is referred to as first stage decomposition. Wang et al. (2018) reported first-stage decomposition for both potatoes cross-linked and uncross-link starch film at 100 ˚C. The polymer chain dehydration of the second stage decomposition for both starches was observed between 300 and 400 ˚C. This is higher than the 150 and 300 °C second stage decomposition by Wang et al. (2018). The final stage decomposition temperature of 900 °C in this study is higher than the 600 $^0$C reported by Wang et al. (2018).

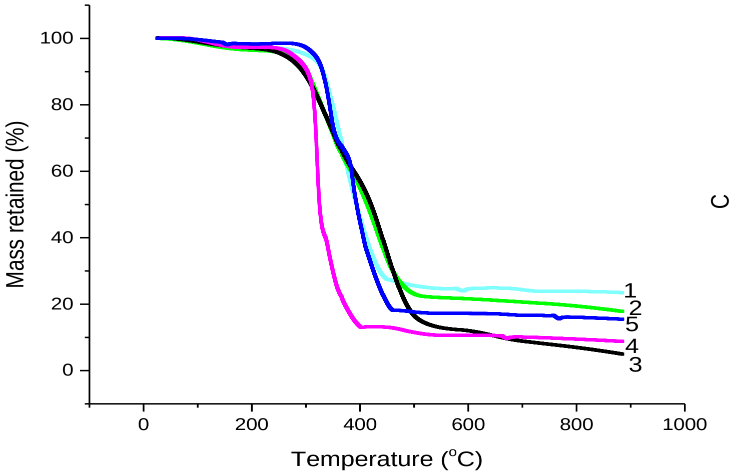

**Figure 8.** Mass retained against exposure temperature of cassava starch film

Figure 9 presents the DTG plots, which provide information on the maximum weight loss rate in relation to the peak temperature ($T_P$). The $T_p$ of the uncross-linked starch film in this is 374.13 ˚C, while that of the cross-linked samples are 385.51, 420.75, 324.42, and 385.32 ˚C respectively. In contrast, it shows that the decomposition of uncross-linked starch film occurs before samples 2, 3 and 5. This implies that bleaching and cross-linking yields a better-ordered structure of the starch, increasing its crystallinity and reducing decomposition rate on heating. However, the decomposition of the uncross-linked starch occurs after that of sample 4. This implies that bleaching and cross-linking led to a reaction that caused modification of order of the starch structure, hence it readily decomposes with an increase in temperature. Wang et al. (2018) reported Tp of 306.1 ˚C for uncross-linked potato starch film and 265.6 to 275.7 ˚C for cross-linked potato starch film. This shows that in terms of thermal stability, cross-linked cassava starch film in this study has better performance.

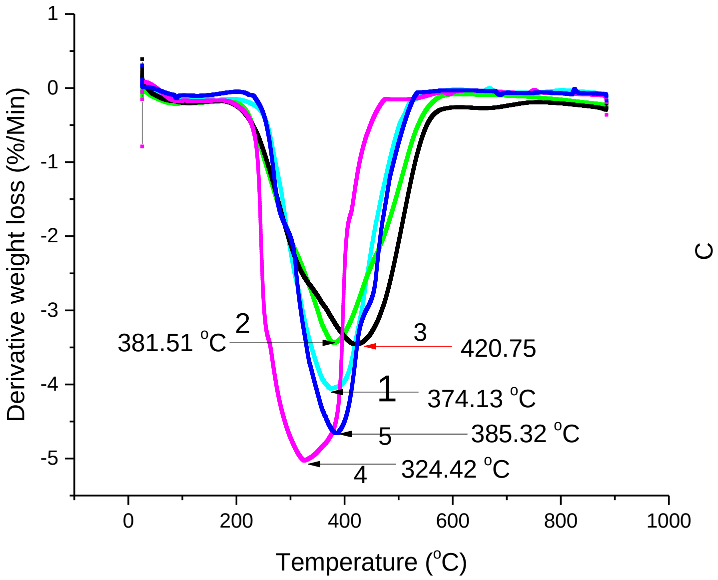

**Figure 9:** Derivative weight loss against Peak Temperature

## 3.5 Implications of the Results of the study of Agri-food security

The development of bleached and cross-linked cassava starch films shows promise for enhancing agri-food security through sustainable packaging solutions (Jeyasubramanian & Balachander, 2016; Rosseto et al., 2019). These films offer a balance between durability and biodegradability, providing a viable alternative to conventional plastics, thus contributing to a more resilient and sustainable food system. The results obtained from this study on the effect of bleaching and cross-linking cassava starch film with oxidized sucrose have several implications for agri-food security. Studies have shown that biodegradable films made from natural polymers like starch can significantly reduce reliance on petrochemical-based plastics, thus contributing to a more sustainable food packaging industry.

The high transparency retention of 88.2% after 96 hours of water immersion suggests that the cassava starch film can be used as a sustainable and biodegradable packaging material. Transparency is often important for food packaging as it allows consumers to see the product, which can be crucial for marketing fresh produce. Durable and water-resistant packaging can help in maintaining the quality and freshness of food products by providing better protection against environmental factors. Improved water resistance and thermal properties extend the usability of these films in various climatic conditions, supporting food security by preserving food quality and reducing waste.

The significant weight loss of 52.02% indicates that the film is biodegradable. This benefits agri-food security by reducing environmental pollution caused by conventional plastic packaging, promoting a more sustainable food system. Moderate water solubility can be advantageous for specific applications where controlled degradation of the packaging is desired, such as single-use packaging that does not require long-term durability. The biodegradability of cassava starch films helps mitigate the environmental impact of plastic waste, aligning with global efforts to enhance agri-food security through sustainable practices.

The thermo-gravimetric analysis (TGA) showed a temperature peak (Tp) of 420.75°C for the treated film, compared to 374.13°C for the control sample. Improved thermal stability means the cassava starch film can withstand higher temperatures without degrading. This is crucial for various food processing and storage stages, where thermal resistance can prevent the packaging from breaking down or compromising the food's safety and quality. Enhanced thermal stability broadens the range of applications for the cassava starch film, making it suitable for packaging food items that require high-temperature sterilization or are stored in warmer environments.

Integrating digitalization technologies into the study of starch modification will enhance research efficiency, sustainability, and innovation in developing non-toxic and high-performance starch-based materials for various industrial applications by allowing for advanced simulations and modeling of chemical processes involved, which could streamline experimental designs, optimize conditions and reduce the need for trial and errors. Automation in experimentation can be enabled through robotics and smart sensors. Digitalization supports sustainability initiatives by optimizing resource use and reducing waste in the starch modification processes.

## 4. Conclusions

Bleaching of cassava starch with $H_2O_2$ brought about improvement on the transparency of the film. This study adopted oxidized sucrose (polyaldehide) for cross-linking of bleached cassava starch. Both bleaching and oxidation of the starch occurred at different operating temperatures, times, and amounts of glycerol, which produced bleached, oxidized cassava starch film. The sample 3 starch film synthesized at treatment temperature of 90 ˚C, in 10 Mins with 0.5 ml of glycerol gave the best transparency ranging from 96.9 % at 0-hour water immersion to 88.2 % at 96 hours of continuous water immersion. The unbleached, unoxidized starch film has poor transparency retention on prolonged exposure to water as 95.54 % transparency was recorded at zero-hour water immersion 76.82 % transparency at 24 hours of water exposure, while further water exposure results in significant degradation of the film.

The unbleached, unoxidized starch film showed poor weight retention after prolonged water immersion. 4.38 % weight loss was recorded at 24 hours of water immersion, after which significant degradation was observed. Sample 3 has the best water stability, with a minimum weight loss of 14.38 % at 24 hours in water immersion and 52.05 % at 96 hours. The bleached, cross-linked cassava starch film of sample 3 in this study has the best thermal stability with Tp of 420.75 ˚C while unbleached, unoxidized cassava starch film has lower thermal stability with 374.13 °C.

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