Synthesis and Characterization of Green Binder from Cassava root as Input for Paper Packaging Industries

Selam Tsegaye Hagos

A Thesis Submitted to

The Department of Chemical Engineering

School of Mechanical, Chemical and Materials Engineering

Presented in Partial Fulfillment of the Requirement of the Degree of Master's in Chemical Engineering (Specialization in Process Engineering)

Office of Graduate Studies

Adama Science and Technology University

June, 2024

Adama, Ethiopia

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DECLARATION

I hereby declare that this Master's thesis entitled "**Synthesis and Characterization of Green Binder from Cassava root as Input for Paper Packaging Industries**" is my original work and That is, it has not been submitted for the award of any academic degree, diploma or certificate in any other university. All sources of materials that are used for this thesis have been duly acknowledged through citation.

Selam Tsegaye _____ _____

Name of student Signature Date

RECOMMENDATION OF ADVISORS

I, the major advisor of this thesis, hereby certify that I have read the revised version of the thesis entitled "**Synthesis and Characterization of Green Binder from Cassava root as Input for Paper Packaging Industries**" prepared under my guidance by Selam Tsegaye submitted in partial fulfillment of the requirements for the degree of Mater's of Science in Chemical engineering (Specialization in Process Engineering). Therefore, I recommend the submission of a revised version of the thesis to the department following the applicable procedures.

Melaku Tesfaye (Ph.D.)	_____	_____
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Co-advisor	Signature	Date

APPROVAL BOARD OF EXAMINERS

We, the advisors of the thesis entitled "**Synthesis and Characterization of Green Binder from Cassava root as Input for Paper Packaging Industries**" and developed by Selam Tsegaye, hereby certify that the recommendation and suggestions made by the board of examiners are appropriately incorporated into the final version of the thesis.

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Co-advisor	Signature	Date

We, the undersigned, members of the Board of Examiners of the thesis by Selam Tsegaye have read and evaluated the thesis entitled "**Synthesis and Characterization of Green Binder from Cassava root as Input for Paper Packaging Industries**" and examined the candidate during open defense. This is, therefore, to certify that the thesis is accepted for partial fulfillment of the requirement of the degree of Master of Science in Chemical Engineering (Specialization in Process Engineering).

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LIST OF ACRONOMYS AND ABBRIVATIONS

ASTM	American Society for Testing and Materials
DMSO	Dimethyl Sulfoxide
DO	Degree of Oxidation
FTIR	Fourier Transmission Infrared Spectroscopy
mS	Modified Starch
nS	Native cassava
OCS	Oxidized cassava starch
NCS	Native cassava Starch
TGA	Thermogravimetric Analysis
XRD	X-ray diffraction
DSC	Differential Scanning Calorimetry
UTM	Universal testing machine
SEM	Scanning electron microscope
PF	Phenol-formaldehyde
UF	Urea-formaldehyde
RSM	Response Surface Methodology
CCD	Central composite design
ANOVA	Analysis of Variance
ISO	International Organization for Standardization

ABSTRACT

Starch is a renewable, biodegradable, and relatively inexpensive natural polymer that originates from different plant sources which attracted much attention in applications of food, binders , additives, and adhesives, because of its non-toxicity, renewability, abundance, and good adhesion. It is widely used in the paper packaging industry but, it cannot provide sufficient strength and durability required for packaging material, because, it consist of long chains of glucose units that are held together by relatively weak intermolecular forces. Native starch also reacts easily with water molecules to form hydrogen bonds, leading to poor water resistance. Non-renewable petroleum-based synthetic binders, such as polyvinyl acetate or SB and SA latex binders, have been widely utilized as binders in paper and packaging applications to increase mechanical qualities. In comparison to their sustainable equivalents, non-biodegradable polymers hinder the biodegradability of paper and make recycling more difficult. Additionally, the prices are expensive. Therefore, it is found essential to modify starch to upgrade its binder performance for different applications and to replace petroleum derivative adhesives which contain carcinogenic, hazardous, and toxic compounds of formaldehyde. In this study, the starch of Cassava (Manihotesculenta Crantz) was extracted using a modified procedure, and its functional modification was done by the oxidation method. The oxidized starch with different degrees of oxidation (Do) was prepared by reacting native cassava starch with Hydrogen peroxide using Copper(II) sulfate pentahydrate as the catalyst. The experiment was designed by central composite design with three factors (the reaction temperature, reaction time and catalyst loading) that affect the degree of oxidation. The experiment found that the optimal degree of oxidation was 56.1%.The FT-IR analysis confirmed the introduction of the carbonyl group in the oxidized starches through a band at 1695 cm-1. X-ray diffraction (XRD) analysis of oxidized starch showed that the crystal structure of native starch was changed to an amorphous state. Scanning electron microscopy (SEM) suggested that starch granules start to rupture different sizes of cracks are formed on their surfaces when oxidation takes place and eroded surface appearances are observed to make a rougher surface than native starch. The thermal analysis of the native and oxidized starch was studied using thermo gravimetric (TGA) analysis and differential thermal analysis (DTG), it was found that the thermal stability of oxidized starch depends on the degree of oxidation. This characterization confirmed the occurrence of structural modification on native cassava starch (NCS) due to the introduction of the carbonyl group. The sample paper, produced using oxidized starch as a sizing agent, was shown to have a base weight of 126 g/m², burst strength of 2.7 kg/cm², breaking length of 3915 m, tear factor of 126.9 m Nm²/gm, tensile strength of 7.4 kg, and porosity of 13 sec. The sample paper, when using oxidized starch adhesive, was shown to have burst strength of 8.5 kg/cm² and crush strength of 28 lb, exceeding the standard values of 7.8 kg/cm² and 25 lb, respectively. This demonstrated improved performance in both metrics.

Keywords: Starch, Oxidation, degree of oxidation, Oxidized starch, Binders

CHAPTER ONE

1. INTRODUCTION

1.1. Background of the study

One of the global industries with(Reddy et al., 2013)the quickest rate of growth is adhesives. Based on data from Globe Newswire (2023), the adhesive industry is estimated to develop at a compound yearly growth rate of 4.9% between 2022 and 2030, reaching a projected market size of around US $63.9 billion by that time. They are widely used in many different industries, including electronics, shipbuilding, wood processing, the paper packaging business, construction, and the aerospace and automobile industries.

Today, petrochemical resources like urea, phenol, and melamine formaldehyde are used to make most commercial adhesives. These resources emit formaldehyde gas and volatile organic compounds that are harmful to both human health and the environment. People are becoming more interested in bio-based adhesives as a way to reduce environmental pressures and address health concerns as petrochemical resources continue to run out and environmental consciousness increases(Arias et al., 2021).

Reddy et al., (2017), state that the possibility of synthesizing polymeric materials from bio-based, renewable resources has received a lot of interest due to growing environmental awareness and the need to reduce dependence on petroleum resources. When discussing adhesive technology, there has been a resurgence of interest in traditional bio-based binders, including starch or renewable rubber. Additionally, there has been an exploration of newer technologies such as the utilization of modified vegetable oils or derivatives of lignin for the synthesis of binders. Whether used in the packaging line or during conversion, adhesives are essential to the structure of most paper and paper board packaging(Altay et al., 2021).

Paper is an excellent material for various applications due to its biodegradability, lightweight, and recyclability. For the production of paper, firstly suitable fibers are needed for end use. Then the filling material, binder and additional materials are required. With the development of the paper industry, great attention has been paid to improving the properties of paper in cost

cost-effective fashion. Paper and board materials made of paper are currently used in e-commerce and food product packaging (Gadhave et al.,2022).

Globally, paper companies apply chemical binders during the paper-making process to attain the target tensile strength of paper. The mechanical and thermal properties of paper and packaging have been enhanced by the widespread use of non-renewable petroleum-based synthetic binders, such as acrylamide, acetaldehyde, urea-formaldehyde, and vinyl acetate. polyvinyl acetate or SB and SA latex binders, as coating binders (Zhu et al., 2018).Compared to their sustainable counterparts, non-biodegradable polymers make recycling paper more difficult and reduce its biodegradability. Paper manufacturers, who utilize SB latex for approximately 35% of global consumption, are forced to face higher production costs due to the rising cost of these petroleum-based materials, which are influenced by both political and economic factors. Sustainable solutions with minimal environmental impact are what paper companies are searching for (Altay et al., 2021)**.**

Different types of bio-based raw materials have been investigated for use in bio-based adhesives as a means of addressing these issues. Plant oils, protein, lignin, tannin and starch are some of these renewable resources. Because of its non-toxicity, abundance, renewability and good adhesion Starch a naturally occurring polymer derived from various plant sources has gained significant attention in the food, paper making, additive, and adhesive industries. It is also relatively inexpensive and biodegradable (Wang et al., 2019).It consists of two distinct polysaccharide components, amylopectin and amylose, which are both made of a glucose monomer with varying sizes and shapes. It is a promising resource for the production of adhesives. Depending on the starch's botanical origin, the ratio of amylose to amylopectin varies, which has an impact on the adhesive's properties (Antov et al., 2020).

Starch is a valuable resource for the paper industry because it is abundant and at a low cost. In general, the paper industry is the largest nonfood application of starches when viewed globally. Nowadays, the majority of starch used in the paper industry is applied on the surface. These mainly consist of pigment coating, functional coating, and surface sizing (Li et al., 2019). However, Starch does not have physical and chemical properties suitable for certain type of processing in its native form due to their poor shear and thermal stability and high degree of retro gradation. Furthermore, native starches can easily undergo syneresis besides

the gelling tendency of the pastes. Therefore, the applications of starch in various industries like food, paper, and textile can be increased by adopting various techniques of modification. To enhance starch's use in the paper packaging industry, its physiochemical and physical-mechanical qualities can be tailored to match the specifications needed for the final system. There exist four fundamental forms of starch modifications: chemical, physical, enzymatic, and genetic (Oyeyinka et al., 2020).Among the advantages of starch oxidation modification for the paper industry are lower costs, better adhesion, stronger materials, and enhanced water resistance. In the paper industry, oxidation modification is viewed as a competitive and promising way to modify the properties of starch because of these advantages. Grain and root crops such as sweet potatoes, maize, wheat, rice, yams, cassava stems, and cassava roots are sources of starch (Zhang et al., 2012).

Cassava starch is a widely utilized crop in Ethiopia, particularly in the southern regions of Wolaita and Sidama (Raya et al., 2022).Different studies on cassava starch have brought the possibility of using cassava starch as pharmaceutical excipients, sizing agent, and nutritional potential as alternatives to common starches e.g. corn and potato. However, there is a lack of comprehensive research and development efforts specifically targeted at optimizing cassava starch as a green binder for paper packaging applications. Moreover, according to the Ethiopian Revenue and Customs Authority (2020), the country met binder demand through importing from abroad. Therefore the research on the synthesis and characterization of green binder from cassava starch for the paper industry mainly focuses on the modification and optimization of cassava starch properties to improve its suitability for papermaking. The research highlights the potential of cassava-based binders in meeting the needs of the paper industry, including environmental conservation, cost-effectiveness, and enhanced durability.

1.2. Statement of the problem

Paper manufacturers use chemical binders all around the world to attain the desired tensile strength for their paper. Acrylamide, urea-formaldehyde, vinyl acetate, and acetaldehyde are a few of the components of these binders. These resources emit formaldehyde gas and volatile organic compounds that are harmful to both human health and the environment (Altay et al., 2021).Compared to their sustainable counterparts, non-biodegradable polymers make recycling more difficult and reduce the biodegradability of papers. Depending on increases in the price of oil, which have an impact on the economy and politics, the cost of these petroleum-based commodities rises. Researchers have looked into substitutes for synthetic paper binders (Gadhave & Gadhave, 2022).

Starch is a renewable, biodegradable, versatile, and useful polymer in process industries, not only because is not expensive but also easy to alter its physicochemical properties through modification for the diverse application in industries including adhesive, pharmaceuticals, plastic,, and textile, beverage, building materials, paper, and dye (Krithika & Ratnamala, 2019).About 60% of Ethiopia's starch needs are met by imports from other Countries, according to the paper packaging sector (Ashebir, 2022). Data gathered from the various manufacturers that were investigated makes it abundantly evident that these local PLCs that extract starches provide 40% of the total starch that the various factories that were surveyed require. This suggests that Ethiopia's paper packaging sector depends heavily on imported starch. In general, starch is imported from a variety of nations, primarily China and India. Ethiopia's paper packaging sector imports starch for USD 2.1 million in foreign currency.

There is a lack of research on synthesizing cassava-based binders from cassava starch for paper packaging industries. There is a growing demand for sustainable and cost-effective alternatives to synthetic chemical binders. To address this, it is crucial to understand modification techniques, optimize the synthesis process, and characterize the properties of cassava starch-based binders. This investigation aims to improve the suitability of these green binders for paper packaging applications, meeting the industry's need for sustainable alternatives.

1.3. Research Questions

The research question for the synthesis and characterization of green binder from cassava root for paper packaging industries could be:

- RQ1.How can starch -based materials are effectively synthesized and utilized as binders for eco-friendly and sustainable paper packaging in the food industry?
- RQ2 .What are the key properties of cassava stem -based binders that make them suitable for paper packaging, and how do these properties compare to traditional petroleum-based packaging materials?
- **RQ3**. In what ways can the synthesis of cassava root-based binders contribute to the development of circular economy principles in the paper packaging industry?

Based on the above research questions the choices of the systems are framed as follows

Cassava root starch is selected as the main raw material due to:

- Its availability, low cost, and desirable functional properties, such as low gelatinization temperature, high viscosity, and clear paste formation, make it a suitable binder for paper packaging

1.4. Objectives of the Study

1.4.1. General Objectives

The main objective of this study was extraction and functional modification of Cassava root as a green binder for paper packaging Industries.

1.4.2. Specific objectives

The specific objectives of this research are

- To conduct the extraction of starch from cassava root and its perspective proximate analysis
- To optimize the reaction parameters (temperature, time, catalyst loading) using response surface methodology to achieve the desired functional properties of the modified cassava root starch for binder synthesis

- To carry out physicochemical characterization of native cassava starch and oxidized cassava starch
- To Validate native and modified cassava starch using characterization instruments (FTIR,XRD,TGA , and SEM)
- To study the effect of starch-based binder on the paper quality using tensile strength, porosity, and contact angle measurements, to assess the suitability of the binder for paper packaging applications

1.5. Significance of the study

The significance of the study lies in its potential to advance the field of green binders by exploring the extraction and functional modification of cassava root starch for the development of a starch-based binder for paper packaging.

This study aims to fulfill the crucial requirement for an environmentally friendly binder, thereby making a substantial contribution toward minimizing the environmental footprint of the packaging industry. Additionally, it focuses on developing a binder that offers cost-effectiveness and easy recyclability, making it a preferable alternative to petroleum-based binders. The paper packaging industry often relies on imported starch binders, which contributes to foreign currency expenditure. By utilizing cassava root, which is easily grown in our country Ethiopia, as a substitute for starch binder, our country can reduce their reliance on imports and decrease their foreign currency costs. The study aims to offer a renewable and biodegradable alternative to traditional petroleum-based packaging materials, potentially leading to a positive impact on both the environment and the industry. Furthermore, the development of sustainable packaging solutions aligns with the growing global emphasis on environmental sustainability, offering potential benefits to society and creating opportunities for eco-friendly packaging innovations in the market.

1.6. Scope of the Study

The scope of this proposal work mainly focuses on the extraction and characterization of cassava root starch. The first step involves the extraction of starch from cassava roots, followed by the characterization of both the native and modified starch. The modification process aims to investigate the effects of various processing parameters, including reaction

temperature, reaction time, mixing ratio, and catalyst loading. To assess the structural and chemical changes in the starch instrumental techniques such as Scanning Electron Microscope (SEM), Fourier Transform Infrared Spectroscopy (FTIR), X-ray Diffraction (XRD), and Thermo Gravimetric Analysis (TGA) are employed. These techniques provide valuable insights into the morphology, functional groups, crystalline, thermal behavior, and degradation properties of the modified and native cassava root starch. Furthermore, the study involves the synthesis of a binder using cassava roots starch as a key component. The effect of the modified starch on the properties of the binder is investigated. This includes assessing its tensile strength, burst strength, porosity properties and contact angle measurement and performance as a binder in paper packaging.

CHAPTER TWO

2. LITERATURE REVIEW

2.1. Biopolymer

Biopolymers are organic compounds that are present in natural sources. The Greek terms "bio" and "polymer," which stand for nature and living things, are the source of the phrase biopolymer. (Jaya et al., 2022).Today's global economy is reliant on fossil hydrocarbon resources, which provide the raw materials for a variety of chemicals and materials used in the production of items for sale(Imam et al., 2013).Biopolymers are sustainable, harmless to the ecosystem, and biodegradable materials, which can be utilized as an ideal substitute for petrol-based polymers that are manufactured (Oliveira et al., 2020).

The majority of renewable polymers are structural polymers, which comprise proteins obtained from agriculture, cellulose, oils, latexes, carbohydrates, and their derivatives. Among the different biopolymers, starches are the most bountiful class of macromolecules. These polymers are highly desirable raw materials for use in consumer goods, specialty chemicals, pharmaceuticals, tissue engineering products, biomedical devices, nanocomposites, bioplastics, packaging, binders, building materials, automotive products, enhanced oil recovery aids, functional foods, and wood adhesives because of their distinctive macromolecular features and range of functional qualities(Shen et al., 2014).

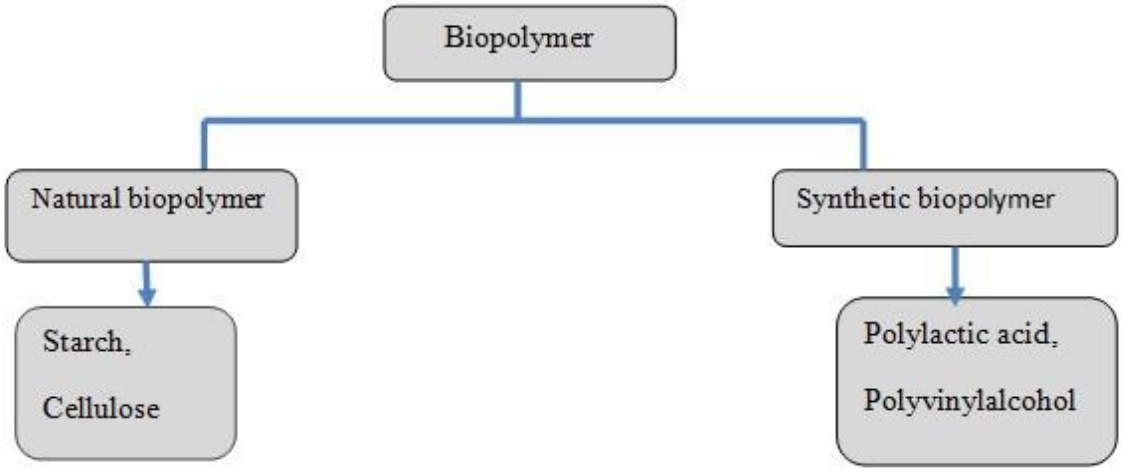

Figure 2-1Classification of biopolymers based upon their origin

2.2. Starch

Starch, composed of glucose monomers, is a significant component in human diets and finds extensive applications in various industries, including food, paper, clothing, and construction. Regardless of its source, starch is considered an excellent choice for the development of biodegradable food packaging. Edible sources of starch, such as corn, sweet potato, cassava, potato, and wheat, are commonly used to create starch-based biodegradable packaging materials (Weligama Thuppahige et al., 2023).

In comparison to petroleum-based polymers, starch is inexpensive, renewable, and easily processed. Its main benefit is that it can be processed like that of synthetic polymers, but it is also biodegradable and has a lower greenhouse gas impact. As a result, the utilization of starches from diverse sources has gained popularity for several innovative, non-food uses, including the production of adhesives, coatings, polymers, and bio composites (P. Choi,.2015).Specifically, starch is a very promising bio macromolecule for the creation of a wide range of materials with various special physicochemical properties that make them appropriate for several applications (Wondimu et al., 2014). To explore the industrial applications of starch, it is essential to understand its structure and key properties.

2.2.1. Structure of Starch

Starch is a naturally occurring polymer with a very high molecular weight and the formula $C_6H_{10}O_5$ (Salt et al., 2019).Starch is composed of two types of glucan polymers: amylose and amylopectin. Amylopectin has a significantly higher molecular weight compared to amylose. On average, the size distribution of amylopectin peaks at around 108 Da , while the size distribution of amylose is approximately two orders of magnitude lower, around 106 Da (Bertoft, 2017).The Starch granules primarily consist of two major polysaccharides: amylose and amylopectin. Both amylose and amylopectin are composed of chains of D-glucose residues linked by α-(1,4) glycosidic bonds. Additionally, they have α-(1,6) glycosidic linkages that create branches within the polymers. Although amylose is traditionally considered to be linear, branched forms of amylose do exist, albeit with fewer branches. Both branched and linear amylose molecules have long chains consisting of hundreds or even thousands of glucosyl units. In most "normal" starch granules, amylopectin constitutes the major portion by weight, accounting for 70-85%, while starch granules (Apriyanto et al.,

2022).amylose makes up 15-30%. However, there are exceptions to this general composition in certain.

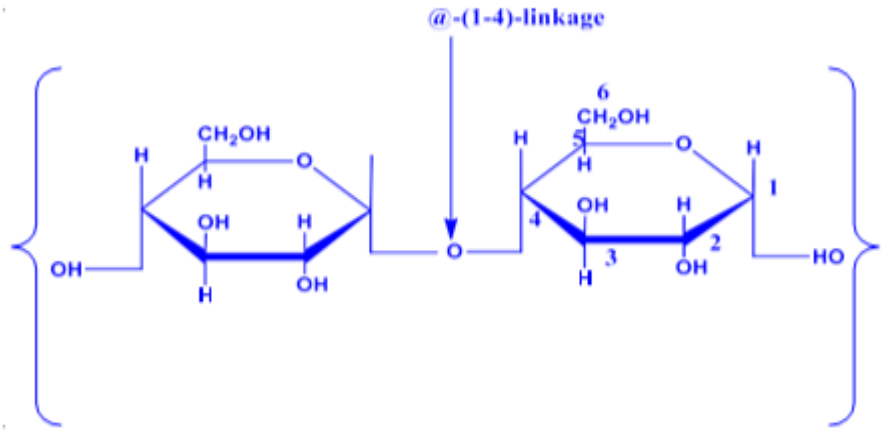

Figure 2-2 linear polymer, amylose (adapted from Somdech et al., 2016)

In contrast, amylopectin is the polysaccharide type that dominates in terms of quantity and largely controls the properties of the starch granule. On the other hand, there can be significant variations in the ratio of amylopectin to amylose (Apriyanto et al., 2022). Amylopectin exhibits a significantly higher degree of branching compared to amylose. Amylose is primarily composed of strictly linear polyglucans with α-1, 4 linkages, although it may contain a small amount of branching. In contrast, amylopectin is a complex mixture characterized by a large number of branches in addition to the α-1,4 linked linear segments. These branches, formed through α-1,6 linkages, contribute to the highly branched structure of amylopectin. A degree of polymerization (DP) ranging from 10 to 20 is created by surrounding α-1,4-linked glucan chains to form the double helices (Bertoft,2017).

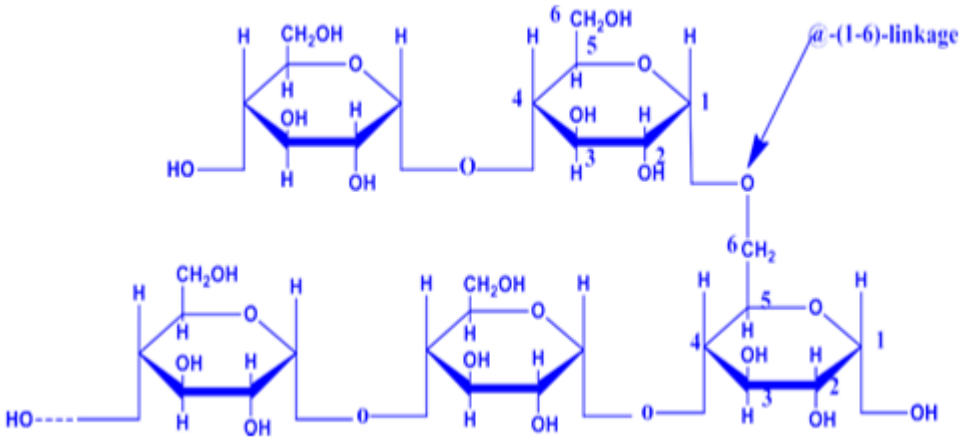

Figure 2-3the branched polymer, Amylopectin (Adapted from (Sorndech et al., 2016)

2.2.2. Functional properties of starch

Starch has several practical qualities and uses in the industrial and biomedical domains due to its compact structure. Starch has a comparatively lower water solubility and oil and water absorption capacity due to its polymeric and branching structure. The ability of starch to bind iodine is good. It also has good swelling power, gelatinization ability, and a reasonably high viscosity. Additionally; it can create thin films and has good pasting capabilities with consistency, smoothness, and clarity. Starch is a good option for a variety of food and industrial compositions because of its freeze-thaw and cold storage stabilities. While starch is vulnerable to hydrolysis by acids and enzymes, it is resistant to mild pressure and temperature. Nonetheless, the enzymatic digestibility values of native starches are comparatively lower (Boukhalfa et al., 2018);(Ajayi et al., 2016).The functional characteristics of starch can be enhanced by a number of physical and chemical processes, which will raise its nutritional, medicinal, and industrial significance (Oyeyinka et al., 2020).

According to Krithika & Ratnamala, (2019)To address these limitations and enhance the properties of starch, extensive research has been conducted on its physical and chemical modification. The most commonly studied methods for starch modification include derivatization through processes like etherification, esterification, cross-linking, and grafting. Additionally, starch can be modified through decomposition via acid or enzymatic hydrolysis, as well as oxidation. Physical treatments such as heat or moisture are also employed to modify starch (Krithika & Ratnamala, 2019).

2.2.3. Application and Uses of starch

Starch is an affordable, readily available, and versatile raw material for the large-scale biomaterial processing industry due to its physio-chemical properties and abundance. Approximately 35 % of all starch in Western nations is utilized as biopolymers in the food, textile, and paper sectors in either its original or modified form (Beckles & Thitisaksakul, 2016).

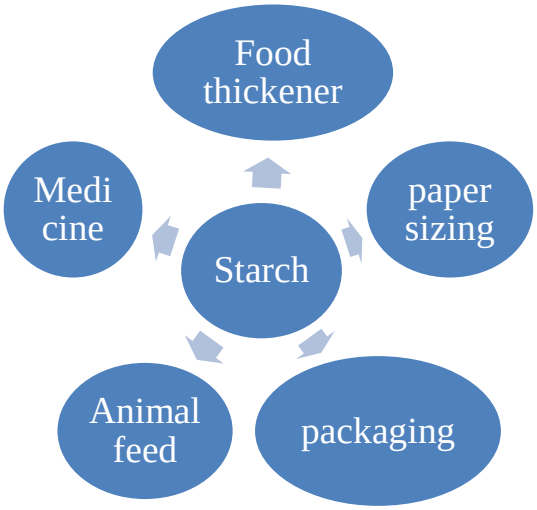

Figure 2-4 Uses of starch

Starch is used for a variety of purposes, including, thickening, stabilizing, texturizing, gelling, film formation, encapsulation, water retention, shelf life extension, coating, and sizing.

Starch as a coating agent

Starch is a readily available, biodegradable carbohydrate. Additionally, it has proven to be a viable and sustainable coating agent in substitute of polymer compounds derived from petroleum. However, starch needs to be modified to improve its low compatibility with other polymers, poor film-forming ability, and hydrophilicity (Z. Lin et al., 2019).

Starch as a sizing agent

Starch is the most often utilized surface-sizing agent in the paper industry, because of its molecular structural resemblance to cellulose, but because the majority of natural starches include a large number of hydroxyl groups, they can create powerful intra- and intermolecular hydrogen interactions. As a result, there is a significant increase in the contact between starch

molecules, which restricts the use of starch as a surface-sizing agent and causes issues like poor adhesion and film formation (Wei et al., 2021).

Starch as a thickening and stabilizing agent

Stabilizers are significant fixings in fabricated dairy items as a result of their capacity to further develop thickness and sensory properties. Stabilizers are synthetic, and many of them have a plant origin, which is considered the least expensive and incorporates the most generally utilized ones (Altemimi, 2018).

Starch as a Renewable Resource for Green binder and Bio-Adhesive

One of the most abundant organic substances is starch, which is used as a binder in the paper and pharmaceutical industries. It is a granulating agent, biodegradable, diluent, and adjustable polymer. Starch is a main raw material in glue and adhesive industries due to its abundantly available and low cost (Wei et al., 2021).Starch has a wide range of applications, including as a bonding agent and filler in tablet manufacturing. While starch is used in the rubber and foam sectors to achieve greater foaming and color, it is also utilized to increase recovery and extend the shelf life of detergents. Its distinct thermal, structural, and functional properties also make it a valuable element in the food, paper, and textile industries (Mohd et al., 2021).

2.2.4. Profiles on the Consumption of starch

The starch has been used in various industries including the manufacturing of textile, paper, and pulp adhesives, pharmaceuticals, flowers, food complexes, and so on. Industries use the product mainly as binding, packing, diluting adhesive, water absorber agent, and sweetener in their production process. The source of supply of starch is imported as well as local, in which 14 productions in the country is insignificant. Data collected from the surveyed different factories has clearly pointed out that these local starches extracting PLCs do supply 40 percent of the total starch demanded by the different factories surveyed. This clearly shows a greater sum of starch is imported from foreign starch extracting factories and as such substantial amount of hard currency is spent for importing about the remaining 60% of the starch demanded by local industries. There is the sense of a growing demand for starch in the international market and Statistics data illustrates a rising increase of starch imports into Ethiopia. A total of 2,658,577 kg of starch is needed as a total demand for Ethiopia.

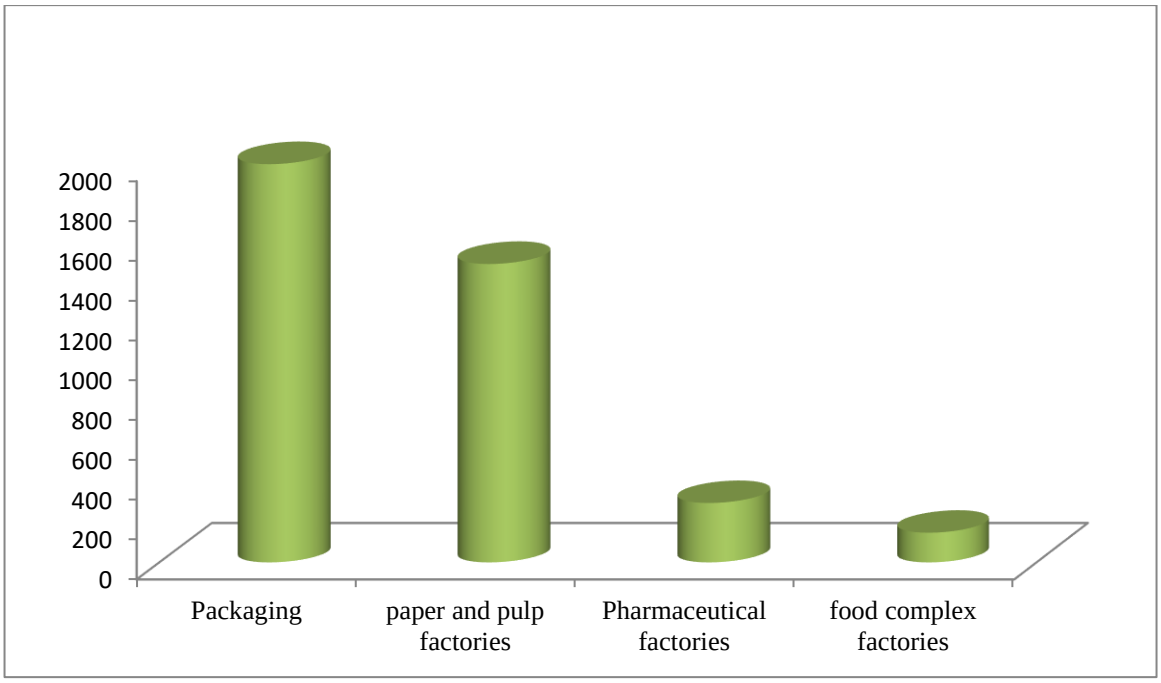

Figure 2-5 Yearly demand of each factories for starch (in kilograms)

2.3. Cassava (*ManihotesculentaCrantz*)

Cassava (*ManihotesculentaCrantz*),commonly known as tapioca, manioc, or yucca, is a perennial crop that belongs to the Euphorbiaceae family. It is primarily cultivated in tropical and sub-tropical regions around the world (Tafesse et al., 2021).Cassava is a tropical crop that is thought to have originated in the Amazon. Cassava is grown either as an isolated crop or in combination with other plants such as oil palm, rubber, vegetables, legumes, and maize. When plants are planted in mixed beds, the risk of damage from pests and bad weather is distributed among plants with varying susceptibilities. One typical tropical plant is cassava. Its culture can be roughly defined as being between 30°N and 30°S latitudes; nevertheless, the majority of cassava growing occurs between 20°N and 20°S. The crop generally needs a warm, humid climate. Temperature matters because, at roughly 10ºC, all growth ceases (Helanto et al., 2019).

Figure 2-6 Cassava root

Cassava (*Manihotesculenta* Crantz) is a critical industrial crop in many tropical and subtropical areas including South America (e.g. Brazil), Africa (e.g. Nigeria), and Asia (e.g. Thailand) (Omojola, 2013). The roots of cassava are rich in starch and approximately half of the total roots produced are utilized for starch production. Although corn has been the leading crop for starch production more than 80% of the worlds starch production. Cassava starch has many advantages compared to other crops including higher starch accumulation capacity, year-round availability, economical price, resilience to drought, poor soil factors, pests and diseases, and a relatively simple starch extraction method (Sugih et al., 2019)

In 2018, the global production of cassava reached 278 million metric tons, with Africa accounting for approximately 61% of the total production. Since 2010, cassava production has seen a significant increase of 240 million metric tons worldwide (FAOSTAT, 2020). According to projections by the Food and Agriculture Organization (FAO), sub-Saharan Africa is expected to contribute around 62% of the global cassava production by 2025 (FAOSTAT, 2020).In Ethiopia, root crops, including potatoes, sweet potatoes, taro, and cassava, occupy more than 2% of the country's total cropping area. Cassava is one of the most extensively cultivated crops in certain districts of the Wolaita Zone, located in the southern region of Ethiopia (Godana &Hussein, 2019).

The majority of Ethiopians, according to Gebremedhin et al. (2001), rely on cereal crops for their food, and despite their significant contributions to food security, income generation, and

the provision of food energy, the food potential of root and tuber crops has not been fully utilized. However, as a dietary staple in places with low soil quality, erratic rainfall, and inadequate market infrastructure, cassava provides a number of additional advantages over rice, maize, and other grains. But for a variety of reasons, policymakers and scholars have neglected cassava, which is also thought to be a food staple for those with low per capita incomes (Tafesse et al., 2021).Cassava's year-round availability, strong resistance to drought and harsh climate conditions, and high yield in poor soil make it one of the most important sources of starch used as a staple meal in the world (Oyeyinka et al., 2020).The granule size of cassava starch ranges from 2 to 32μm, and its shape is described as round, truncated, and oval. Up to 80% of the dry weight of cassava root is made up of starch, the primary ingredient.

2.3.1 Uses and Composition of Cassava (*ManihotesculentaCrantz*)

Cassava is mainly cultivated in the tropics for its starchy tuberous rootwhich is widely used around the world for various purposes**.**Cassava roots are either directly consumed by humans as food, used as animal feed, or for industrial use. Cassava is a significant crop in Ethiopia, particularly in the southern and southwestern parts of the country, where it serves as both a food security and cash crop for small-scale farmers(Ashebir, 2022).In the Wolaita region of Southern Ethiopia, cassava serves multiple purposes. It is a staple food, providing sustenance through dishes like boiled cassava and cassava bread. Cassava cultivation serves as a source of income for farmers, as they sell surplus cassava in local markets. The plant also contributes to animal husbandry, with its leaves and stems used as livestock feed and cassava used as traditional medicine.

2.3.2 Composition of Cassava (*ManihotesculentaCrantz*)

The nutritional composition of cassava root based on the wet weight basis of the sample is shown in the table below.

Table 2-1 Nutritional composition of cassava root (Somendrika, M., 2017)

Sample	Moisture	Ash	fat	Crude protein	Crude fiber	Carbohydrate
Cassava	58.88	1.51.34		1.23	1.72	35.83

Table 2-2 Proximate composition of Cassava (w/w % in dry basis) (Charles et al., 2005)

Sample	Moisture (%)	Crude protein (%)	Crude fiber (%)	Ash (%)	Carbohydrate	Energy **(kJ 100 g^{-1})**
Cassava	10.3	1.5	2.5	1.8	83.8	1430

2.4. Extraction and Physio-chemical characterization of cassava starch

According to their report, cassava starch has unique structural and functional properties, which differentiate it from other starches like corn, anchote, and potato, including granule size, shape, morphology, thermal stability, and crystallinity. These properties are crucial for developing optimal extraction methods and modifying starch for various applications. WeligamaThuppahige et al (2023) reported the extraction of the cassava starch using a modified procedure. To separate the starch from the pulp in the extractor, fresh roots are washed, chopped, and grated in water containing sulfur (Figure 2-7). Following this, the pulp is separated from the starch fraction, which is then dried after being dewatered. To prevent microbial growth, the starch can be stored in Na2S2O5 solution before drying (Weligama Thuppahige et al., 2023).Many variables can impact the amount of starch produced, such as the drying state of the raw materials when the roots are harvested, and how they are stored. Ultimately, up to 80% of the dried weight of the cassava root can be produced as starch. However, varieties that are well suited for this use, such as those with a high dry matter content and thin peel thickness, can yield even higher amounts of starch (Godana &Hussein, 2019)

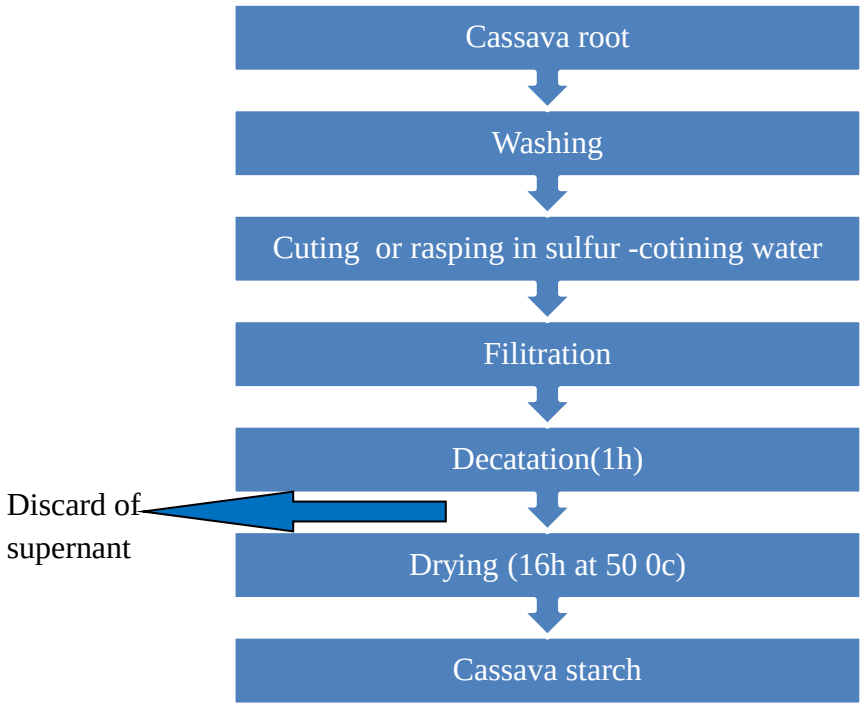

Figure 2-7 Isolation and purification Process of cassava starch

The physicochemical characterization of cassava starch involves the analysis of several properties, including the granule size, swelling power, solubility, paste viscosity, brightness, amylose content, and carbonyl and carboxyl contents(He et al., 2020). The morphological structures of cassava starch granules were evaluated using SEM and the size of granules varied from 1.17 to 22.22 μm. It was too smaller than potato starches. The x-ray diffraction study of the starch displayed an A-type pattern with a distinctive maximum peak at around 17.0^0 2θIt has also a greater gelatinization temperature of 64.54 °C, which indicates that the more crystallinity or high amylopectin component in cassava starch. This property contributes to the strength and stability of the starch paste, making it a more effective binder.The retrogradation rates of cassava starch paste increase with temperature (He et al., 2020).Additionally, the Fourier Transform Infrared Spectrometer (FTIR) ratios of specific bands in cassava starches vary, indicating differences in granule size, crystallinity, short-range order, water and oil absorption capacities, solubility, and transparency based on the variety of cassava.

2.5. Methods of starch modification

According to Sweedman et al, (2013) native starches are rarely consumed in their original form and are typically utilized by industries without significant modification. However, the direct application of native starches is limited due to their instability when subjected to temperature, pH variations, and shear forces. Native starches have a tendency to decompose and retrograde, which hinders their functionality. Furthermore, certain starch granules are inert and insoluble in water at room temperature, making them highly resistant to enzymatic hydrolysis and lacking in desirable functional properties. To overcome these limitations, native starches are commonly modified to acquire specific characteristics such as solubility, texture, adhesion, and tolerance to the heating temperatures employed in industrial processes. The physical modification of starch involves techniques such as moisture, heat, shear, or radiation, and has gained attention due to its non-reliance on chemical reagents for starch modification. This method offers an alternative approach to modify starch without the use of chemicals. On the other hand, chemical modification is a widely employed and common method to alter the properties of starch for various applications. Chemically modified starches exhibit a diverse range of physical and chemical properties that make them suitable for different uses. These modified starches demonstrate improved physicochemical properties compared to their native counterparts, enhancing their functionality and expanding their potential applications (Krithika & Ratnamala, 2019; Masina et al., 2017; Sweedman et al., 2013)

Table 2-3 Related work in Modification of starch

Modification method	Treatment	Change in starch structure	Change in starch properties	Reference
Oxidation	oxidizing agent-induced addition of carboxyl and carbonyl groups to natural starch	The starch undergoes depolymerization, which delays the process of recrystallization because carbonyl and carboxyl groups are incorporated.	It decreases the starch's dispersion viscosity but increases the stability, clarity, and biding qualities.	Boukhalfa, F. et al. (2018)
Etherification				
Hydroxyethylation	Addition of an ethyl hydroxyl group to the starch.	Changes in the granular structure.	Increases the capacity of some anticancer and other drugs to bind to their targets.	Paleos CM. et al. (2018)
Hydroxypropylation	Addition of hydroxyl propyl group on the starch.	It damages the hydrogen bonds between and within molecules of starch, weakening its granular structure. In amorphous regions, it enhances the motional freedom of starch chains.	It raises the starch's peak viscosity, enzymatic digestibility, swelling power, water binding capacity, and solubility.	Lee HL. Et al. (2011)
Esterification				
Acetylation	Reaction between a polymeric starch's hydroxyl group and acetyl group	It retards the crystallization or retro gradation in starch granules	It increases the viscosity and swelling capacity of granules while preventing the formation of intra molecular hydrogen bonds. It lessens irrationality	Thirumdas R et al.(2017)

2.5.1. Starch oxidation

The process of producing oxidized starch involves reacting starch with a predetermined quantity of oxidizing reagent at a controlled pH and temperature. Depolymerization from oxidation produces a decrease in dispersion viscosity and the introduction of carbonyl and carboxyl groups, which hinder recrystallization (Krithika & Ratnamala, 2019).

The three available hydroxyl groups are targeted for oxidation during the oxidative process to produce new starch derivatives. Oxidized starches have been demonstrated to have improved physiochemical properties, such as film formation and adhesively in some formulations, promoting a controlled release of active agents in drug delivery systems. However, the nature and properties of the oxidized starch derivative depend on the nature of the oxidative process (Masina et al., 2017; Oyeyinka et al., 2020; Salt et al., 1992; Wondimu et al., 2014).The oxidation process involves treating a starch suspension with an oxidizing agent containing 6-9% available chlorine. This treatment leads to the introduction of carboxyl and carbonyl groups within the starch molecules. These newly formed functional groups play a significant role in impeding the retro gradation process, which refers to the tendency of starch molecules to reassociate and form a gel-like structure upon cooling. By hindering retrogradation, the presence of carboxyl and carbonyl groups enhances the stability of the modified starch, making it less prone to gel formation and suitable for various applications (Zhang et al., 2017).

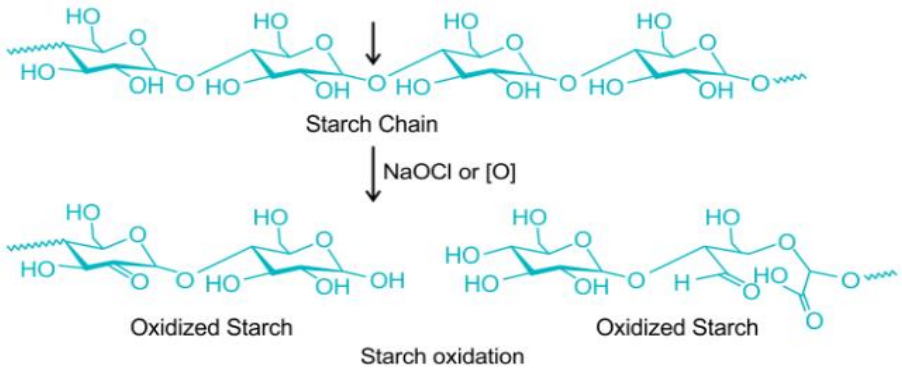

Figure 2-8 oxidation of starch

Reduced viscosity, high clarity, and low temperature stability are typical physicochemical characteristics of the oxidized derivatives, which lead to increased applications in the food,

biotechnology, and pharmaceutical industries. The oxidized starch matrices' surface morphology varies as well, mostly depending on how long the chemical reaction takes. Changes in viscosity and thermal stability can have more significant effects and opportunities for functionalization. Matrix fictionalization is also greatly impacted by surface morphology modification because variations in this attribute can lead to the starch matrix's controlled biodegradation (Apriyanto et al., 2022; BeMiller, 2018; Masina et al., 2017).

Table 2-4 Related work on oxidation

Starch source	**Oxidizer concentration (%)**	**Reaction time(min)**	**pH**	**Reaction temperature (c^0)**	**Reference**
Cassava	3 % sodium hypochlorite	30, 60, 120	8, 9, 10, 11	40	Sangseethonf et al .(2009)
Cassava	0.12–2.89 % H2o2 using cuso4 as a catalyst	50	1.64–8.36	20–45	Dias et al. (2011)
Banana	1.0 sodium hypochlorite	30–240	7.5, 11.5	35	Sánchez-Rivera et al. (2009)
Corn ,potato		30		15–60	Zhang et al. (2012)

2.6. Overview of Binder

Binders and adhesives are two terms that are often used interchangeably depending on the application. Both serve as examples of polymeric materials with the ability to adhere to one another and to two or more surfaces in order to form composites. In the manufacturing of wood (plywood or compressed sawdust-based wood composites), for instance, thermoset synthetic resins like urea-or phenol-formaldehyde are commonly referred to as adhesives or glues. Yet, the term "binders" is frequently used to describe polymers, such as polysaccharides, that are obtained from naturally occurring renewable resources and utilized as binder materials by the food, paper, and pharmaceutical industries (Kumari et al.,

2021).Binding could be a simple physical attraction between two or more materials or it may be mediated by more complex chemical interactions influenced by their surface chemistry, as well as their inter and intra-molecular interactions. The majority of commercial binders, especially those used in the production of wood, are synthetic resins made from petroleum chemicals that are harmful to the environment and human health. As an example, bio-based binders have primarily taken hold of niche markets in the pavement, paper coatings, and microsurgery industries; however, a growing number of end users in other industrial sectors have recently started to exhibit a noticeable shift in attitude and approach towards bio-based binders (Imam et al., 2013).In order to encourage granules and provide cohesion compact during direct compression, binders can be introduced as dry powders during granulation (Kumari et al., 2021).

2.6 .1 Classification of Binder

This section discusses Binders categories from a variety of perspectives, including source, function, physical form, application manner, and context

2.6.1.2 Classification of Binder based on physical form

Binders can be classified into two categories based on their physical form: powder binders and liquid binders. Powder binders are used in both wet granulation and dry granulation processes. These are added to powder blends in the dry form and granulated in situ by the addition of water, alcohol, or hydro alcholic solution. Powder binders such as cellulose, methyl cellulose, polyvinyl pyrrolidone, PEG Solution binders: gelatine, PVP, HPMC, PEG, sucrose, starch are commonly used as direct compression binders due to their high flow ability and compressibility. Liquid binders, on the other hand are more effective than those in dry form. They are used in the wet granulation process and are added in solution or suspension form. Commonly used liquid binders include polyethylene glycol (PEG), hydroxypropyl methylcellulose (HPMC), and sodium alginate. These binders are used to improve the plasticity of other binders and may prolong disintegration time when used in high concentration (Kumari et al., 2021).

2.6.1.2. Classification of Binders by Sources

Natural Binder

A natural binder refers to a substance derived from natural sources, typically plants, that is used to enhance the cohesion and binding properties of pharmaceutical formulations. These binders are obtained in various forms such as powders or solutions and are known for their biocompatibility, low toxicity, and eco-friendly characteristics. Examples of natural binders include natural gum(acacia), dried fruit, starch, and gelatin (Kumari et al., 2021). Natural binders like various starches, gums, mucilages, and dried fruits have strong binding capacity as compared to others such as disintegrants, filler, and sustain release, and these polymers are safer than polymers like PVP.

Synthetic Binder

Synthetic binder refers to a binder that is chemically synthesized or modified to possess specific properties for different applications. These binders are typically produced through various chemical processes. Synthetic binders are available in different forms, including powders and liquids, and exhibit adjustable viscosity and adhesive properties. Synthetic binders include cellulose derivatives (e.g. methylcellulose, hydroxypropyl cellulose),polyvinylpyrrolidone(PVP), and polyethylene glycol(PEG) (Liew et al., 2022).

2.7. Starch based binder

Starch has various applications in the production of food and other non-food industries (Liew et al., 2022). As the most abundant natural polysaccharide macromolecules, starch has a potential application in the starch-based binder. Also, it has been extensively investigated and widely used in the adhesives industry due to its relatively great adhesion performance and zero formaldehyde emission to the environment. But its bonding strength is insufficient for bonding structural products (Altay et al., 2021). It is an attractive green material to replace petrochemical-based ingredients in adhesives. Since the demand for adhesives is increasing in recent year's application of substitute raw materials will be very important.

Some starches are recognized for their ability to bind, including rice, maize, potato, wheat, and corn starches. However, other starches, like Enset starch and banana starch, can also be used as binding agents (Shiva et al., 2010). Starch is mostly used as thickening, stabilizing, gelling,

and filling agent in many pharmaceutical formulations. It is mainly used in tablets as filler, binder, or disintegrant. Starch is the main source of carbohydrates found in plant tubers and seed endosperm (Beckles & Thitisaksakul, 2016). Plant proteins, namely soybean protein, and wheat gluten, after denaturation were used as bulk binders for cellulose fibers in paper composite instead of synthetic adhesives and yielded excellent paper strength.

The efficiency of a binder is influenced by the characteristics and properties of starch. Starch binders possess desirable traits such as excellent ductility, strong adhesion properties, self-curing capabilities, and resistance to hygroscopicity. Hygroscopicity resistance refers to the binder's inability to absorb water, thus preventing swelling. To enhance the structure and binding properties of starch, it can be subjected to modifications through physical or chemical methods (Mohd et al., 2021).

Chemical modifications have been developed to overcome the weakness of native starch such as water repellence, failure of granules to swell and develop viscosity in cold water, and uncontrolled viscosity after cooking. An effective method to improve the functionality of starch is a chemical modification which can adjust physicochemical properties by bringing in new functional groups in starches (Sukhija et al., 2016).

2.8. Starch consumption in the paper packaging industry

Starch plays a significant role in various types of paper production (Flory et al., 2013). It ranks as the third most consumed component by weight in papermaking and paper conversion processes, following cellulose fiber and mineral pigments. Starch serves multiple purposes, including acting as a flocculant and retention aid, a bonding agent, a surface size, a binder for coatings, and an adhesive in products like corrugated board, laminated grades, and other applications (Maurer, 2009).

Around the world, paper manufacturers utilize chemical binders in the paper production process to achieve the desired strength of the paper. As paper mainly consists of cellulose, a polymer, it is feasible to stimulate the formation of a cell wall by using enzymes to apply and interconnect other components of the cell wall. An essential characteristic of printing and writing papers is their ability to withstand the penetration of water-based liquids (Flory et al., 2013). Paper manufacturers frequently incorporate sizing agents into paper to reduce the rate at which liquids penetrate its capillary structures. Sizing agents are typically categorized as

either internal or surface sizing agents. Internal sizing agents are added to the pulp slurry during the papermaking process, while surface sizing agents are applied to the paper's surface after the sheet is formed. Both types of sizing agents enhance the paper's water-repellent properties. Additionally, surface sizing agents have the ability to decrease the quantity and dimensions of pores, reduce paper roughness, and modify the surface energy of the paper (Maurer, 2009).

2.8.1. Starch usage as coating binders

Coated paper is a type of paper that comprises a base paper and a layer of coating. The coating layer is applied to the base paper during the manufacturing process to enhance its properties. Coating color, which is used for the coating, is composed primarily of pigments, binders, and various additives. Binders constitute the second most abundant component in the coating color, following the pigments (Li et al., 2019). Coated paper employs binders of natural origin, such as starch and protein, or synthetic latex like styrene-butadiene, polyvinyl acetate, and polyacrylates. Starch, being a cost-effective natural binder, is limited in its use due to insolubility in cooled water, retrogradation tendencies, and loss of viscosity and thickening power during cooking and storage. Consequently, starch modification is necessary. Modified starches are typically added to coating formulations to the maximum extent possible while meeting specific end-use requirements. The inclusion of modified starch helps regulate reheology, prevent pigment flocculation, and enhance water retention. Research by Chen et al. indicates that increased starch content can elevate ultimate tensile strength and elastic modulus, while decreasing elongation at break(Chen et al., 2014). On the other hand, adding too much starch to the coating formulation could reduce picking resistance and drying rate (Hashemi Najafi et al., 2018)., and increase crack area (J. J. Choi et al., 2020).

2.8.2. Starch usage as surface sizing agent

Surface sizing involves the application of a sizing agent material onto the surface of paper or cardboard using suitable systems. The purpose of surface sizing is to enhance the appearance and printability of paper and cardboard products. Natural or synthetic binders are utilized as surface sizing agents, including Sodium Carboxyl methyl Cellulose (SCMC), Polyvinyl Alcohol (PVOH), and various types of starches. Currently, size presses are the most commonly used machines for surface sizing during the papermaking process. These size

presses have been further improved by incorporating additional features. The utilization of starch as a surface binder contributes to the overall quality enhancement of paper and cardboard materials (Salt et al., 2002).

2.9. Tensile strength, Water resistance, and contact angle measurement evaluation

A paper sample's tensile strength is the highest stress it may withstand before breaking under the force applied in opposite directions. It is among paper and paperboard's most significant physical characteristics. The tensile strength of paper is influenced by factors like fiber properties, sizing agents, and coating materials. Improving tensile strength enhances the durability and quality of paper products (Axelsson, 2009).

The contact angle measurement of paper is conducted using ASTMD724, which is the standard test method for the surface wet ability of paper (Angle of contact method). This test involves applying a drop of liquid to a paper specimen and measuring the angle of contact, providing insights into the paper's wettability and suitability for various applications like printing and writing. The initial contact angle and the angle after a defined period are typically measured, with an angle between 90-100 degrees considered optimal for water-based inks(Jin et al., 2022).This method is valuable for assessing the quality and performance characteristics of paper surfaces.

CHAPTER THREE

3. MATERIALS AND METHODS

3.1. The Study Sites Description

Synthesis and characterization of green binder form Cassava root for paper packaging industries carried out in Chemical Engineering Laboratory of Adama Science and Technology University (ASTU). Some characterizations were performed in different places due to the lack of some instruments. SEM characterization was performed in the biology laboratory in ASTU. TGA and XRD characterization were also carried out in the Materials Science Engineering Laboratory, and FT-IR was performed in Addis Ababa University. Paper quality test was conducted in pulp and paper Company laboratory. The cassava was collected from an area in the Wolaita zone of Ethiopia, located between the coordinates 6.4°N - 7.1°N and 37.4°E - 38.2°E, Southern Ethiopia; they were collected in plastic bags and transported to the laboratory.

3.2. Chemicals and material

All chemicals and reagents were used for the synthesis of cassava-based binders were purchased commercially from local chemical markets.

3.2.1. Chemicals

In this research work different chemicals and samples, such as Tap water, Ethanol, Deionized water, Copper sulfate pentahydrate ($CuSo_4,5H_20$) Sodium hydroxide (NaOH), Sodium meta bisulfite ($Na_2S_2O_5$), Hydrogen peroxide (H_2O_2), Sodium hypochlorite (NaClO), Hydrochloric acid (HCl),Bromine, Acetic acid, Iodine solution and Potassium iodide. Other chemicals and reagents were used for the synthesis of starch-based binder for paper packaging.

3.2.2. Apparatus and Instruments

The apparatus and equipment's that were used during this research work are : - Tensile strength tester, Fourier Transform Infrared Spectroscopy(FTIR), Thermal Gravimetric Analysis (TGA), Scanning electron microscope (SEM), Digital balance, Soxhlet extractor, Ball mill, Mechanical blender, Mixer, Sieve with 250µm, Knife, Beakers, Flasks, Measuring Cylinder, Spatula, Petridish, Gloves, Pipette, Dropper, ice bath, Water bath, Filter paper,

Analytical balance, Vacuum desiccator, pH meter, Flasks, oven drier, Magnetic strier, Temperature controlled reactor, Oven and Universal indicator.

3.3. Methods

3.3.1. Sample collection and preparation

Freshly harvested Cassava roots samples were collected from an area in the Wolaita zone of Ethiopia, located between the coordinates 6.4°N - 7.1°N and 37.4°E - 38.2°E and transported to the chemical engineering laboratory of Adama Science and Technology University. The cassava roots were washed, grated or crushed, and then stored at ambient temperature for extraction processes.

3.3.2. Extraction of starch from Cassava roots

The process of extracting starch from raw Cassava roots involves several steps. Initially, the cassava roots was washed to remove any debris present on the surface, was followed by peeling. The peeled cassava was cut into approximately 1 cm cubes. These cubes were further reduced in size using a mechanical shredder for duration of 5 minutes, resulting in uniformly crushed cassava roots. A 10 % (w/v) crushed Cassava and tap water suspension was prepared. The suspension was filtered with a 150μm sieve and the filtrate was kept for 3 h. Each treatment was replicated three times to ensure accuracy and reliability. The resulting filtrate was allowed to settle, leading to the formation of a firm layer containing starch and other heavy particles. The supernatant was decanted, and the starch-containing sediment was subjected to at least two additional washes and subsequently dried. The sediment was dried at 50 °C for 48 h in an oven. The starch powder was made from dried sediment using a ball mill.

$$\text{Starch yield (\%)} = \frac{\text{dry weight of extracted starch(g)} * 100\%}{\text{dry weight of raw materials (g)}} \qquad 3.1$$

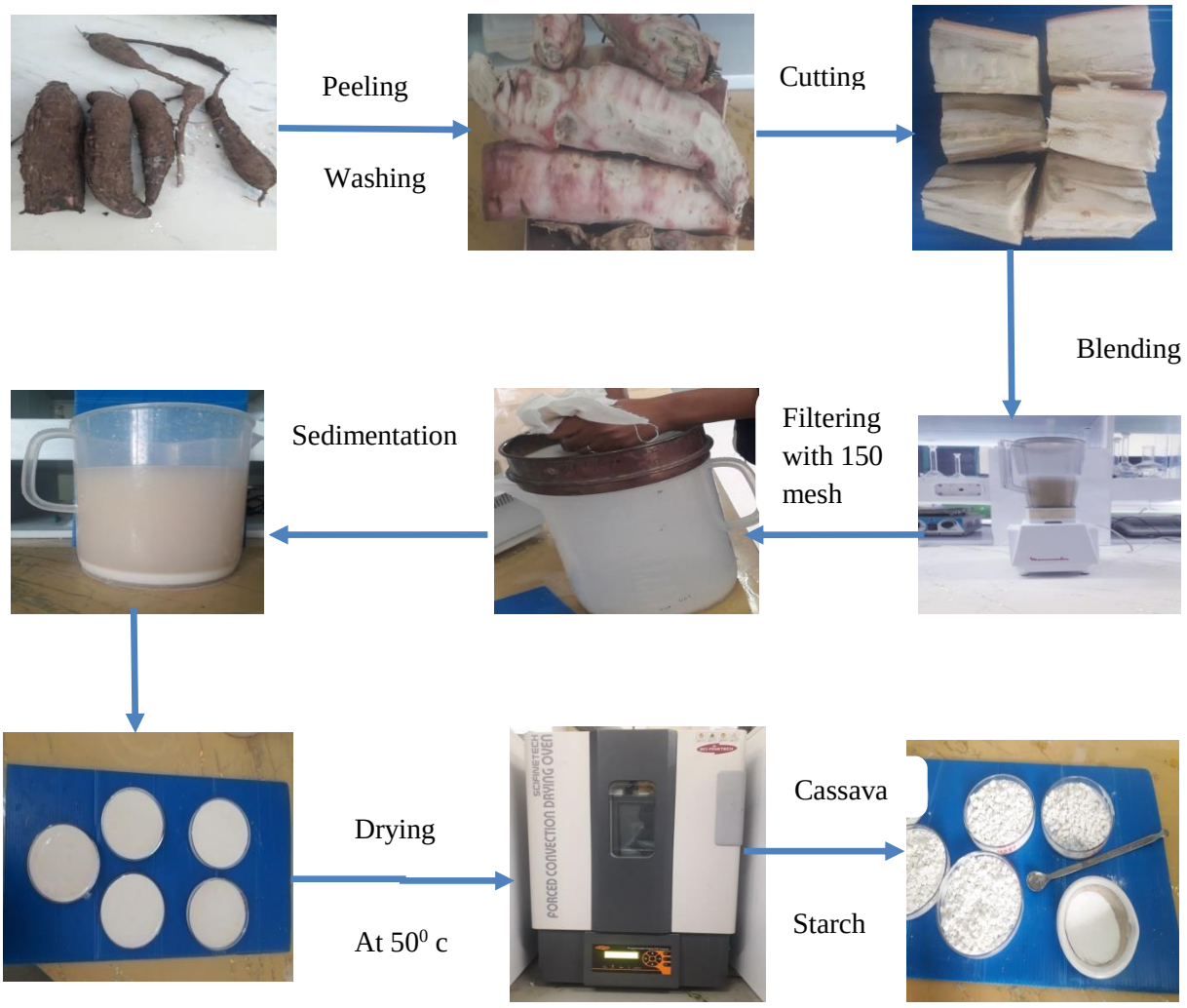

Figure 3-1 Experimental procedure to extract starch from cassava roots

3.3.3. Modification of Cassava roots Starch

The oxidation procedure was modified according to the method of Wang et al. (2007). Starch slurry was prepared by adding 10 g starch and 100 mL distilled water into a 250 mL round bottom flask equipped with a magnetic rod and heating device (hot plate).The mixture heated to 50 ◦C with modest stirring to gelatinize the starch about 30 minute. After that, the temperature was decreased to reaction temperatures ranging from 30 ^{0}C- 70 ^{0}C. The $CuSO_4 \cdot 5H_2O$ was dissolved in10 mL distilled water before being added to the starch. The $CuSO_4$ solution was first added to the starch solution. The pH was then adjusted to 9 by addition of NaOH (concentration of 1N). When the pH had reached the value of 9, was followed by the addition of H_2O_2 in half an hour. The pH was maintained constant by continuous addition of NaOH.The addition of Hydrogen peroxide was repeated 6 times, every

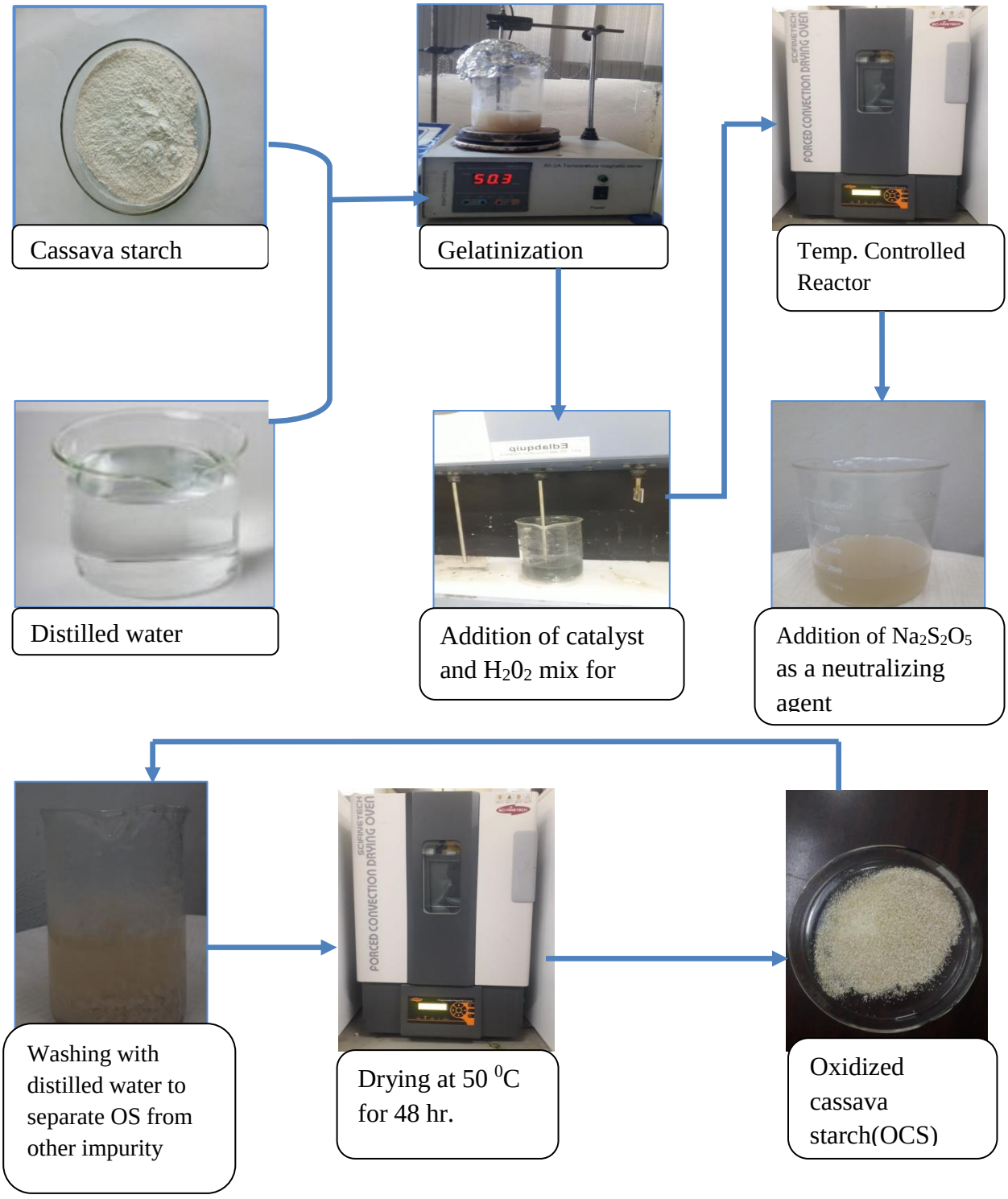

Figure 3-2 Experimental procedures for modification of cassava

10 minutes, until reached a total amount of 2.5% by weight of dry starch and the residual peroxide was neutralized by adding a small excess of starch Sodium meta bisulfate

($Na_2S_2O_5$).the oxidized starch was washed using distilled water until desired purity obtained. The obtained slurry was filtered and was dried in an oven at 50° C. for 24 hours.

3.3.4. Determining degree of oxidation

The degree of oxidation was expressed as the number of total carboxyl and carbonyl groups per 100 glucose units. The content of carboxyl groups was determined by titrating a sample solution with a standard NaOH solution, while the carbonyl group content was determined by reacting carbonyl groups with hydroxylamine reagent and then back-titrating with an HCl solution. A simpler method was developed to determine the total degree of oxidation of oxidized starch according to the literature (Kuakpetoon&Wang, 2001; Wing&Willett, 2005) with some modifications. A dry sample (0.1 g) was placed in distilled water (50 mL) and then 10 mL of 0.1 M NaOH was added. After that, the slurry was heated to a boil to make it completely soluble. The cooled solution was adjusted to a pH value of lower than 7.0 with 10 mL of 0.15 M HCl aqueous solution. Because of the water evaporation in the process of heating, some water was added to keep the solution content the same as before heating. Then, the solution was heated to boil again for 1 min and the mixture was rapidly back-titrated with 0.10 M NaOH to the phenolphthalein end-point. A blank test was performed with nature starch. All samples were tested three times.

$$DO = \frac{C_{NaOH}V_{NaoH} - C_{HCl}V_{HCl}}{m/162} * 100\% \qquad 3.2$$

$$DOS = DOT - DOB \qquad 3.3$$

Where C_{NaOH} and C_{HCl} represented the concentrations of NaOH and HCl solutions, respectively; V_{NaOH} and V_{HCl} were the volumes of used NaOH and HCl solutions; m was the weight of dry or oxidized starch; DOS represented the DO of the samples, and DOB represented the DO of the blank sample.

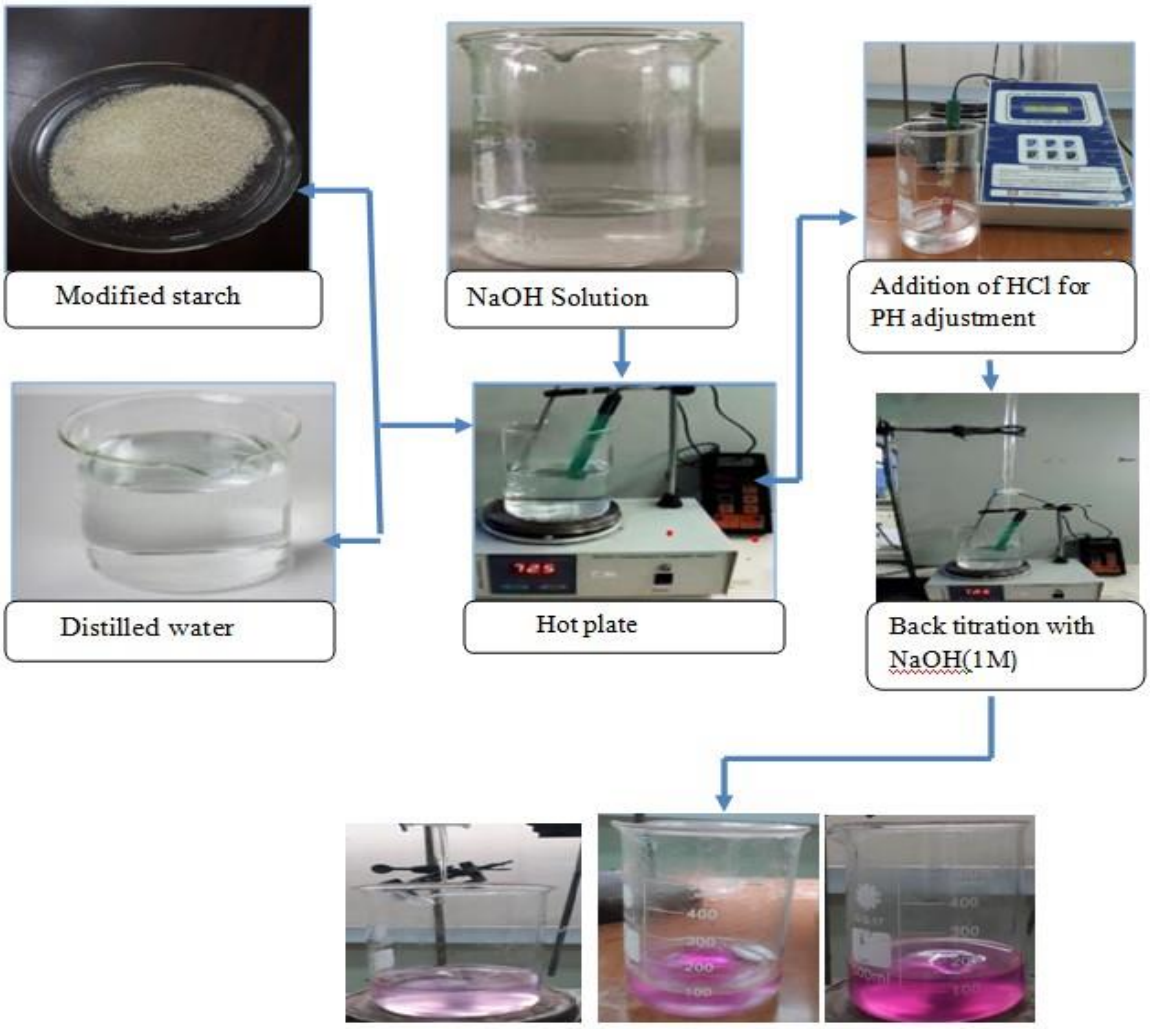

Figure 3-3 Experimental procedures for Degree of oxidation

3.4. Response Surface Methodology and Experimental Design

Response Surface Methodology (RSM) is an important statistical and mathematical tool for optimization. The experimental values were used to determine the effect of three operating variables such as time, catalyst loading and temperature on the degree of oxidation. Design Expert software version 13 was used to design the experiments and to analyze the results. Central composite design (CCD) was used to optimize the modification of starch. Three process variables (time, catalyst loading , and temperature) was studied at three levels as shown Table 3-1The effects and impacts of each factor and levels as well as interactions between factors and levels on the responses degree of oxidation was analyzed by analysis of

variance (ANOVA). The experimental ranges and levels of the mentioned independent variables are shown in Table 3

Table 3-1 Independent variables and response of degree of oxidation

Independent variables	**Symbols**		
		(-1)	(1)
Time (minute)	A	30	120
Reaction temperature(^{0}c)	B	30	70
Catalyst loading(%w/w)	C	0.1	0.4

Central composite design (CCD) was used to clarify the relationship between the independent variables and the response function. In this work, a three-level factorial Central composite design (CCD) with 20 experimental runs was applied.In order to study the effect of the Reaction parameters on the percentage of Degree of oxidation, a second –order polynomial response surface can be fitted in to the following equation.

$Y= \beta_0+\beta_1X_1+\beta_2X_2+\beta_{11}X^21+\beta_{22}X_2^2+\beta_{12}X_1X_2$

Where Y is the response(Y=Degree of oxidation); β_0 is a constant; β_1 and β_2 represent the regression co-efficient; while β_{11} andβ_{22} are the quadratic coefficients: and β_{12} is the interaction coefficient.

3.5. Characterization

3.5.1. Proximate analysis of Cassava roots starch

Determination of Moisture Content

The oven was used to determine the moisture content of the starch samples. The crucibles was washed, dried in the oven, and allowed to cool in the desiccators. Then the weight of the crucible was noted (W1).starch sample was put in the crucibles and both the crucible and the sample was weighed and registered as (W2). The crucibles containing the samples were then dried in the oven at 105^{o}C for 3 hours. Finally, the crucibles was taken out and allowed to cool in the desiccators and the weight was noted as (W3). The process of drying, cooling, and

weighing was continued until constant weight W3 was obtained (AOAC, 1975), The percentage moisture was calculated as follows:

$$\% \text{ Moisture content} = \frac{\text{Weight lost}}{\text{Weight of sample}} * 100 \qquad 3.5$$

$$\% \text{ Moisture Content} = {}^{(W1-W2)}\!/_{W1} * 100 \qquad 3.6$$

Determination of Ash Content

Each Starch sample was put in pre-weighed clean and were dried crucibles weighting (W_1) and the weight of the crucible and the samples was noted as (W_2). The crucibles were then transferred into a muffle furnace at 650ºC for 4 hours to burn off the organic matter until grey/white ash – is obtained. The crucibles were then removed, allowed to cool in the desiccators and the weights of the crucibles and the ash contents was noted (W_3) (AOAC, 1999).

The ash content was calculated as:

$$\% \text{ Ash} = \frac{\text{WeightofAsh}}{\text{Weightofsample}} * 100 \qquad 3.7$$

$$\% \text{ Ash} = {}^{(W3-W1)}\!/_{(W2-W1)} * 100 \qquad 3.8$$

Determination of Crude Fat

The fat contents of the samples were determined using the Soxhlet extractor as used by Oladebeye, A. (2009). A known weight of each sample was weighed (W_1) on a pre-weighed filter paper weighting (W_2), folded neatly and the total weight of the filter paper and the sample was noted (W_3). The filter papers, holding the samples were then inserted into the extraction unit and extraction was carried out with petroleum ether (b.pt. 40 ^{0}C - 60 ^{0}C) for 5 hours. After the extraction, the filter papers were removed, dried in the oven at 100ºC for about 30 minutes, allowed to cool in the desiccators, and the weights were noted as (W_4). The crude fat percentage was then calculated as:

$$\% \text{ Crude fat} = \frac{\text{Loss in weight}}{\text{weight of sample}} * 100 \qquad 3.9$$

$$\% \text{ Crude fat} = {}^{(W3-W4)}\!/_{W1} * 100 \qquad 3.10$$

Amylose content estimation

The amylose content (%) of the starch was determined by a colorimetric assay using the method described by Tessema, A. (2021).The standard stock solution of amylose was prepared by dissolving 0.1 g with 1 mL of ethanol and 9 mL 1 N sodium hydroxide (NaOH) in a 100 mL volumetric flask. The mouth of the flask was covered with a stopper and the contents were mixed well. The samples were boiled for 10 min in a boiling water bath to gelatinize the starch. The samples was removed from the water bath and was cooled to room temperature, then fill up to the mark with distilled water and shaken thoroughly. A portion of the stock solution was pipette into another 100 mL volumetric flask to prepare the standard amylose solutions of 50, 40, 30, 20, and 10%, then 1 mL of 1 N acetic acid and 2 mL of iodine solution (0.2 g I_2 and 2.0 g KI in 100 mL of distilled water) was added and made up to volume (100 mL) with distill water to develop a dark blue color. After 20 min the sample was shaken and the absorbance reading was taken at 600 nm using UV Spectrophotometer (UV-1800, Shimadzu, Japan). The blank solution contained 1 mL of ethanol and 9 mL of sodium hydroxide was boiled and filled up to the mark with distilled water. Finally, 5 mL was then pipette into a 100 mL volumetric flask, 1 mL of 1 N acetic acid and 2 mL of iodine solution was added and then filled up to the mark. This was used to standardize the spectrophotometer at 600 nm. Likewise, absorbance readings of the pure amylose solutions of starches were taken at the same wavelengths. The amylose content of starches was estimated from the standard calibration curve using a relationship between concentrations and absorbance of known mixtures of amylose solutions. The experiment was performed in triplicate and the mean values will be taken

3.5.2. Determination of physicochemical properties of Cassava starch

Gelatinization Temperature

1.5g of starch sample was dissolved in a beaker with 10ml of distilled water, the mixture was stirred, a thermometer was inserted and the beaker was placed in a water bath. The solution

was stirred continuously until its color became milky and thickened. This is the gel point and the temperature at this point was read off as the gelatinization temperature.

Swelling power

A modified version of Tester and Morrison's method was used to determine the swelling power (by weight) of starch. A 0.2g amount of cassava starch was dissolved in 20 mL of water. The suspension was centrifuged for 15 minutes at 2,200 rpm after being heated to 85°C in a water bath for 30 minutes with vigorous shaking every 5 minutes. The swelling power was computed and reported as a percentage using the sediment's weight. Three copies of the decision were made. This is how the swelling power was computed.

$$\textbf{Swelling power} = \frac{\text{Weight of sediment}}{(\text{weight of dry starch} - \text{weight of dissolved starch})} \qquad 3.11$$

Viscosity

Viscosity Utilizing a viscometer (Brookfield, RVDVII+ PRO,China) with spindle no. RV O2 and 200 rpm at 25 °C, the viscosity of a 2% w/v starch suspension was measured. After rotating for thirty seconds, the viscosity readings were obtained. Every measurement was done three times.

Solubility

A 10-gram starch sample was suspended in 40 mL of purified water. It was heated for 30 minutes while being constantly shook to the appropriate temperatures of 60, 70, and 80 degrees Celsius. For fifteen minutes, the mixtures were centrifuged at 100 rpm. At 130°C, an aliquot of supernatants (5 mL) was evaporated and weighed. The percentage ratio of the dried supernatant's mass (g) to the dry starch's original mass (g) indicated the starch's solubility.

3.6.2. Characterization of native and modified Cassava starch

3.6.2.1. Scanning electron microscopy (SEM) analysis

The morphologies of native and modified cassava root starch were observed using SEM (Hitachi S-3000N, Tokyo, Japan). Before testing, the samples were mounted on the SEM stubs with double-sided adhesive tapes and then were coated with platinum under vacuum to make the sample conductive. Scanning electron photomicrographs were recorded at various magnifications to ensure clear images.

3.6.2.2. X-ray diffraction analysis (XRD)

X-ray patterns of native and modified Cassava root starches with different DS values was analyzed between 2θ = 5° and 2θ = 55° using an X-ray diffractometer (Rigaku D/Max-B, Tokyo, Japan) with Cu Kα radiation at a voltage of 40 kV and 40 Ma

3.6.2.3. Fourier transforms infrared spectroscopy analysis (FTIR)

FTIR spectra of native and modified cassava root starches were measured using an FTIR spectrometer (Nicolet Avatar 360, Madison, WI).Samples were diluted at 1:20 with KBr before acquisition. A background of pure KBr was acquired before the sample was scanned. For each spectrum, the DRIFTS were set with an angle of 5°, and 128 scans were run. The FTIR spectra of the native and modified were recorded by using an FTIR spectrophotometer (model IS50-ABX) in the range of between 400 and 4000 cm^{-1}.

3.6.2.4. Thermo gravimetric testing (TGA)

Thermo gravimetric analysis (TGA) of native and modified cassava roots starch samples (4–5 mg) was carried out by using a NETZSCH thermal analyzer (TG209F1, NETZSCH-Gerätebau GmbH, Selb/Bavaria, Germany) under nitrogen atmosphere at a heating rate of 10 ^{0}C/min after the samples were kept in a vacuum oven at 60 ^{0}C for 48 h. The range of scanning temperature was from 40 ^{0}C to 600 ^{0}C.

3.7. Paper formulation and quality test

Prepare slurry was prepared by making the cellulose fiber and oxidized cassava starch in appropriate proportions. the oxidized starch acts as a binder to hold the fibers together. Initially, 80g of oxidized starch was combined with 320 mL of water and thoroughly mixed. The resulting mixture was then cooked, and the gelatinization temperature was measured using a thermometer. Subsequently, 800 mL of water was added to the cooked starch solution to adjust its viscosity, which was measured using a viscometer. A 400 mL weight/volume (w/v) pulp solution was prepared separately by mixing pulp with water. To incorporate the oxidized starch, 15ml volumes of the previously prepared starch solution were added to the pulp solution, followed by thorough mixing. The resulting mixture was Molded by using sheet Molding and then transferred to an oven for drying under specified conditions. Once dried, the

paper samples were removed from the oven to test tensile strength and tearing resistance using standard procedures. The starch acts as a binder to hold the fibers together.

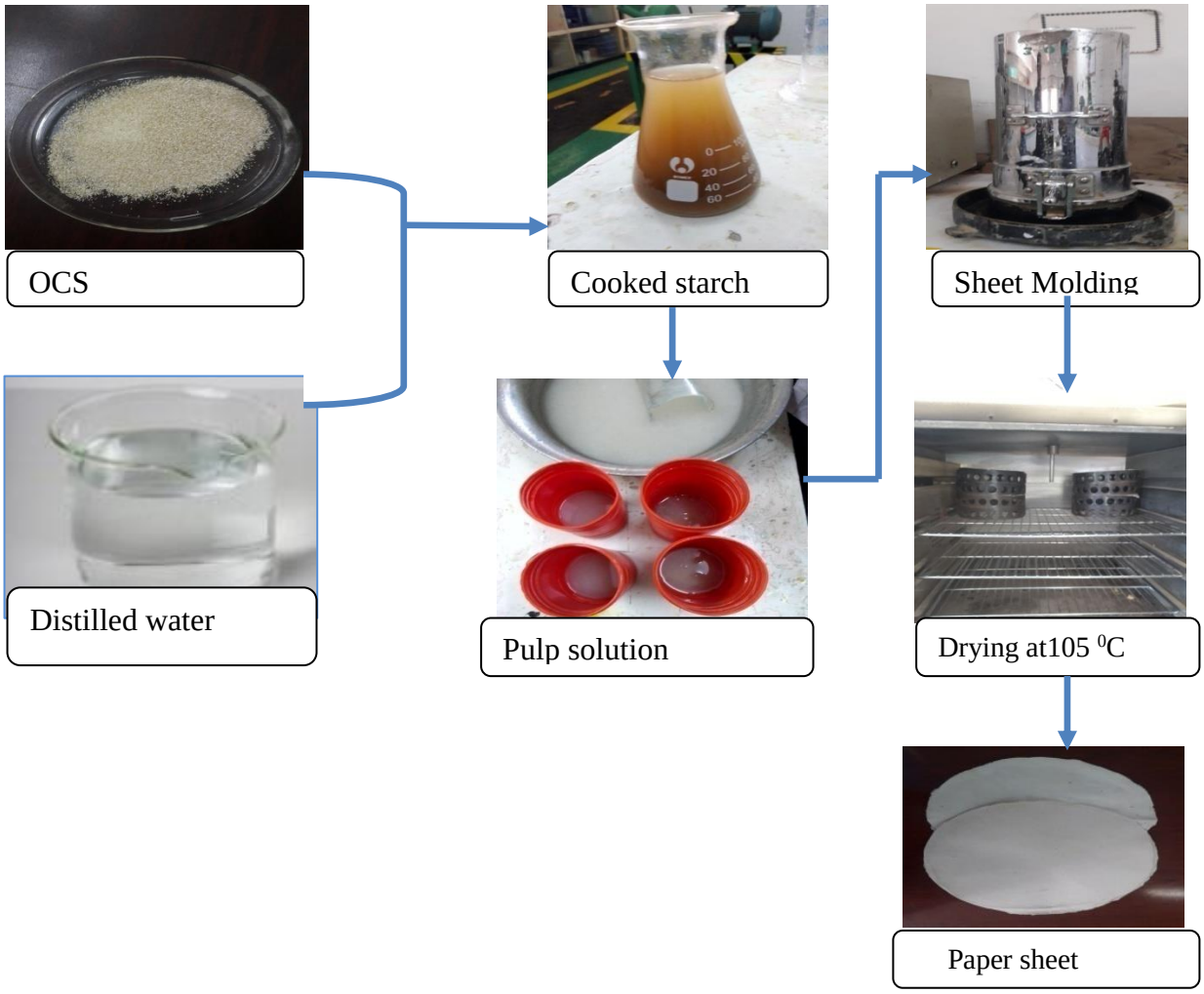

Figure 3-4 Experimental procedures for paper formulation

3.7.1. Tensile strength

The tensile strength of the paper was measured using a tensile tester (XLW-B, China), and the paper was cut as a long strip with 150 mm × 15 mm. Tear resistance was tested with a tearing tester (SLY1000, China) with a cutting paper as 63 mm × 75 mm. Burst resistance was tested using a bursting tester (BSM-1600, China) with cutting paper as Φ = 80 mm. The tensile

strength of paper is influenced by factors like fiber properties, sizing agents, and coating materials. Improving tensile strength enhances the durability and quality of paper products.

3.7.2. Porosity

This was a test of the openness of papers. The test was conducted according to TAPPI Test Method T460, using a Gurley porosity tester. The instrument measures porosity by forcing air through the sheet and measuring the rate of flow. More open sheets allow air to pass through the sheet more rapidly.

3.7.3. Tearing strength measurement

The tearing strength of the paper was measured using the Elmendorf tear tester according to ISO 2000 and TAPPI T414 standards. Representative paper samples were cut to 63 mm x 75 mm and conditioned at 23°C and 50% relative humidity for 24 hours. An initial tear was made using a standardized cut, and the samples were mounted on the tester. The force required to propagate the tear was measured in millinewtons (mN) or grams-force (gf). Each sample underwent at least ten measurements to ensure statistical reliability, and the average tearing strength and standard deviation were calculated. This methodology ensures consistent and accurate assessment of the paper's tearing strength, essential for quality control and performance evaluation in various applications.

3.7.4. Bursting strength measurement

The bursting strength of paper was determined using a normalized bursting tester (Yamauchi & Tanaka, 2002)according to standard STN EN ISO 2758 for the bursting strength of paper. Determination of the bursting strength is considered to be an empirical procedure and for its simplicity and authenticity in paper, rupture is widely used in practice. The bursting strength presents the combined strength and stretch of a paper as measured by the ability of the paper to resist rupture when pressure is applied under specified conditions to one of its sides by an instrument used for testing the property reported in kPa.

3.8. Formulation of corrugating binder using Oxidized starch

Corrugated cardboard consists of gluing a corrugated sheet of paper between two flat layers. corrugated cardboard production is a need for glue to bond the layers together. For the bonding of these layers, starch is used as an adhesive to prepare the adhesive solution for

corrugated paper production, 69 grams of starch was measured and added to a tank containing 238 milliliters of water. The mixture is stirred for 5 minutes. Separately, a sodium hydroxide solution was prepared by dissolving 2 grams of sodium hydroxide in 10 milliliters of water. This sodium hydroxide solution was then combined with the starch mixture, and the combined solution was stirred for a few more minutes to ensure thorough mixing then apply to the sheets. After that the crush burst test was conducted.

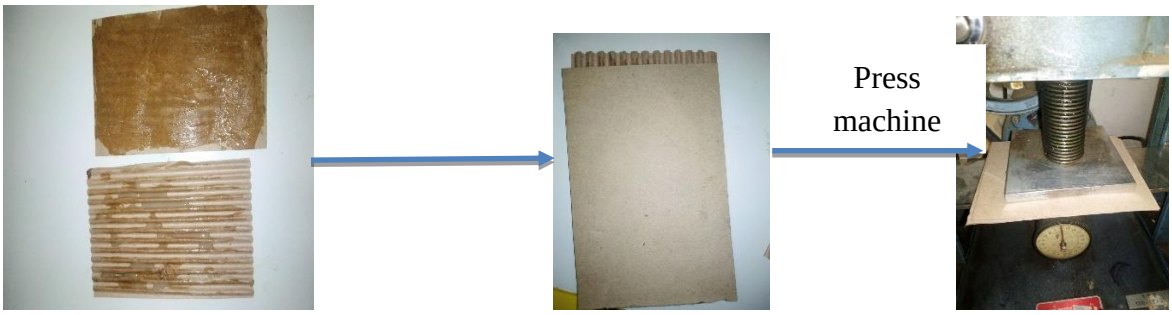

Figure 3- 5 Experimental procedures for formulation of corrugated binder using OS

CHAPTER FOUR

4. RESULT AND DISCUSSIONS

4.1. Proximate analysis of native cassava starch

The proximate analysis (moisture content, crude protein, crude fat, gelatinization temperature, and ash content) of cassava starch is shown in Table 4.1.The moisture content of cassava starch in this work was (10.60 ± 1.25%) which is almost the same previously reported work of Andriansyah, R. et al, (2017).The ash content (0.13± 0.06%) is the non-volatile inorganic matter of a compound which remains after subjecting it to a high decomposition temperature. During heating, the organic compounds are decomposed or released leaving behind the residue which consists mainly of other inorganic. In this work, cassava starch had ash content slightly lower than previously reported work (0.19 ± 0.05) of Berhanu Bilate Daemo et al,(2017). This value indicates that cassava starch had fewerinorganic compounds like calcium (Ca), iron (Fe), and phosphorous (P) relative to other root tubers like potato, sweet potato, and anchote. The crude fat content in cassava starch was (0.28±0.5%) which was relatively higher than previously stated work. This is due to a slight modification in determining the method of the fat content of cassava starch from previous work. The amylose content (22.4%) was within the range reported for different varieties of cassava starches (Defloor et al., 2015; Ogunmola et al., 2001). In the estimation of amylose content, amylose solutions, as well as their mixtures stained with iodine solution, showed a linear relationship between absorption and concentration at 600 nm. According to the standard linear curve equation A = 0.0166X + 0.054; R2 = 0.9995; where A is absorbance value, X is the concentration of amylose (%)], the amylose contents of the starches was estimated to be 22.4% as shown in Table 4.1

Table 4-1 Proximate analysis of cassava starch

Sample	**Moisture content (%)**	**Ash content (%)**	**Gelatinization temperature (^{0}C)**	**Crude fat %**	**Amylose content %**	**Amylopectin Content %**	**Yield %**
Cassava starch	10.60± 1.25%)	0.13± 0.06%	55	0.28%	22.4%	87.6%	32.2%

4.2. Physicochemical Properties of the Native and Oxidized Cassava Starch

The Physicochemical characteristics (gelatinization temperature, Swelling power, solubility, and viscosity) of Native cassava starch(NCS) and oxidized Cassava starch(OCS)are shown in Table 4.2.Oxidized starch exhibited a higher gelatinization temperature of 68 ^{o}C Compared to 55^{o}C for native cassava starch, indicating that it required more heat to begin the gelatinization process which is almost the same previously reported work by Zang et al,(2021) This chemical modification was also resulted in a substantial increase in swelling power, with oxidized starch swelling to 13% whereas native cassava starch was swelled only to 5%.Furthermore,oxidized starch showed greater solubility at different temperatures: at 60 ^{o}C, it was 38.5%. at 70 ^{o}C, it was 42.5%, and at 80 ^{o}C, it was 52.8%.Significantly higher than the native cassava starch at these temperatures, which were 21.8%, 32.5%, and 38.8%, respectively. The viscosity of NCS and OCS was 11 and 19 N·s m^{-2}respectiveliy which is slightly different from the previous work of Sondari et al,(2021).These differences were attributed to the structure changes induced by oxidation, which enhance the starch's interaction with water, increase its thermal stability, and alter its physical properties.

Table 4-2 Physicochemical Properties of the Native and Oxidized Cassava Starch

Type	**Gelatinization temperature**	**Swelling power (%)**	**Solubility**	**Viscosity**
Native cassava starch	55 ^{o}C ± 0.50	5.00± 0.20	60^{o}C,21.8±0.20 70^{o}C,32.5±0.30 80^{o}C,38.8±0.20	11 ± 0.50
Oxidized cassava starch	68^{o}C ± 0.50	13 ± 0.06	60^{o}C,38.5±0.20 70^{o}C,42.5±0.30 80^{o}C,52.8±0.50	19 ± 0.4

4.3. Optimization of degree of oxidation (DO)

In this work, mathematical models were developed for the performance namely the degree of oxidation. Response surface methodology Approach was used to determine the optimum degree of oxidation parameters that were got higher degree of oxidation from modified cassava starch. In this study, three parameters namely reaction time, reaction temperature and

catalyst loading were identified and the ranges of the parameters namely were selected based on the preliminary experiments. Twenty experiments were carried out and the degree of oxidation was obtained by using titration method.

Table 4-3 1 Factor and the response (Degree of oxidation)

Std	**Run**	**Factor1 A: time minute**	**Factor 2 B:reaction temperature**	**Factor 3C: catalyst loading (w/w%)**	**Response 1 Degree of oxidation(DO)**
8	1	120	70	0.4	43.5
13	2	75	50	0.1	49
9	3	30	50	0.25	37.7
4	4	120	70	0.1	39.7
5	5	30	30	0.4	26.8
14	6	75	50	0.4	54.2
1	7	30	30	0.1	22.4
3	8	30	70	0.1	32.7
16	9	75	50	0.25	56.6
15	10	75	50	0.25	52.08
6	11	120	30	0.4	39.6
7	12	30	70	0.4	28.5
10	13	120	50	0.25	50.3
12	14	75	70	0.25	46.5
17	15	75	50	0.25	51.8
11	16	75	30	0.25	28.9
18	17	75	50	0.25	54
20	18	75	50	0.25	48
2	19	120	30	0.1	36.9
19	20	75	50	0.25	54

4.3.2. Regression Analysis and Model Fitting

The adequacy of the developed models was tested at a 95% confidence interval using the ANOVA technique, and the results of the linear and quadratic order response surface model fitting in the form of ANOVA are given in Table 4-4. The test for the significance of the regression models, the test for the significance of the individual model coefficients, and the lack-of –fit test were performed using the statistical Design –Expert 13.1.1 software package. By selecting the step-wise regression method, which eliminates the insignificant model terms automatically, the result is presented as shown tables 4.3 below.

Table 4-4 ANOVA analysis for the quadratic model

Source	**Sum of squares**	**Df**	**Mean square**	**F-Value**	**p-value**	
Model	1949.50	9	216.61	15.07	<0.0001	**Significant**
A-Reaction time	386.88	1	386.88	27.47	0.0004	
B-Reaction temperature	133.96	1	133.96	9.51	0.00116	
C-Catalyst loading	14.88	1	14.88	1.06	0.3282	
AB	3.13	1	3.13	0.2218	0.6477	
AC	5.45	1	5.45	0.3865	0.5480	
BC	6.48	1	6.48	0.4600	0.5130	
A^2	118.60	1	118.60	8.42	0.0158	
B^2	455.31	1	455.31	32.32	0.0002	
C^2	2.93	1	2.93	0.2082	0.6579	
Residual	140.86	10	14.09			
Lack of Fit	99.00	5	19.80	2.80	0,1633	**Not significant**
Pure error	41.86	5	8.37			
C or Total	2127.04	19				

The Model F-value of 15.07 implies the model is significant. There is only a 0.001% chance that an F-value this large could occur due to noise. P-values less than 0.0500 indicate model terms are significant. In this case A, B, BC, A^2, B^2 are significant model terms. Values greater than 0.1000 indicate the model terms are not significant. If there are many insignificant model terms (not counting those required to support hierarchy), Model reduction may improve your model.

Lack of fit was also given in Table 4-4 .the lack-of-fit test ($p>0.05$)was used to examine the model's"fitness" which showed that it was suitable for correctly predicting the variation (Prasad et al.,2011).The degree to which the models fit the data is measured by lack of fit. The lack of fit F-Value of 2.36 implies the lack of fit is not significant relative to the pure error. There is a 18.33 chance that a lack of fit F-value this large could occur due to noise. Non – significant lack of fit is good for the model to fit. Therefore, the model adequately explained the response.

Table 4-5 Model Adequacy measures for degree of oxidation

Std.Dev.	**2.75**	**R^2**	**0.968**
Mean	43.67	Adjusted R^2	0.940
C.V%	3.54	Predicted R^2	0.852
		Adeq precision	15.2291

The Predicted R^2 of 0.852 is not as close to the Adjusted R^2 of 0.94 as one might normally expect;i.e. the difference is not more than 0.2.The difference between the adjusted R-square is 0.088(i.e. they are close to each other) and this indicates the close fit of the model to the actual response data. According to several Literature investigations, the model's suitability was demonstrated by the determination coefficient R- square value being greater than 0.75 (Subramanianet et al., 2015).In the present study, the value of R-square for the developed correlation is 0.968: this indicates that 96.8% of the oxidation of cassava starch is a success in the experimental studies. That indicates the model was adequate in the optimization study. The model's Adjusted was extremely comparable to each of their respective values, demonstrating a strong correlation between the predicted and observed values. Adeq. Precision measures the

signal-to-noise ratio and a ratio greater than 4 is desirable. Therefore, in this study, the ratio of 15.2291 indicates an adequate signal, and this model can be used to navigate the design space.

4.2.3. Effect of Independent Variable interaction on the degree of oxidation(Y)

Based on the predicted model, the effect of independent variable interaction (Reaction Temperature, Reaction time, and catalyst loading)is explained by Plotting contour and three-dimensional (3D) plots. All other independent variables are expected at centered levels.

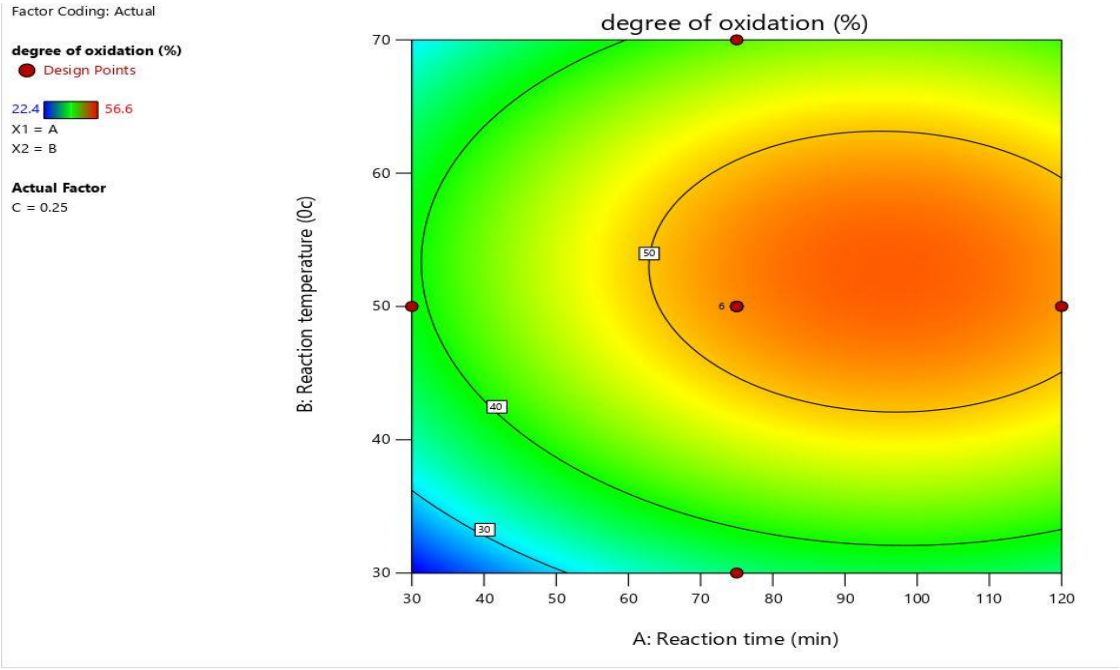

Figure 4-1Response contour plots of predicted degree of oxidation as function of Reaction temperature and Reaction time

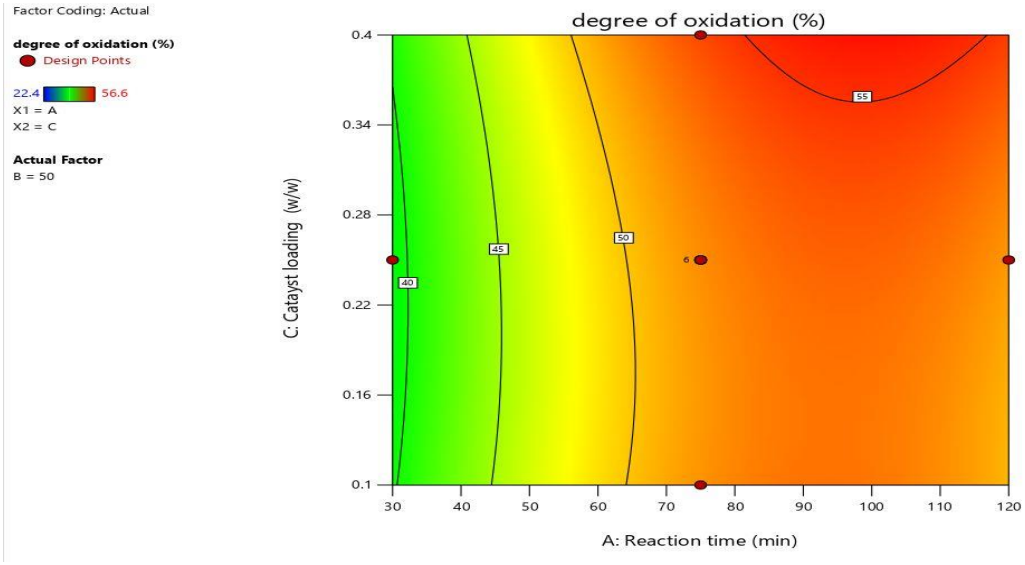

Figure 4-2. Response contour plots of predicted degree of oxidation as a function of Reaction time and Catalyst loading

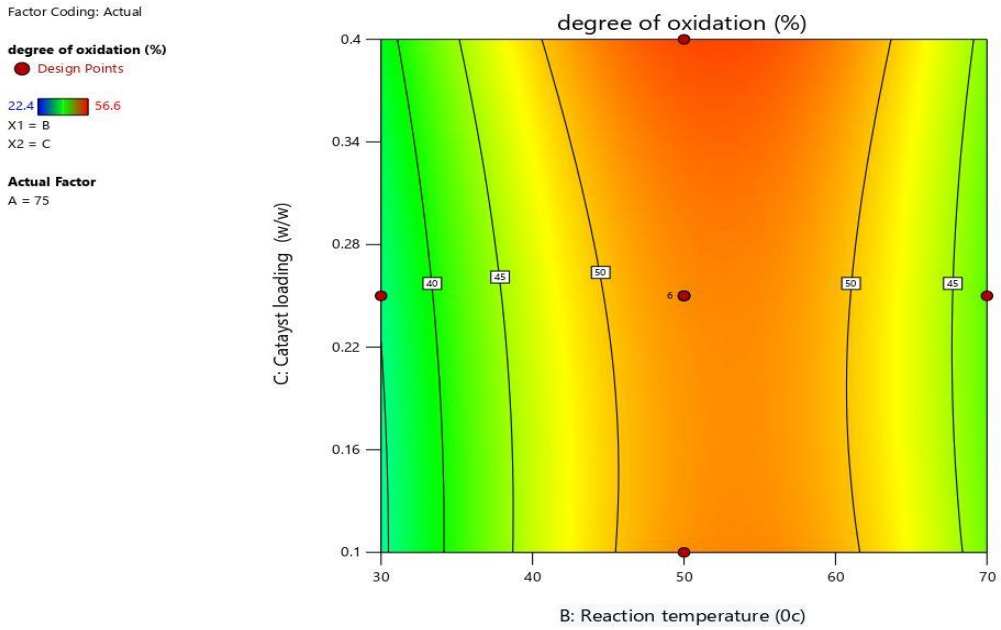

Figure 4-3 Response contour plots of predicted degree of oxidation as function of Reaction temperature and Catalyst loading

Second–order polynomial mathematical models for the oxidation of starch were obtained by conducting a multiple regression analysis. These mathematical Models were applied to develop a relationship between independent and response variables. The final quadratic

Polynomial equations for oxidation of Starch were formulated by using the regression coefficient values while ignoring insignificant terms and are given by the following equations.

$$Y=51.87 + 6.22A+3.66B+0.9C-0.6250AB+0.8250AC-0.9BC-6.57A^2-12.87B^2+1.03C^2$$

From this quadratic regression model equation, it was observed that the linear variables A, B, and C,$C^{2,}$ and the interaction variables AC, have a positive effect on the oxidation of starch whereas other terms have a negative effect.

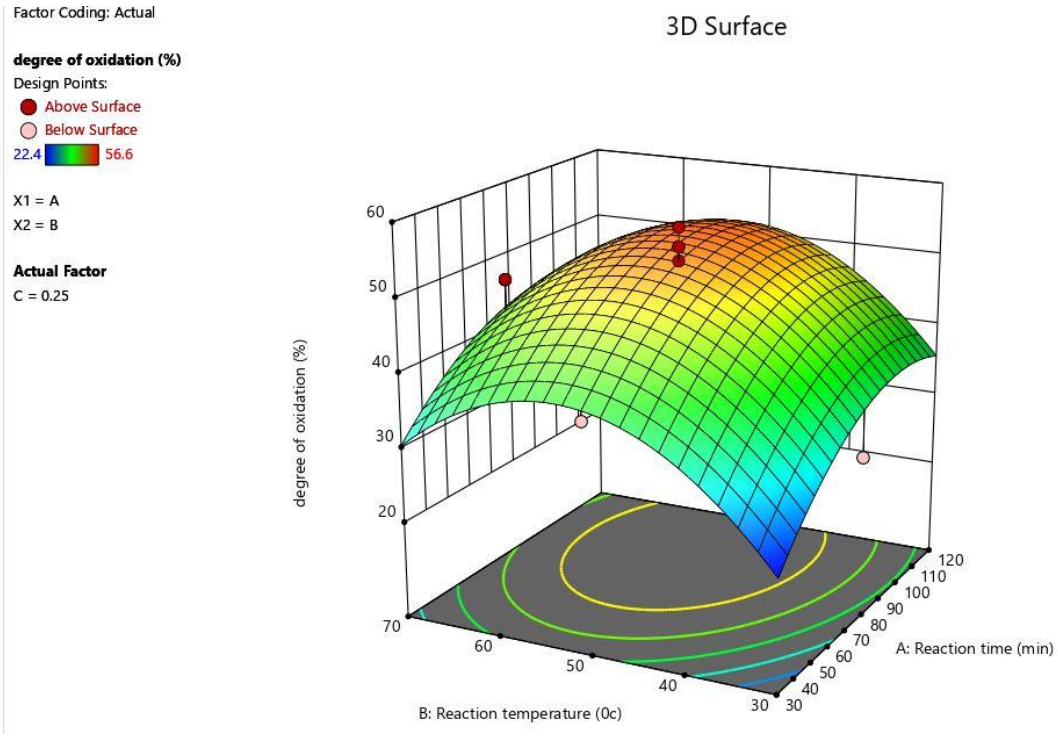

Figure 4-4 Response surface plots of degree of oxidation as a function of Reaction temperature and Reaction time

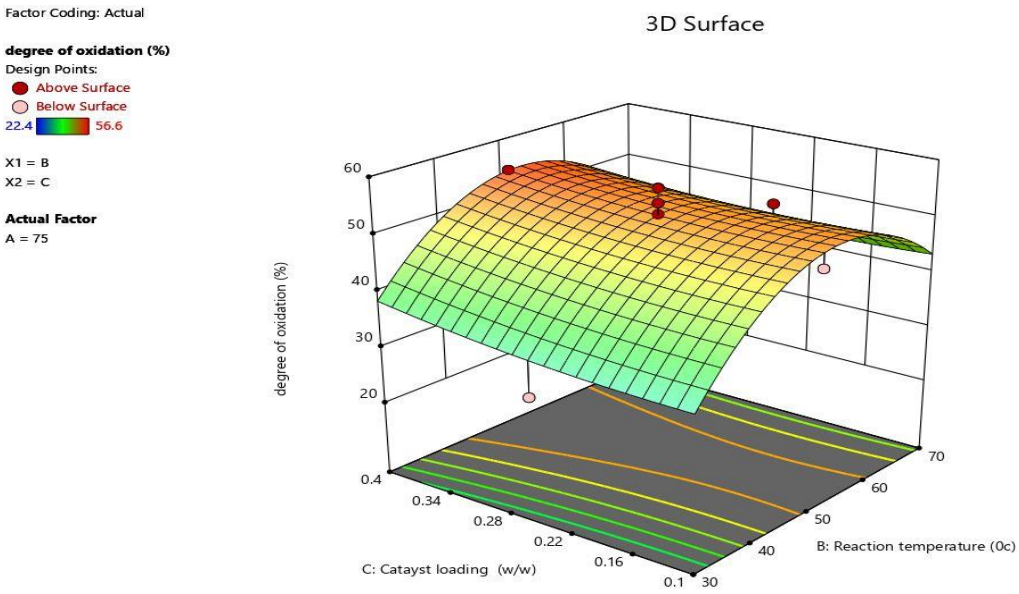

Figure 4-5 Response surface plots of the degree of oxidation as a function of Reaction temperature and Catalyst loading

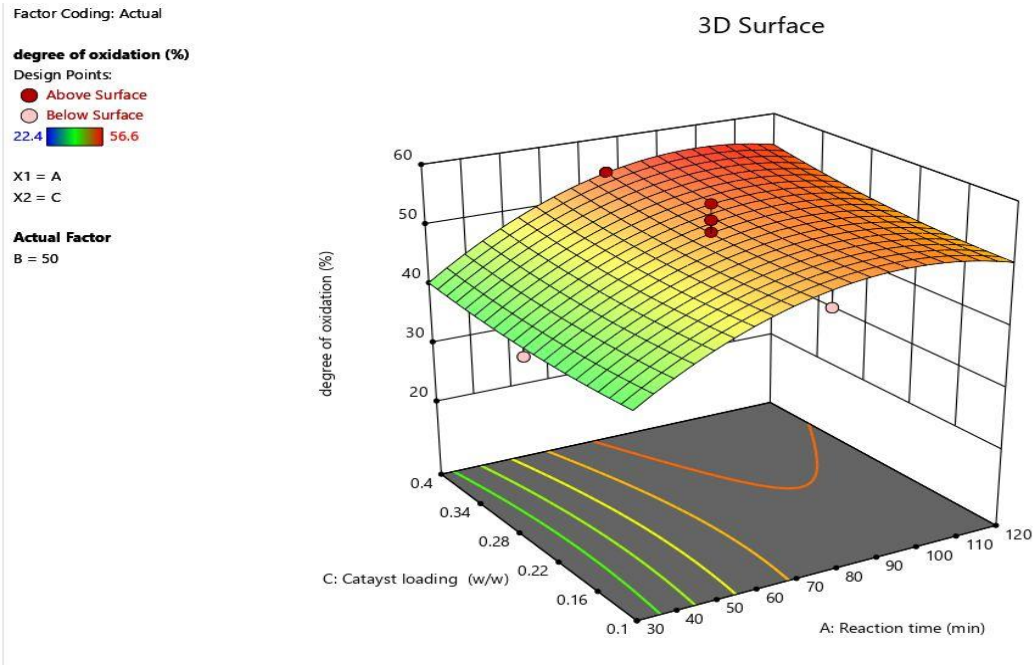

Figure 4-6 Response surface plots of degree of oxidation as function of Reaction time and Catalyst loading

The three – dimensional (3D) response for oxidation of cassava starch are shown in fig 4-3,4-4 and fig 4-5,which indicates the effect of the significance terms on the tested response. The degree of oxidation parameters such as Reaction temperature (30-70 ^{0}C), Reaction time (30-120min), and catalyst loading (0.1-0.4 w/w) influence the degree of oxidation. The 3D curves showed the main and interaction effect between two oxidation parameters on the degree of oxidation by maintaining the third parameter as zero level. Fig 4-3, 4-4and Fig 4-5 exhibited the main (A,B and C) and interaction (AB,AC and BC) on the degree of oxidation.

The effect of Reaction temperature and Reaction time on the degree of oxidation are shown in fig 4.3.higher degree of oxidation were attained at reaction temperature of 50 ^{0}C and reaction time around 75 - 80min. Fig 4-3 also provides information on the interaction among degree of oxidation ,reaction temperature and reaction time. When the reaction temperature increase from 3o to 60^{0}C and the reaction time from 30 min to 75min , Degree of oxidation increases from 22.4% to 56.6%, but when reaction temperature and tine continues to increase from 60 ^{0}C to 70 ^{0}C,The degree of oxidation(DO) drops to 46.5%. For instance, rising temperature would cause the hydrogen per oxide to activate more and cause the starch gels to enlarge. That being said, oxidant degradation occurs at temperatures greater than 60^{0}C, which lowers DO. This finding is in good agreement with previous work (Zhang et al., 2012).

Fig 4.4 showed the 3D response curve of the main and interaction effect (BC) of Reaction temperatures and the catalyst loading on the degree of oxidation at a constant Reaction time. The degree of oxidation of cassava starch significantly increased with catalyst loading from 0.1 to 0.25 w/w% and the Reaction temperature 30 to 60^{0}C and thereafter both the degree of oxidation slightly decreased. When the catalyst is too high, there won't be enough oxidant available for the catalysis, and the excess catalyst won't be able to demonstrate its catalytic capabilities. Nonetheless, carboxyl functionalities in the modified starch allow heavy metals to be maintained and oxidized starch has good complex characteristics. Unwanted coloring was resulted from modified starch's high metal level (Idris et al., 2023).therefore 0.25% Cu2+ was chosen as optimal catalyst dosage (Nimenibo-Uadia R et al., alCymbopogon, 2020).

As illustrated in Fig 4.5 which showed how the reaction time and catalyst loading affect the degree of oxidation. As Catalyst loading increased from 0.1to 0.28w/w% and the reaction time increased from 30 to 80 min the degree of oxidation increased from 22.4 to 56.6% .However, a

further increase in the catalyst loading and reaction time decrease the degree of oxidation from 56.6 to 50%.at the beginning the concentration of the oxidizing agent is higher and the oxidation is easier. Initial oxidation is simpler and occurs at a higher concentration of the oxidizing agent. Due to the oxidant being consumed earlier in the reaction, the efficiency of the reaction was decreased (Setyaningsih et al., 2021). the optimum degree of oxidation 56.1 % was obtained at 98minute, 51^0c and 0.4 catalysts loading with 95% validation

A plot of predicted degree of oxidation versus actual degree of oxidation is given in Figure 4.5. As showed from the above figure, predicted degree of oxidation represent nearly 96.8%of actual degree of oxidation values, indicates the significance of the model.

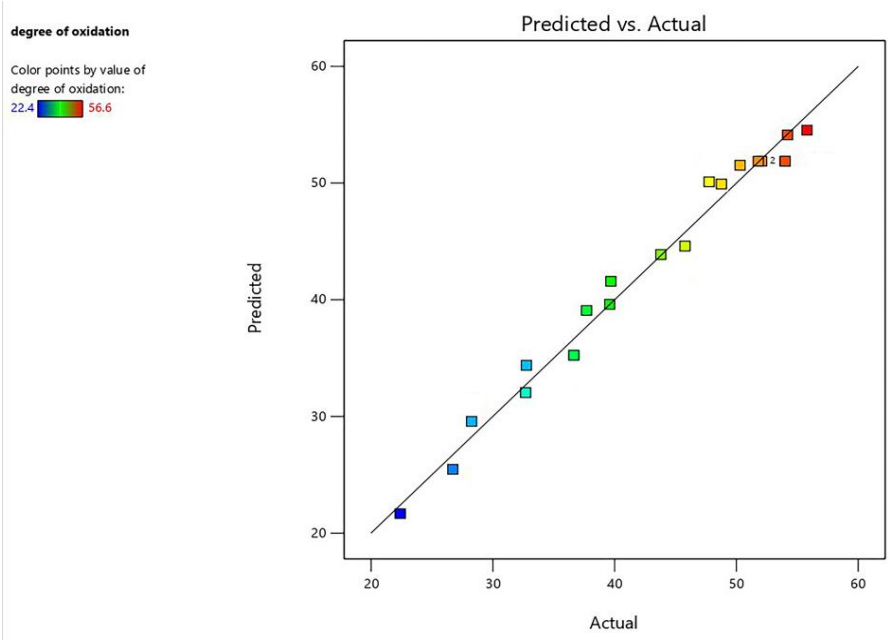

Figure 4-7 Relationship between predicted and actual values of degree of oxidation

The effect of main parameters are illustrated in figure 4.6 .effect of reaction Time (A), reaction temperature (B) and Catalyst loading (C) that are linear and quadratic on a considerable degree of oxidation was found.

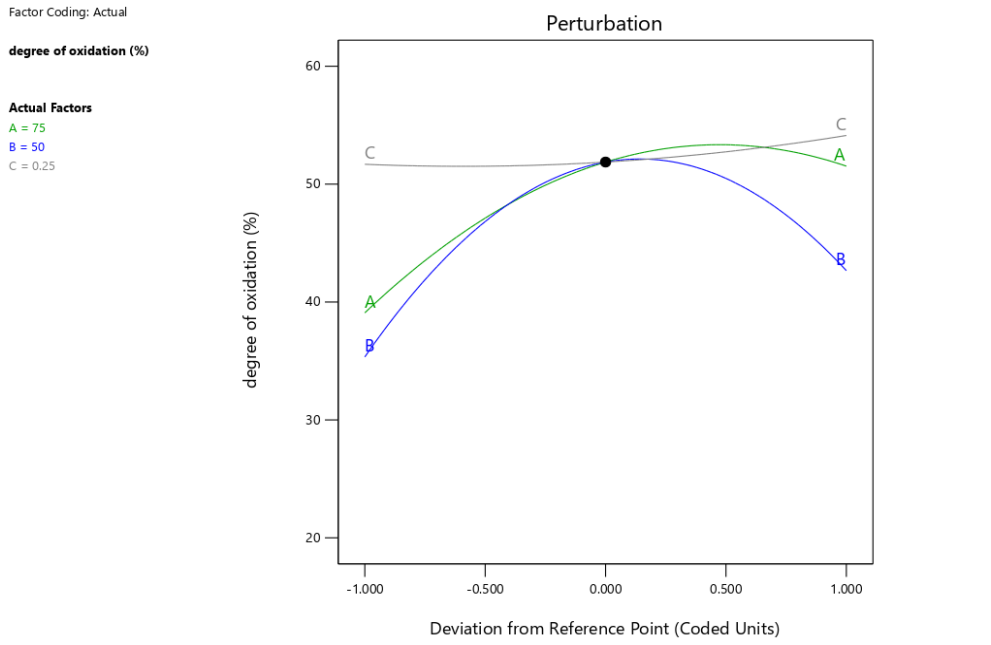

Figure 4-8 effect of reaction Time (A), reaction temperature (B), and Catalyst loading (C)

4.3. Physiochemical Characterization of Cassava starch

4.3.1. Morphological analysis of native cassava starch

The morphological characteristics of cassava starch granules were determined by using a Scanning electro microscope. The SEM image in fig 4.6 shows the morphological characteristics of cassava starch granules.the observed microscopic appearance of cassava starch granular shape is same from the previously done literature .from SEM results, in accordance with the observation R. H. Lin et al., (2020) native cassava starch granulers had round shape with a truncated end on the one side .the surface of native starch granules was smooth. According to Lindeboom et al., (2004), the granules size distribution obtained in this study can be classified as very small to medium size. Starch granule size influences water absorption, solubility, and swelling. Small granules have a high surface area that can lead to high water absorption capacity. the smaller size of cassava starch granules compared to anchote and potato is attributed to their higher surface area to volume ratio, which facilitates faster water absorption and mobilization (Dereje et al., 2021).The cassava starch granules size, mean width, and the length are tabulated as follows.

Table 4-6 Cassava starch granule size

Sample	Mean width	Width range	Mean granule length	Length range
Cassava starch	8.85µm	1.31-17.26µm	11.50µm	3.35- 18.09µm

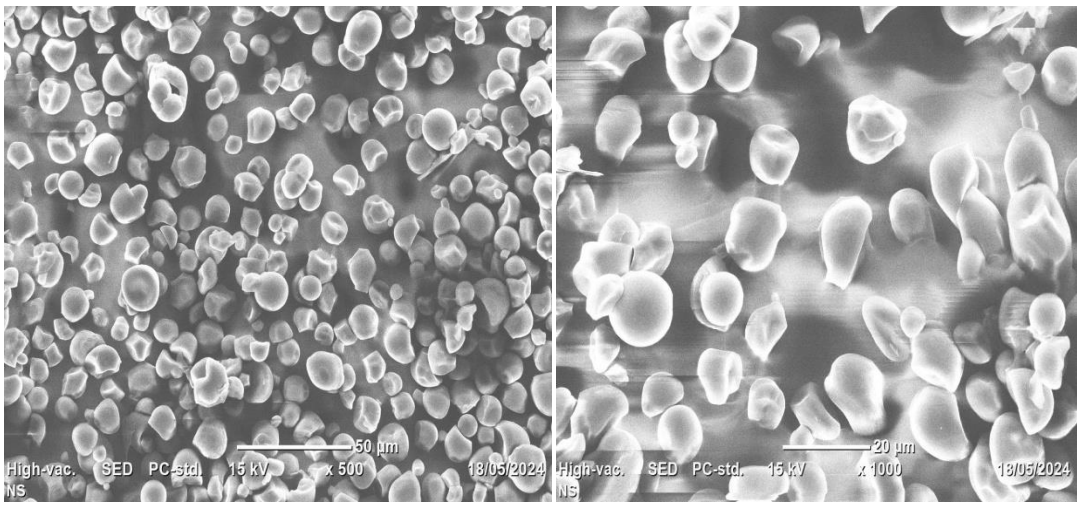

Figure 4-9 SEM image of native cassava starch

4.3.2. FTIR analysis of Native Cassava starch

The Fourier Transform infrared spectroscopy (FTIR) spectra of cassava starch are presented in Figure 4-9 below. The FTIR spectra of native cassava starch typically show characteristic peaks that correspond to specific functional groups present in the starch molecule. These peaks provide valuable information about the molecular structure of the starch. This starch showed different bands due to vibration modes of amylose and amylopectin structures (Sharif et al., 2015).A broad peaks in the range of 3200-3600cm-1 were typically observed, representing the stretching vibration of the hydroxyl groups present in cassava starch and a similar result was also reported by Cuenca et al., (2020).A peak around 2930cm-1 was observed, corresponding to the stretching vibration of the C-H bonds in the starch molecule and similar result also reported by (Zang et al., 2020).a peak around 1640-1650cm-1 indicates the bending vibrations of the hydroxyl groups, often associated with absorbed water molecules. The absorption Peaks in the range of 1400-1500cm-1 are associated with the symmetric deformation CH_2 of groups in the starch molecule. The Peaks around 1350-1370cm-1 represented the symmetric bending vibration of the C-H bonds (Sharif et al., 2015).The Peaks around 1050-1150cm-1 was

observed, corresponding to the stretching vibrations of the C-O bonds present in the starch molecule(WeligamaThuppahigeetal.,2023).

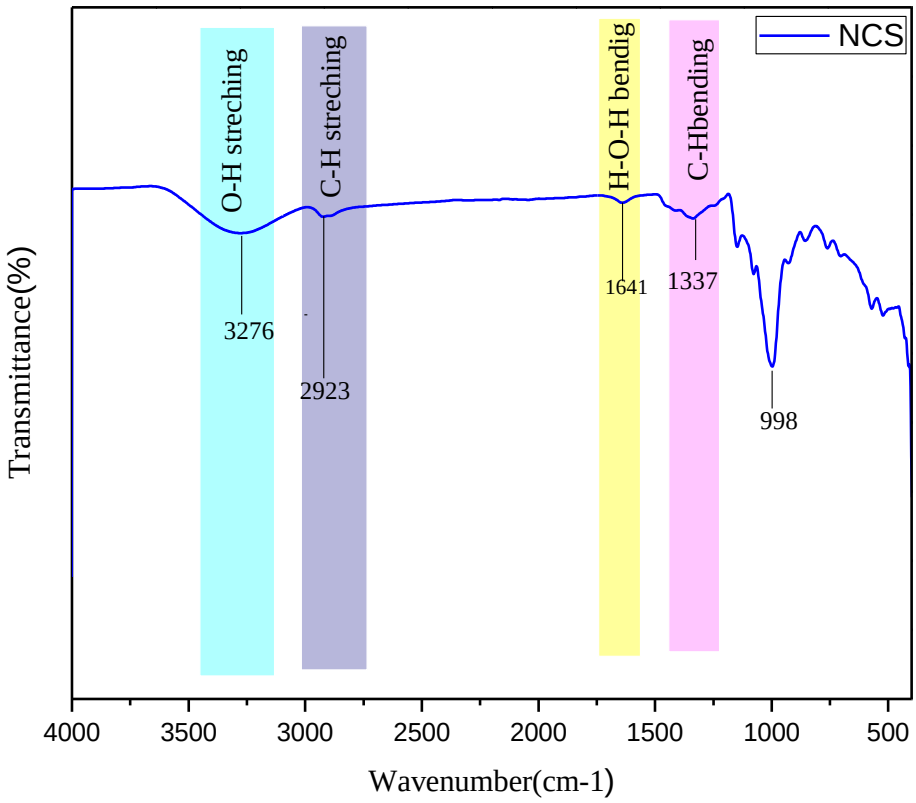

Figure 4-10 FT-IR spectra of Native cassava starch

4.3.3.Crystallinity analysis of native Cassava starch

X-ray diffraction was used to observe the crystalline polymorphs of native starch. The cassava starch's x-ray diffraction pattern is displayed in image 4.10 below. The diffraction patterns provide information on the arrangement of the amylopectin chain in double helices. The x-ray pattern of starch has been classified as A-type, B-type , and C-type starches. A-type starch is typical for cereals starches that have a doublet at around 17° and 18° of 2θ and present strong diffractionpeaksabout15°and23°of2θ.BtypeistypicalforintubersStarchesandpatternsidentifiedby astrongpeakat17°of2θandacharacteristicpeakabout5.6°,15.26°,17.21°,19.75°,22.32°and24.08°o f2θ.

In addition to these peaks, it has weak diffraction peaks at 2θ = 5.81° and 26.10°. C-type starch patterns are a combination of A-type starch and B-type starch. The characteristic diffraction peaks of type C starch were observed at 2θ = 15.06°,17.09°,19.34°and22.86°(Abera et al., 2019).(R. H. Lin et al., 2020)Cassava starch showed strong diffraction peaks at 17° of 2θ with characteristics peak at 5.6°, 15.26°, 17.21°, 23.1° and 25.08° of 2θ. According to these diffraction peaks, cassava starch is a B-type starch which is similar to the previous work by Segura et al., (2013).

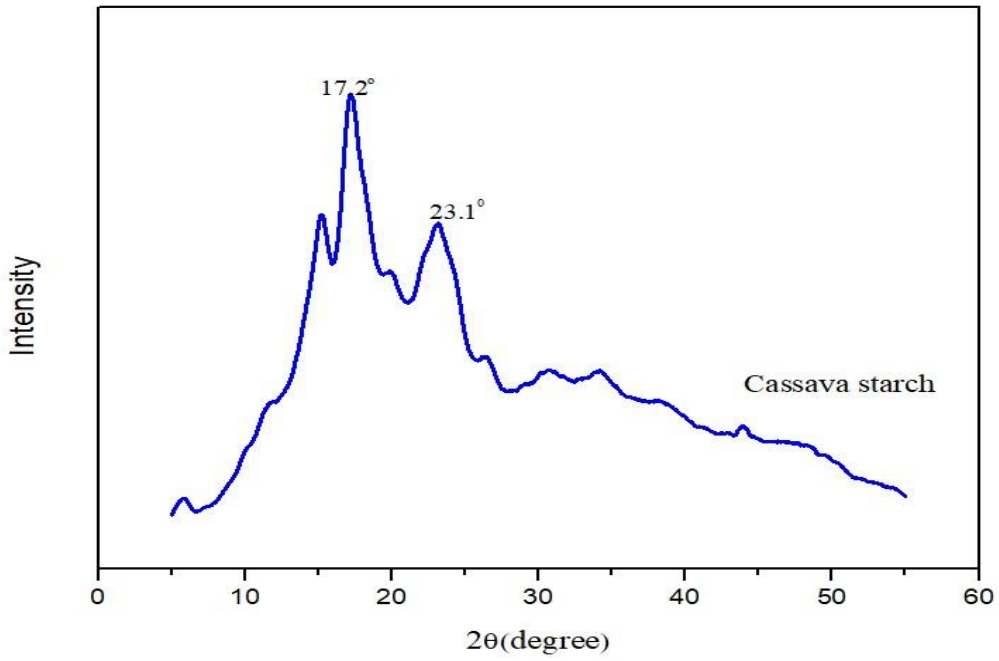

Figure 4-11 XRD image of native starch

4.3.4. Thermo gravimetric analysis (TGA) Native cassava starch

Thermal gravimetric analysis measures the mass loss of the sample as a function of temperature.TGA with DTA was used to assess the Native cassava starch's thermal stability. The TG of the obtained cassava starch (Figure 4.12) showed mass losses in three steps and thermal events corresponding to these losses. The first weight loss (14.236 %) was observed in the 30 –278.6 ℃ temperature range. and it indicates the evaporation of absorbed moisture or the release of volatile components. The second weight loss (74.8%) took place in the 278.6–331.7 ℃ temperature range and was assigned to starch decomposition process of the main sample component. this phase is marked by a significant mass loss which could be attributed to the thermal degradation of organic compounds of starch. As shown in the DTG curve in Fig

4.12 the highest decomposition occurred in the 306 ℃.The third weight loss (0.8%) took place at the temperature of 452 ℃ corresponding with the weight loss in the TGA curve, indicating the further decomposition of remaining residues. The DTG curve confirms these findings by showing endothermic peaks at this temperature, indicating energy absorption associated with thermal evens. Overall the sample exhibited significant thermal degradation, with a total weight loss of 99.2% by 600℃.

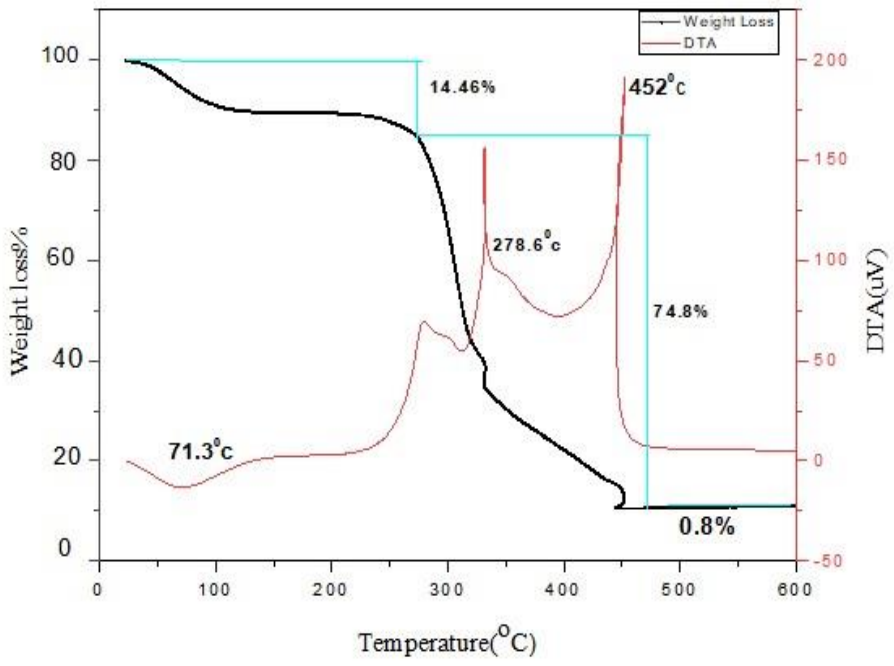

Figure 4-12 TGA and DTA curves of Native cassava starch

4.4. Modification/oxidation of starch

The oxidation of starch primarily involves the conversion of hydroxyl groups to carbonyl and carboxyl groups, which modifies the functional properties of starch. This process can be carried out using various oxidizing agents like sodium hypochlorite, hydrogen peroxide, and ozone. Such oxidation occurs primarily on the hydroxyl groups at the C-2, C-3, and C-6 positions. In this study, we focused on the Oxidation reaction of starch with hydrogen oxide as an oxidizing agent and $CuSo_4$ catalyst (Muflihati et al., 2019).Oxidation happens as a result of a radical chain reaction. Hydrogen peroxide breaks down quickly in the presence of a metal catalyst to produce hydroxyl radicals (OH). By removing hydrogen atoms from C-H groups on sugar rings, these extremely potent free radicals react with carbohydrates quickly to produce

new radicals (R-CHOH) (Fig4-12). Peroxide oxidation is the primary process that forms the carbonyl functional group; carboxyl groups are created in lower quantities during this process (Sangseethong et al., 2010).

In the hydrogen peroxide oxidation reaction, a peroxide anion is formed,

$$H_20_2 + Cu^{+2} \xrightarrow{Cu\,SO_4.5H_20} OH + OH^- + Cu^{3+} \quad (1)$$

The hydroxyl radical formed oxidizes an alcohol group forming a radical,

$$RCH_2OH + OH \longrightarrow R.CHOH + H2O. \quad (2)$$

This radical reacts with copper ions,

$$R{\cdot}CHOH + Cu^{+3} \longrightarrow RCHO + H^+ + Cu^{2+} \quad (3)$$

And hydrogen peroxide

$$R.CHOH + H_2O_2 \longrightarrow RCHO + OH + H_2O \quad (4)$$

The carbonyl functional group is primarily formed during peroxide oxidation; a smaller amount of carboxyl groups are formed during this process.

This treatment leads to the introduction of carboxyl and carbonyl groups within the starch molecules. Oxidized starches tend to have reduced viscosity, swelling power, retrogradation tendency, and pasting temperature these newly formed functional groups play a significant role in impeding the retro gradation process, which refers to the tendency of starch molecules to re-associate and form a gel-like structure upon cooling. By hindering retrogradation, the presence of carboxyl and carbonyl groups enhances the stability of the modified starch, making it less prone to gel formation and suitable for various applications (Zhang et al., 2017).This is leading to the change in morphological properties, crystalline properties, gelatinization properties, and gelatinization enthalpy of the starch. The changes in Cassava starch before and after oxidation with different degrees of oxidation were investigated by FTIR, SEM, TG–DTG, and XRD.

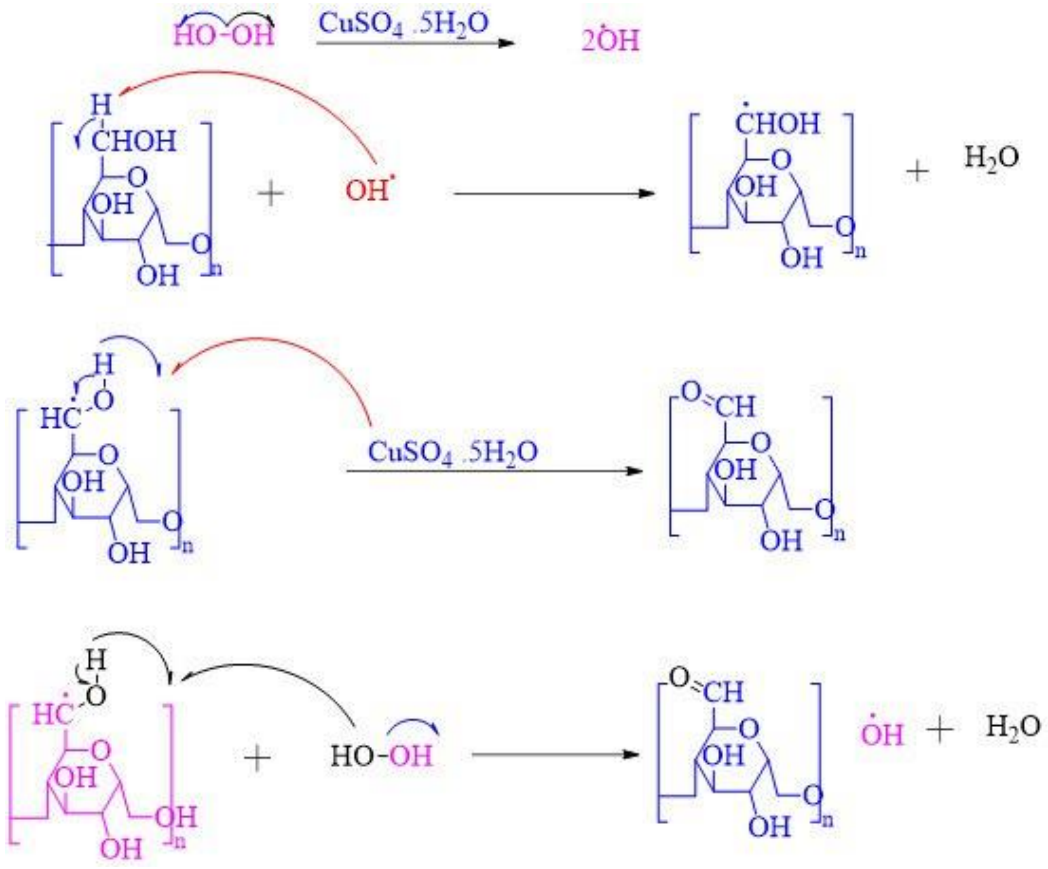

Figure 4-13 Reactions mechanism of oxidation starch

4.4.1. Morphological analysis of Modified Cassava starch

The scanning electron micrographs (SEM) of the native and Oxidized cassava starch granules are shown in Fig. 4.14(a). The SEM technique was applied in order to evaluate whether the Modification treatment was changed the structure of starch granules significantly, compared with Native cassava starch. Similarly to observations of Klein et al., (2014), our native cassava starch showed round shape with a truncated end. Fig.4.14 (b) shows the microphotograph of oxidized cassava starch with a high Degree of oxidation. The morphology of the starch granule shows a clear external structural difference between native cassava starch and oxidized cassava starch. Additionally, the starch granules start to rupture and different sizes of cracks are formed on their surfaces when oxidation takes place.th oxidized cassava starch granules in fig 4.14(b) seem more swollen or distorted, with irregular shapes and disrupted(rough) surfaces, which is slightly different from the previous work of Zang et al., (2020).This is due to the introduction of carboxyl groups. Therefore, the above results show that the external, as

well as internal parts of the starch granules, are influenced by the chemical Oxidation processes, which means that the crystalline of the starch decreases significantly. The introduction of carboxyl groups brought significant changes in the shapes and the sizes of the starch granules which occur not only in some surface modification.

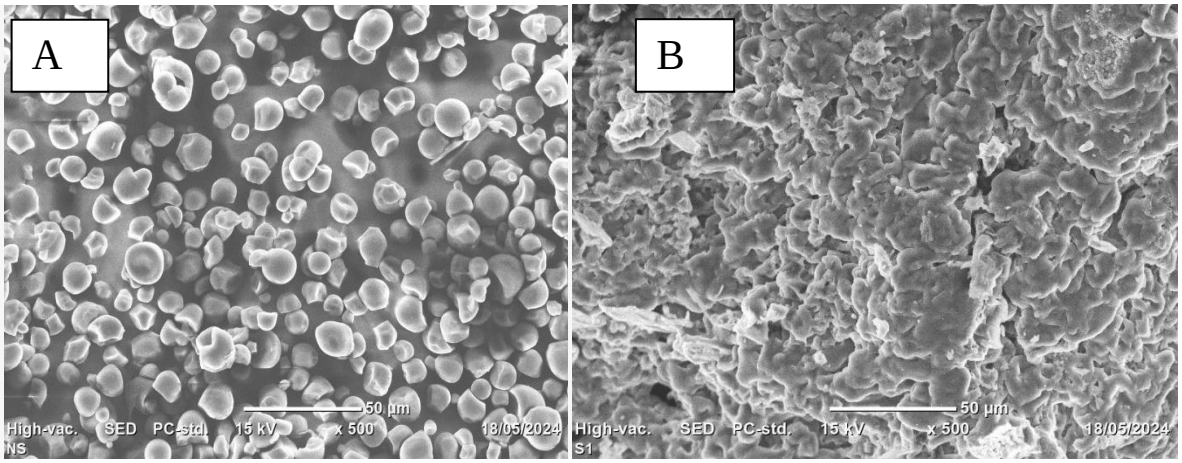

Figure 4-14 Morphology of (a) native and (b) Modified Cassava starch

4.4.2. FTIR analysis of Modified starch

The oxidation reaction between cassava starch and hydrogen per oxide, which used Cupper (II sulphate pent hydrate as a catalyst, was confirmed by FTIR Spectroscopy. The FTIR spectra of native and oxidized starches are shown in Fig. 4.15. Native cassava starches (NCS) are shown in Fig. 4. 15.there are several clear absorbencies at 3276,2923.5,1641 cm-1, 1337cm-1and 998 cm-1represents the stretching vibrations of O-H groups, the Stretching vibration of C-H in CH2,Stretching of H-O-H , O–H bending vibration of adsorbed water molecules of H–O–H, C-O stretching vibrations and: C-O-C stretching vibrations in the glycosidic linkages respectively (Zang et al., 2020).In the case of OCS a peak at 3324 cm-1 was observed, corresponding to O-H stretching vibrations and it indicated hydrogen-bonded hydroxyl groups. Both NCS and OCS have prominent hydroxyl group peaks, but the peak for OCS is slightly shifted, which may indicate changes in hydrogen bonding due to oxidation. The band at around 2925 cm-1 is assigned to CH2 symmetrical stretching vibrations. a new absorption at 1695 cm-1 was seen and it is assigned to C=O stretching vibrations, This bond confirms the introduction of –COOH group into the starch molecule. Which is similar to the previous work by Sangseethong et al., (2010).This suggested that more carbonyl and carboxyl groups were

formed. The results indicate that native starch was successfully oxidized by hydrogen peroxide, and hydroxyl groups were changed to carbonyl and/or carboxyl groups.

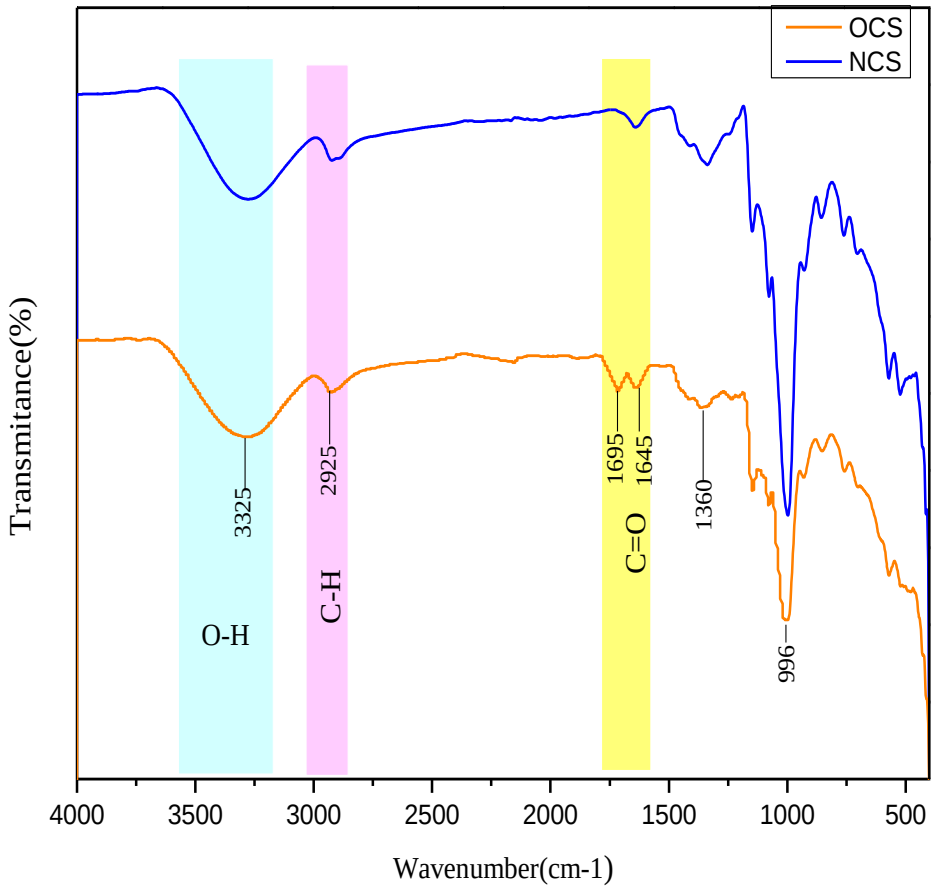

Figure 4-15 FT-IR spectra of Native and oxidized cassava starch

4.4.3. XRD analysis of Modified starch

Measurements of X-ray diffraction (XRD) were performed to see if starch's Crystallinity was altered by oxidation.. The X-ray diffraction spectra of native cassava starch and oxidized Cassava starches are presented in Fig.4.15 below. The native cassava starch had sharp diffraction peaks at 17° (2θ) and a few characteristics peaks at 5.6°, 15.26°, 17.21°, 23.32°, and 25.08°, which indicated a typical B-type pattern. However, and at DO –51% and DO-56% oxidized starch except one all sharp peaks were disappeared as shown in Fig.4.15. These X-ray diffraction (XRD) results indicated that with Oxidation modification, the crystalline

structure of native starch was damaged and new structure of oxidized cassava starch was formed. As a result, the degrees of crystallinity decreased with increasing the DO from DO-0% to DO-56.6%. This is due to intra- and inter-molecular hydrogen bonds were responsible for the highly ordered crystalline structure. During the oxidation modification process, Oxidation reactions often involve the addition of functional groups, such as carbonyl (C=O) or carboxyl (COOH) groups, this reduces the formation of intermolecular hydrogen bonds and thereby destroying the ordered crystalline structure (Rahaman et al.,2021).This suggests that oxidation can impact the crystalline structure of starch, potentially converting it into an amorphous state. As the DO of the oxidized starch increased from DO-0 to DO-56.6%, there was increased destruction or even loss of the ordered crystalline structure (Lin.Y et al., 2020).

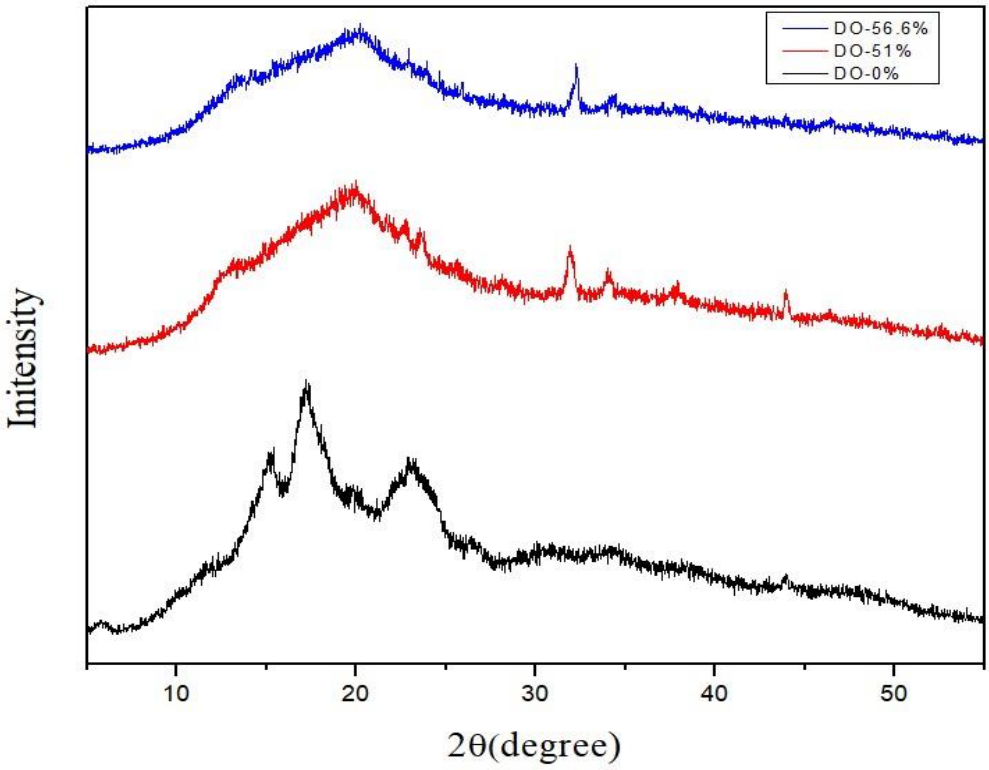

Figure 4-16 XRD of (DO-0%, DO-51% and DO- 56.6%)

4.4.4. Thermo gravimetric analysis (TGA) of Modified starch

Thermo gravimetric analyses (TGA) curves were used to see the change of thermal stability caused by the oxidation of starch and to determine the weight loss of the starch on heating. The TGA and DTG curves for the native (DO-0) Cassava starch and oxidized cassava starch

with DO (56.6%) were shown in Fig.4.16 a and Fig.4.In general, there were three phases to weight loss. The first weight loss (11.236%) was observed in the 29 ℃ –310 ℃ temperature range and it is attributed to the removal of physically adsorbed water, volatile components and hydrogen-bonded water that remained in starch even after preconditioning. The endothermic peak at 77.39^0C corresponds to the initial weight loss. The second weight loss (16.5%) occurs between 310–352 ℃ representing the main decomposition phase of the sample. The most substantial weight loss was occurred at a temperature 381.72℃. As shown in the DTA curve in Fig 4.16, the endothermic peak at 381.7℃ aligns with the significant weight loss in the TGA curve, indicating the onset of the primary decomposition phase. The decomposition of starch is a result of the inner and intermolecular dehydration reaction of starch molecules, with water as a main product of decomposition. Energy absorption is associated with the breakdown of chemical bonds and the release of decomposition products. The last weight loss (0.63%) at 518.4 ^{0}C indicates the decomposition of any remaining residuals .the small weight loss of 0.63% suggests that only minor components of the sample were stable to higher temperatures.

As shown in Fig 4-17 15% weight loss of native cassava starch (NCS) occurred at 240℃, 50,% weight loss at 308℃,85 % weight loss at 449℃ and maximum degradation temperature (T max) occurred at 306℃.For oxidized cassava starch, 15 % weight loss occurred at 275 ℃, 50% weight loss at 320 ℃, 85 % weight loss at 390℃ and maximum degradation temperature (Tmax) occurred at 338 ℃.

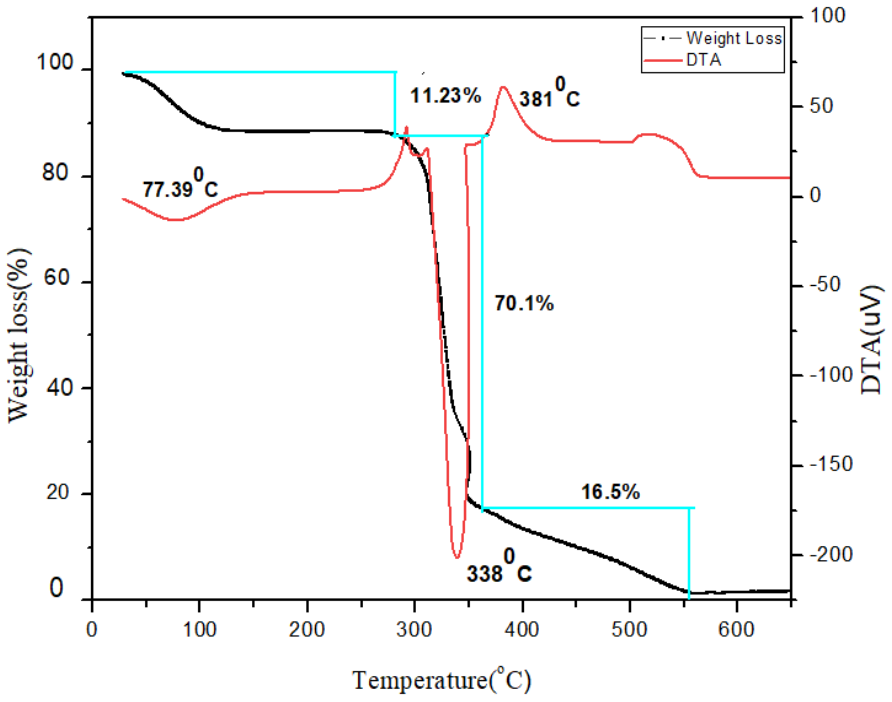

Figure 4-16 TGA curves of oxdized cassava starch

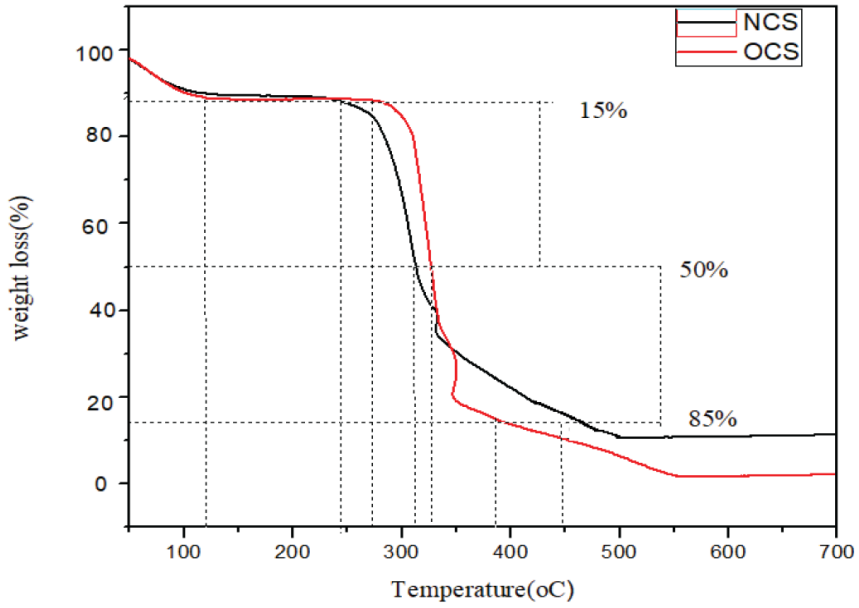

Figure 4-17 TGA curves of native cassava starch and oxidized cassava starch

Native cassava starch shows significant decomposition at lower temperatures compared to oxidized starch and also it shows a higher weight loss percentage in its major peaks compared to the oxidized starch. In general, oxidation of starch has been reported to result in increased thermal stability, which is characterized by single DTA peaks that occur at higher temperatures than the one found for native starch decomposition. The increase in thermal stability was due to the low amount of remaining hydroxyl groups (OH) in starch molecules after modification. Oxidation reactions can result in the formation of larger molecular-weight starch derivatives. Higher molecular weight compounds due to oxidation of the hydroxyl group (OH) exhibit better thermal stability due to their increased chain length and more extensive intermolecular interactions (Costa et al., 2011).

4.5. Paper quality test

4.5.1. Determination of tensile strength

The tensile strength measurement is a critical parameter for evaluating the performance and durability of paper materials. In this study, the tensile strength of the sample paper was compared with that of a standard paper under controlled conditions. Both the sample and standard papers were subjected to a drying time of 25 minutes at a temperature of 105°C. The base weight of the sample paper was 126 g/cm², while the standard paper's base weight ranged between 120 and 130 g/cm²

Table 4-7Tensile strength of sample paper and standard paper

	Base weight	**Time(min)**	**Temperature(^{0}C)**	**Tensile strength(kg)**
Sample paper	126g/m^2	25 min	105(^{0}C)	7.4 kg
Standard paper	120-130 g/m^2	25min	105(^{0}C)	7.1 -7,5kg

The tensile strength of the sample paper was measured at 7.4 kg f. In comparison, the tensile strength of the standard paper varies between 7.1 and 7.5 kg f. These results indicate that the

sample paper's tensile strength was at the higher end of the standard paper's range, demonstrating that the sample paper performs equivalently to or slightly better than the standard paper under the tested conditions. This comparison is useful for evaluating the quality of the sample paper relative to the standard paper.

4.5.2. Determination of breaking strength

Breaking length is a measure of the intrinsic strength of paper and is defined as the length of a strip of paper that would break under its own weight if suspended vertically. It is a crucial parameter in assessing the durability and strength of paper relative to its weight.

Table 4-8 breaking length of sample paper and standard paper

	Base weight	**Time(min)**	**Temperature(^{0}C)**	**Breaking length(m)**
Sample paper	126g/m^2	25 min	105(^{0}C)	3915m
Standard paper	120-130 g/m^2	25min	105(^{0}C)	3910-3920m

The table compares the breaking length of sample paper and standard paper under identical conditions of a 25-minute drying time at 105°C. The sample paper, with a base weight of 126 g/cm², has a breaking length of 3915 meters. In comparison, the standard paper, with a base weight range of 120-130 g/cm², shows a breaking length range of 3910 to 3920 meters. This indicates that the sample paper's breaking length is within the range of the standard paper, suggesting that the sample paper performs comparably in terms of strength and durability. These findings validate the quality and reliability of the sample paper, suggesting that it meets the performance criteria of the standard paper.

4.5.3. Determination of the Burst strength

Burst strength is an important property of paper, indicating its resistance to rupture when subjected to pressure. It is a critical parameter for assessing the durability and robustness of

paper products, especially for applications such as packaging, where the paper must withstand significant stress and handling.

Table 4-9 Bursting strength of sample paper and standard paper

	Base weight	**Time(min)**	**Temperature(^{0}C)**	**Burst length(kg/m^2)**
Sample paper	126g/m^2	25min	105^{0}C	2.7kg/m^2
Standard paper	120-130 g/m^2	25 min	105^{0}C	2.5- 2.8 kg/m^2

The burst strength of the sample paper was measured at 2.7 kg/cm² under controlled conditions of 25 minutes drying time and 105°C, with a base weight of 126 g/cm². In comparison, the standard paper, with a base weight range of 120-130 g/cm², exhibited burst strengths between 2.5 and 2.8 kg/cm². This demonstrates that the sample paper's burst strength is within the standard paper's range, indicating comparable resistance to rupture

4.5.4. Determination of Tear Factor and Porosity

Table 4-10 Tear factor and Porosity of sample paper and standard paper

	Base weight	**Time(min)**	**Temperature(^{0}C)**	**Porosity (sec)**	**Tear factor (m Nm^2/gm)**
Sample paper	126g/cm^2	25min	105(^{0}C)	13 sec	2.7m Nm^2/gm
Standard paper	120-130 g/cm^2	25 min	105(^{0}C)	15-19 sec	2.5-2.8 m Nm^2/gm

The comparison of porosity and tearing strength reveals that the sample paper performs similarly to the standard paper in terms of tearing strength and lower porosity while offering. The tearing strength of 2.7 kg/cm² for the sample paper is within the standard range of 2.5 to 2.8 kg/cm², ensuring it is robust and durable. Additionally, the sample paper's porosity of 13

seconds, lower than the standard paper's 15 to 19 seconds, suggests enhanced permeability, which can be beneficial for quicker ink absorption and drying.

4.6. Determination of burst and crush tests for corrugated cardboard

The table presents the results of the burst and crush tests conducted on the corrugated cardboard. These tests measure the cardboard's strength and durability, which are critical for evaluating its suitability for various packaging applications.

	Burst (kg/cm^2)	**Crush (lb.)**
Standard	7.8 kg/cm^2	25 lb.
Measured	8.5 kg/cm^2	28 lb.

The test results for the corrugated cardboard were analyzed, focusing on burst and crush strength. The burst strength was measured at 8.5 kg/cm^2, surpassing the standard value of 7.8 kg/cm^2. This indicates that the cardboard demonstrates superior resistance to rupture under pressure. Additionally, the crush strength was recorded at 28 pounds, exceeding the standard requirement of 25 pounds. This higher crush strength suggests enhanced resistance to compression, providing better protection during stacking and shipping. Overall, the sample corrugated cardboard exhibits improved strength and durability compared to standard specifications, making it a more reliable choice for packaging applications. These findings validate the sample's potential for effectively protecting goods during transportation and handling.

CHAPTER FIVE

5. CONCLUSION AND RECOMMENDATION

5.1. Conclusion

This research focuses on extracting and structurally modifying cassava (*Manihot esculenta*) starch to develop a green binder for use as an input material in the paper packaging industries. Starch was extracted and characterized from cassava (*Manihot esculenta*) root from Wolaita zone (6.4°N - 7.1°N and 37.4°E - 38.2°E), Ethiopia. The physiochemical analysis confirmed that the gelatinization temperature of native cassava starch was 55 ^{0}C, it exhibited a swelling power of 5.00 ± 0.20, and its solubility ranged from 21.8 to 38.8. And also, a viscosity of 11± 0.5 mpa.s was obtained. The SEM analysis confirmed that most of its granules were round shape with a truncated end on the one side and the size of the granules varied from 3.35-18.09µm. It gave B-type starch by showing a strong peak at 17^0 of 2θ when analyzed by x-ray powder diffraction (XRD).FTIR analysis observed A broad peaks in the range of 3200-3600cm-1 typically observed for native cassava starches indicate the stretching vibrations of O-H groups. The highest decomposition occurred in the range of 310–352 ℃, and the temperature of maximum weight loss rate (Tmax) of native starch occurred at 338℃ when analyzes by TGA/DTG.

Cassava starch possesses several properties that make it a promising candidate for utilization as a paper binder in the production of starch-based products. Oxidized cassava starch were prepared by reaction of native starch with hydrogen per oxide using Copper(II) sulfate pent hydrate ($CuSo_4.5H_20$) as a catalyst. The optimization of modification parameter (reaction temperature, reaction time and catalyst loading) was successfully carried out using response surface methodology central composite design. The optimized condition was validated and found to be fitted with the experimental values. The optimum degree of oxidation 56. % was obtained at 98minute, 51^0c and 0.4 catalysts loading with 95% validation.

Structural modification of starch resulted in substantial changes in the physicochemical properties of the native starch. The FT-IR spectra confirm that the peak of the carbonyl group (C=O) appeared at 1,695 cm–1 for due to the introduction of the carbonyl group on native cassava starch. X-ray diffraction (XRD) approved that the crystal structure of native starch was disappeared and gradually converted to an amorphous structure for 56% DO. The

scanning electron microscopy (SEM) images indicated a substantial variation in starch morphology and the smooth surface of the starch granules converted rough surface as Degree of oxidation (DO) increases, oxidation of starch has been reported to result in decrease thermal stability, which is characterized by a single DTG peaks that occur at lower temperatures than the one found for native starch decomposition. According to TGA/DTG results, the thermal stability of oxidized starch which was 338^0c is higher than the native starch at 306 ℃. This was due to introduction of new functional groups or modification of existing groups within starch molecules. These changes can alter the molecular and interactions, potentially leading to a increase in thermal stability.

The sample paper, produced using oxidized starch as a sizing agent, was shown a base weight of 126 g/m², burst strength of 2.7 kg/cm², breaking length of 3915 m, tear factor of 126.9 m Nm²/gm, tensile strength of 7.4 kg, and porosity of 13 sec. The sample paper using oxidized starch adhesive showed burst strength of 8.5 kg/cm² and crush strength of 28 lb, exceeding the standard values of 7.8 kg/cm² and 25 lb, respectively. This demonstrates improved performance in both metrics. Compared to the standard paper, these values fall within or exceed the typical ranges, indicating that the sample paper meets or surpasses standard performance metrics in most parameters.

5.2. Recommendation

The extraction and structural modification of cassava starch (***Manihot esculenta***) for binder application in the paper packaging industries was studied. The modified starch has a promising property for use in the paper packaging industry with the required characterization such as tensile strength, burst strength, and water resistivity. Due to financial and technical instrument constraints, the scope of thesis work was limited at this level. Based on the present study, some recommendations can be made for future work.

- Since the paper quality tests, such as tensile strength, burst strength, porosity, and contact angle measurement, were conducted using only one concentration of oxidized starch, we suggested that optimizing the parameters that determine paper quality.
- In this study, the extraction of cassava starch was conducted using wet method. To optimize the yield, it is recommended to explore and implement alternative extraction methods.
- Further studies are needed to explore the potential application of Ethiopian cassava starch.
- It is recommended to conduct an economic analysis and feasibility study on the extraction and modification of cassava starch for use in the paper packaging industries.

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APPENDIXES

Cassava root

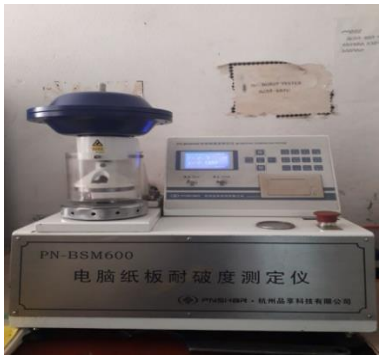
Cassava starch

gelatinization of nS

Tensile tester

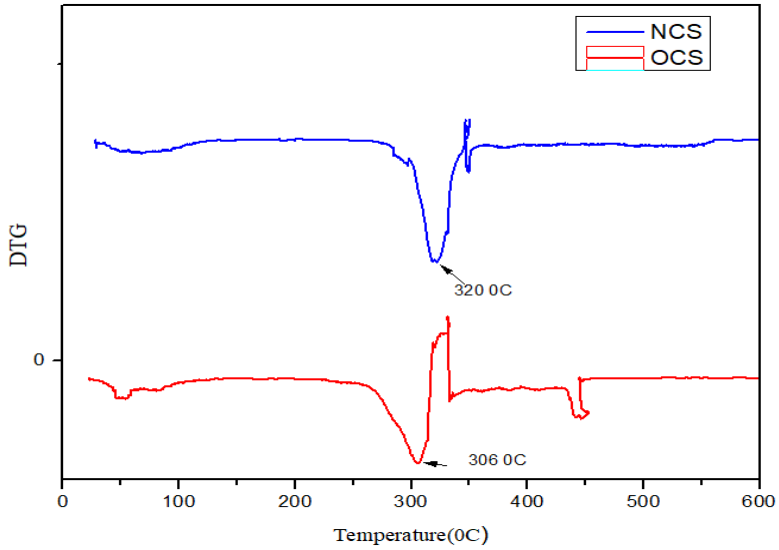
Gurley porosity testers

Tearing strength tester



Bursting strength tester

DTG figure of oxidized cassava starch and native cassava starch



Moisture content determination of native cassava starch

Ash content determination of native cassava starch